

THIRTY-SEVEN YEARS OF ARCHIVES OF ENVIRONMENTAL PROTECTION

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Keywords: *Archives of Environmental Protection*, environmental engineering and protection, journal's anniversary, Institute of Environmental Engineering of PAS.

Abstract: *Archives of Environmental Protection* is the oldest Polish scientific journal regarding environmental engineering and protection. It has been published by the Institute of Environmental Engineering of PAS in Zabrze since 1975. The Committee on Environmental Engineering of PAS became its co-publisher in 2011. The quarterly publishes original articles (earlier, also announcements) concerning broadly understood areas of the environmental engineering and protection. The subjects include: air, land and water protection; technologies of flue gases, soil and wastewater treatment; transformations and transportation of pollutants in the environment; measurement techniques used in research and engineering as well as environmental monitoring. The published articles also focus on the reclamation and management of derelict lands, environmental management and other questions related to the environmental engineering and protection.

The journal has been abstracted by Thomson Scientific since 2006 in the following databases: Science Citation Index Expanded, Biological Abstracts and BIOSIS Previews. Moreover, the journal was given the impact factor (IF) in 2010. The following article presents statistical data as well as a brief history and description of the journal.

INTRODUCTION

The Institute of Environmental Engineering of PAS in Zabrze is the oldest Polish scientific institution that conducts complex basic and applied research into the environmental engineering and protection. Its employees created the basis for the environmental engineering and contributed significantly to define this research area as the new science at the 2nd Congress of the Polish Science in 1973.

The Institute was formed in January 1961. It was first known as Zakład Badań Naukowych Górnośląskiego Okręgu Przemysłowego Polskiej Akademii Nauk (Research Centre of PAS in the Upper Silesian Industrial Region)¹. Its predecessor was Komitet Naukowy PAN ds. Górnośląskiego Okręgu Przemysłowego (Scientific Committee of PAS on the Upper Silesian Industrial Region), which had been working since 1954. It was established by Professor Eugeniusz Zaczyński, who was also its first director.

¹ Translator's note: Translations of Polish titles and names of institutions are given in brackets. This information serves solely to clarify the meaning of the titles and names to the English-speaking readers.

The Centre was reorganized in June 1970 and its name was changed to Zakład Ochrony Środowiska Regionów Przemysłowych PAN (Centre of the Environmental Protection of PAS in Industrial Regions). Finally, the Centre was transformed into the Institute of the Environmental Engineering of PAS in May 1975. It has been functioning in this form ever since. Professor Eugeniusz Zaczyński continued to be the director of the Centre after its first transformation. Later, the Centre and then the Institute were managed by prof. dr hab [full professor]² Jan Paluch (November 1964 – November 1974), prof. dr hab [full professor] Stefan Jarzębski (December 1974 – December 1983), doc. dr hab. inż. [assistant professor] Jan Kapała (January 1984 – October 2001) and prof. dr hab [full professor] Czesława Rosik-Dulewska (November 2001 – April 2012). Dr inż. [Doctor of Science, Eng.] Franciszek Pistelok has been holding the position of the director since April 2012.

The Institute coordinated complex programmes concerning environmental protection and management in the Upper Silesian Industrial Region and other Polish regions in 1970s. In the years 1986–1990, it also managed the programme of “Biochemiczne i fizyczne przemiany zanieczyszczeń i odpadów przemysłowych oraz ich interakcja ze środowiskiem” (“Biochemical and Physical Transformations of Pollutants and Industrial Waste and Their Interactions with the Environment”), which constituted a part of the Centralny Program Badań Podstawowych (Central Basic Research Programme). The Institute of Environmental Engineering is an active participant in all types of scientific research, including those financed by the EU’s Framework Programmes or Ministry of Science and Higher Education and other scientific institutions as well as those not subsidized by the government budget.

Conducting scientific research on the environmental engineering and protection would be futile if its results were not popularized and used in practice. For this reason, the Institute publishes journals and a series of monographs. The first issue of *Prace i Studia (Works and Studies)*, a serial monograph publication, appeared in February 1969. The first issue of *Archives of Environmental Protection* was published in May 1975. The journal has been abstracted by Thompson Scientific since 2006 in the databases of Biological Abstracts and BIOSIS Preview. Furthermore, it has been given IF since 2010 (2009 = 0.284, 2010 = 0.188 and 2011 = 0.444). The quarterly has also been registered in the Index Copernicus since 2002. The IC index attained the values of 3.75 (2002), 3.73 (2003), 3.73 (2004), 4.46 (2005), 9.00 (2007), 9.00 (2008), 9.00 (2009) and 10.61 (2010). At present, a publication in *Archives of Environmental Protection* is given 13 points by the Ministry of Science and Higher Education.

The Institute of Environmental Engineering of PAS celebrated its 50th anniversary in 2011. Since *Archives of Environmental Protection* is its flagship, the following article presents short description and selected statistical data relating to the journal.

SUBJECTS COVERED BY ARTICLES PUBLISHED IN *ARCHIVES OF ENVIRONMENTAL PROTECTION*

Articles published in *Archives of Environmental Protection* regard four main areas, i.e. air, land and water protection as well as waste management.

Works on air protection concern the research into the physical and chemical content of the primary and secondary aerosols necessary for the evaluation of their impact on

² Translator’s note: Polish scientific titles are given in their original form. The information given in square brackets serves solely to clarify the meaning of the title to the English-speaking readers.

health and environment. They also look into the air pollution impact on climate changes. They investigate quantity and content of pollutants emitted from energy plants and industry, specifically when it comes to dangerous substances, chemical and physical properties of substances emitted into the air, emission rates. Studies also cope with the subject of air quality management on local and regional scales.

The majority of articles on water protection discuss problems of water and wastewater treatment for industrial purposes and research into the recovery of biogenic substances from municipal and industrial wastewater. They also concentrate on the changes in the aquatic ecosystem in the process of anthropogenic water reservoirs reclamation.

Studies on land protection deliberate over methods determining the influence of point and non-point sources of pollution, including waste disposal sites, on the environment. There are also articles focusing on the formation of technogenic magnetic and geochemical anomalies in the local and national systems by means of geomagnetic parameters. Some works focus on the examinations of soil magnetic susceptibility as the factor of land pollution caused by the industrial activity. Other papers concentrate on the use of minerals and waste materials as effective and economical sorbing agents of heavy metals and organic pollutants in the remediation of water, wastewater and soil. One can also find publications on the natural and technological bases for the soil-less reclamation of post-industrial areas and waste dumps. Finally, some of the researchers present their findings relating to the use of waste energy of discharge waters from electricity production processes and geothermal water in soil heating for plant production.

Waste management issues discussed in the published articles embrace the research into chemical, physical and technological properties of waste as well methods of protecting the environment against the negative waste impact. The reports also encompass determining various methods enabling waste disposal and recovery. They also focus on the assessment of coal mining and other industrial waste in terms of its short and long-term impact on the environment including directives on its safe disposal and recovery. There are also studies on various chemical binding forms of metals in waste and other environmental samples determined with sequential chemical extraction methods.

Apart from the afore-mentioned topics, *Archives of Environmental Protection* also publishes articles on the broadly understood environmental engineering and protection. By submitting the typescript, the author states that his/her article has not been published or submitted in any other journal. At present, it is also possible to send the paper via e-mail. Afterwards, the author completes the copyright statement and sends it by post. The decision on the article publication depends on the opinions of two independent reviewers and the editorial board acceptance. Authors of the published works receive one author's copy. The articles are also published in the on-line version of the journal. It is worth mentioning that 1,693 articles were submitted to *Archives of Environmental Protection* in the years 1975–2010. 443 papers were rejected after reviewing, which makes 26.2% of the total article number.

HISTORY OF *ARCHIVES OF ENVIRONMENTAL PROTECTION*

The Editorial Committee (Editor-in-Chief, Members and Editorial Assistant) managed editing of the journal in the years 1975–1996. The following persons held the position of the Editor-in-Chief (issues they edited are given in brackets):

1. Jan Paluch (1/1975),
2. Stefan Jarzębski (2/1976 – 3–4/1984),
3. Stefan Godzik (1–2/1985 – 2/1992),
4. Jan Pałasz (3–4/1992 – 3–4/1996).

At that time, 25 people were Members of the Editorial Committee, including:

1. Roman Andrzejewski (1/1979 – 3–4/1984),
2. Jan Bender (1/1979 – 1–4/1982),
3. Jerzy Chmielowski (2/1976 – 3–4/1978),
4. Stanisław Chróściel (1–2/1983 – 3–4/1984),
5. Bohdan Głowiak (2/1976 – 1–4/1982),
6. Stefan Godzik (1/1979 – 3–4/1983),
7. Seweryn Gołwin (1/1984 – 1–2/1988),
8. Andrzej Grossman (2/1976 – 1–4/1982),
9. Zdzisław Harabin (1–2/1983 – 3–4/1984),
10. Stefan Jarzębski (1/1975),
11. Jan Juda (1/1975 – 1–4/1982),
12. Alina Kabata-Pendias (1/1984 – 1–2/1988),
13. Jan Kapała (1–2/1985 – 3–4/1996),
14. Zdzisław Małecki (3–4/1988 – 3–4/1996),
15. Korneliusz Miksch (3–4/1988 – 3–4/1996),
16. Jan Paluch (2/1976 – 1–4/1982),
17. Zygmunt Pociecha (1/1979 – 3–4/1984),
18. Krzysztof Rostański (3–4/1992 – 3–4/1996),
19. Jan Siuta (3–4/1988 – 3–4/1996),
20. Tadeusz Skawina (1/1975 – 3–4/1978),
21. Karol Starmach (1/1975 – 3–4/1978),
22. Zygmunt Strzyszc (1–2/1985 – 2/1992),
23. Mieczysław Sądelski (1–2/1985 – 1–2/1988),
24. Irena Twardowska (3–4/1992 – 3–4/1996),
25. Tomasz Winnicki (1–2/1983 – 3–4/1984).

The following persons held the position of the Editorial Assistant:

1. Zygmunt Strzyszc (1/1975 – 3–4/1983),
2. Stefan Godzik (1/1984 – 3–4/1984),
3. Tomasz T. Suchecki (1–2/1990),
4. Marek Szpor (1–2/1985 – 3–4/1989),
5. Antoni Moskwa (1–2/1990 – 3–4/1996).

Archiwum Ochrony Środowiska (the Polish title was then used) had been a multi-language journal when it became officially bilingual – Polish-English – in 1997 (even though summaries in Russian still appeared). It was also given the new graphic design and its title was changed to *Archiwum Ochrony Środowiska – Archives of Environmental Protection*. The title changed again to *Archives of Environmental Protection – Archiwum Ochrony Środowiska* in 2000. The journal has been a regular quarterly since 1998. The Editorial Committee was divided into the Editorial and Advisory Editorial Boards. The Editorial Board consists of the Editor-in-Chief, Section Editors and Editorial Assistant.

Editors-in-Chief:

1. Tomasz T. Suchecki (1–2/1997 – 1/2002),
2. Korneliusz Miksch (1/2002 – 2/2004),
3. Czesława Rosik-Dulewska (3/2004 to date).

Section Editors:

1. Jan Koniecznyński (3/2004 to date),
2. Korneliusz Miksch (1–2/1997 – 1/2002, 3/2004),
3. Zygmunt Strzyszcz (1–2/1997 to date),
4. Tomasz T. Suchecki (1/2002 – 2/2004),
5. Jerzy Zwoździak (1–2/1997 – 2/2004),
6. Jan Suschka ()

Chairs of the Advisory Editorial Board:

1. Jan Kapała (1–2/1997 – 1/2002),
2. Czesława Rosik-Dulewska (1/2002 – 2/2004),
3. Lucjan Pawłowski (3/2004 to date).

At that time, the Editorial Advisory Board was constituted by 28 people, including members from Poland (11 persons), the USA (3 persons), India, Norway, China and Japan (2 persons from each country), France, Australia, Germany, Lithuania and the Netherlands (1 person from each country).

The journal has been published solely in English since 2005. Moreover, it has been published under exclusively English title, i.e. *Archives of Environmental Protection*, since 2008. At present, its Editor-in-Chief is Professor Czesława Rosik-Dulewska and Professors Jan Koniecznyński, Zygmunt Strzyszcz and Jan Suschka are its Section Editors. Dr [DSc] Antoni Moskwa worked as the Editorial Assistant until 2010. Currently, mgr [MSc] Dorota Konieczna holds this position. Lucjan Pawłowski is the Chair of the Advisory Editorial Board, which consists of 21 persons, including 12 foreign members.

STATISTICAL DATA CONCERNING ARCHIVES OF ENVIRONMENTAL PROTECTION³ IN THE YEARS 1975–2011

Thirty-seven volumes of *Archives of Environmental Protection* were published in the years 1975–2011. They contained 107 issues consisting of 1,310 articles, whose total number of pages amounted to 17,689. Table 1 presents detailed statistical data concerning particular volumes, which includes information on the percentage of studies written by the Institute's employees as well as the percentage of works published in English and those written by foreign authors.

Statistical data is also given in Figures 1–5. They show respectively: the number of issues in particular years, number of pages and publications as well as the information on the percentage of studies prepared by the Institute's employees, works published by foreign authors and articles written in English.

³ By using the title of *Archives of Environmental Protection* and due to the serial publication character of the journal, authors pay attention to all stages of its development regardless of the title the journal had in the specific historical period.

Table 1. Statistical data concerning Archives of Environmental Protection in the years 1975–2011

Volume	Year of publication	Number of issues	Total page number	Number of articles	Publications of the Institute's employees (%)	Publications of foreign authors (%)	Publications in English (%)
1	1975	1	238	8	50	0	0
2	1976	1	272	17	18	0	6
3	1977	3	602	30	57	7	20
4	1978	3	494	27	41	0	19
5	1979	3	478	22	45	0	0
6	1980	3	560	46	26	0	4
7	1981	2	344	32	13	44	59
8	1982	1	124	8	25	0	0
9	1983	2	312	21	33	5	19
10	1984	3	574	37	49	0	5
11	1985	2	348	26	11	0	4
12	1986	1	198	14	21	0	0
13	1987	2	422	40	5	8	8
14	1988	2	342	25	8	0	16
15	1989	2	414	23	22	0	9
16	1990	2	426	35	11	3	51
17	1991	3	552	43	23	2	14
18	1992	3	606	53	38	0	11
19	1993	2	474	34	44	3	9
20	1994	2	466	34	35	3	26
21	1995	3	594	53	0	50	100
22	1996	2	360	27	33	0	15
23	1997	2	470	37	19	0	8
24	1998	4	634	45	26	2	18
25	1999	4	664	43	14	2	19
26	2000	4	604	39	18	0	26
27	2001	4	646	39	25	3	15
28	2002	4	566	46	26	2	35
29	2003	4	596	52	15	0	13

Volume	Year of publication	Number of issues	Total page number	Number of articles	Publications of the Institute's employees (%)	Publications of foreign authors (%)	Publications in English (%)
30	2004	4	616	49	12	0	16
31	2005	4	488	40	15	2	100
32	2006	4	428	33	6	0	100
33	2007	4	408	34	32	3	100
34	2008	5	760	68	6	12	100
35	2009	4	570	49	10	10	100
36	2010	4	524	41	7	15	100
37	2011	4	515	40	13	10	100

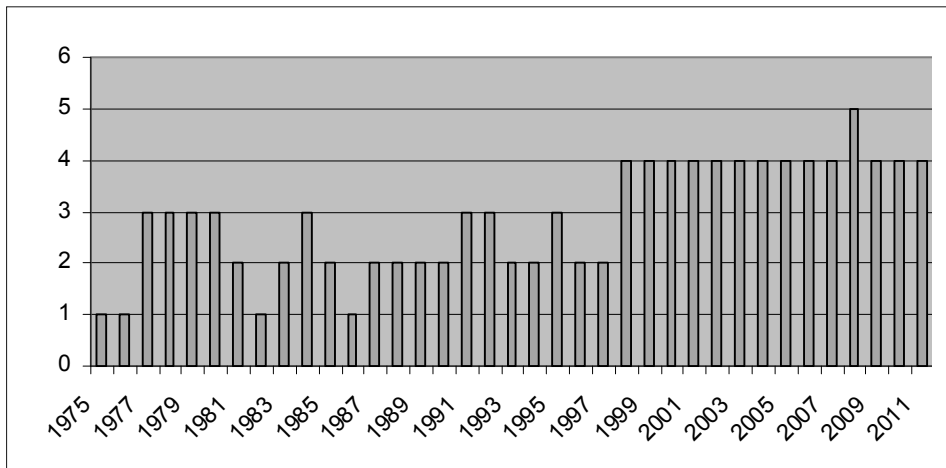


Fig. 1. Number of *Archives of Environmental Protection* issues published in particular years

Information given in Figure 1 indicates that the number of *Archives of Environmental Protection* issues changed. Only one issue was published in the years 1975, 1976, 1982 and 1986. Two issues appeared in the years 1981, 1983, 1987–1990, 1993, 1994, 1996 and 1997. Three issues were available in the years 1977–1980, 1985, 1991, 1992 and 1995. The journal has been published as a regular quarterly since 1998 with an exception of the year 2008, when an additional issue concerning the conference on *International Scientific Thematic Network for Environmental Technologies* was published.

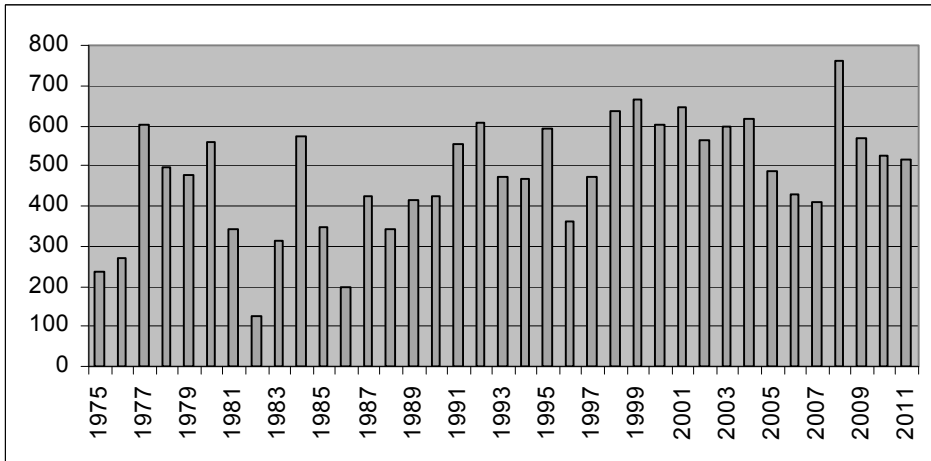


Fig. 2. Number of pages in particular volumes of *Archives of Environmental Protection* published in the years 1975–2010

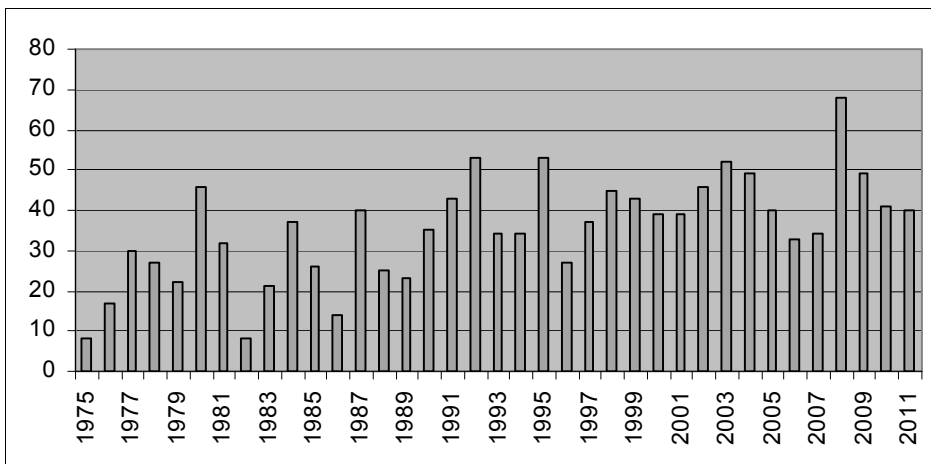


Fig. 3. Number of publications in *Archives of Environmental Protection* in particular years

The number of issues published in particular years determined the total number of pages and publications. The lowest number of pages was published in 1982 (124), whereas the highest one (760) appeared in 2008 due to the publication of the special issue no. 5. The median value is 475 for the years 1975–2010. Nevertheless, this value is higher (approx. 600 pages/year) for the issues circulated since 1998, i.e. the period in which the journal has been published regularly as a quarterly.

The median number of articles published in the years 1975–2010 is approx. 37/year. Nevertheless, it has been regularly exceeded in recent years (see Fig. 3). Obviously, there were volumes in which this value was much lower (1975, 1982) and much higher (1991, 1995, 2008).

It ought to be emphasized that the first publication on the history of the Institute (issue no. 1/1975) was “Nauka a przestrzenny rozwój kraju” (“Science and the spatial development of the country”). It was authored by Witold Nowacki, Kazimierz Kopecki, Tadeusz Klarner, Zdzisław Kaczmarek, Stanisław Leszczycki, Elżbieta Lissowska, Marian Madeyski, Bolesław Malisz, Czesław Mejro, Zbigniew Sufin, Aleksander Tuszko and Władysław Wyrzykowski.

It would be difficult to describe each article published in *Archives of Environmental Protection* within the last thirty-six years. However, many of the articles prove to be tremendously important, innovative, and still influential. These include:

- Stanisław Leszczycki’s “Badania Komitetu GOP-u nad kształtowaniem środowiska człowieka w Górnośląskim Okręgu Przemysłowym w latach 1954–1960” (“The research into the formation of human environment in the Upper Silesian Industrial Region in the years 1954–1960 conducted by the Scientific Committee on the Upper Silesian Industrial Region”) (issue no. 1/1977, pp. 9–24),
- Andrzej Grossman’s “Dorobek naukowy i osiągnięcia Instytutu Podstaw Inżynierii Środowiska Polskiej Akademii Nauk w Zabrze w latach 1961–1976” (“Scientific achievements of the Institute of Environmental Engineering of PAS in the years 1961–1976”), (issue no. 1/1977, pp. 25–42),
- Stefan Kozłowski’s “Ochrona środowiska przyrodniczego w planach przestrzennego zagospodarowania kraju do roku 2000” (“Environmental protection in the plans of the national land management until the year 2000”), (issue no. 1/1981, pp. 97–114),
- Jan Kapała’s “35 lat działalności Instytutu Podstaw Inżynierii Środowiska PAN w Zabrze” (“Thirty-five years of the Institute of Environmental Engineering of PAS in Zabrze”), (issue no 1–2/1997, pp. 7–20),
- Jan Siuta’s “Struktura przestrzenna wieloczynnikowej degradacji środowiska w Polsce” (“Spatial structure of multi-factor environment degradation in Poland”) (issue no. 1/1998, pp. 7–16).

The authors of *Archives of Environmental Protection* also remembered about researchers who had passed away but whose lives and achievements proved to be influential to younger generations of scientists. Among them, articles paying tribute to the memory of the following professors were published:

- Stanisław Byrdy (issue no. 1–2/1993, pp. 7–8).
- Stanisław Jerzy Chróściel (issue no. 3–4/1993, pp. 7–10).
- Roman Andrzejewski (issue no. 1/1999, pp. 78).
- Janina Szulicka (issue no. 2/1999, pp. 7–8).

Issue no. 4/1999 contained the full list of contents regarding all volumes of *Archives of Environmental Protection* in the years 1975–1994. It also comprised an index of authors published in the years 1975–1999. Full English versions of publications have been available on-line at the Institute’s website since 2009. Their Polish versions have also been available since issue no. 4/2011. *Archives of Environmental Protection* has been made available in the international platform Versita in the open access mode since 2012.

Archives of Environmental Protection has never been a periodical devoted solely to the publications written by the employees of the Institute of the Environmental Protection of PAS in Zabrze. Information presented in Fig. 4 shows that the median number of the employees’ articles in the years 1975–2010 was nearly 24%. At the beginning, almost

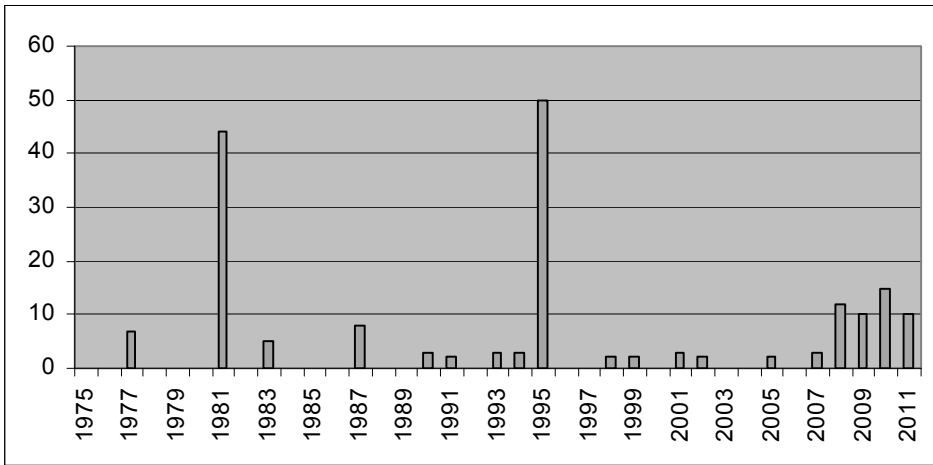


Fig. 4. Publications of the Institute's employees (%) in *Archives of Environmental Protection* in particular years

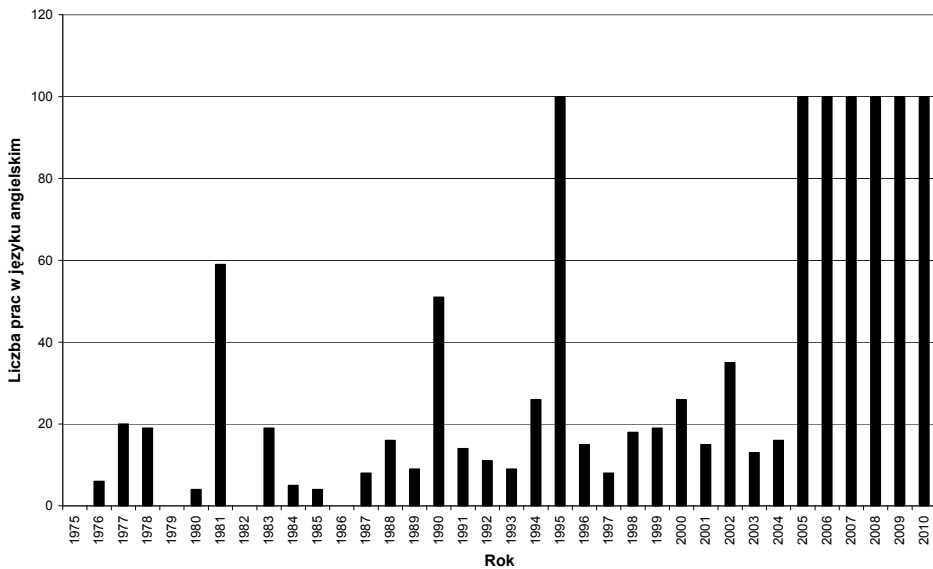


Fig. 5. Publications in English (%) in *Archives of Environmental Protection* in particular years

half the studies were authored by the Institute's staff. This value has been systematically decreasing as the quarterly has become more international in the editorial, authorship and readership terms.

Maciej Kostecki (63 articles) and Czesława Rosik-Dulewska (25 articles) were the most prolific *Archives of Environmental Protection* authors. 13 researchers published at least 10 studies. 51 persons publicized between 5 and 9 papers and 1,178 scientists had between 1 and 4 articles printed. The total number of authors whose works could be found in the journal in the years 1972–2010 was 1,244. They are mainly employed at Polish

R&D institutions. However, the number of the foreign authors has been systematically increasing.

Bolesław Raczyński and Jean Guichard had their “Filtration des aérosols par les lits fixes de billes de verre” published in French (issue no. 1/1977, pp. 111–142) whereas Zygmunt Strzyszc, Rainer Tölle and Joachim Katura wrote their “Zur Anwendung eines hochfrequenten Messverfahrens für den Nachweis von ferromagnetischen Eisen in der Umwelt” in German (issue no. 3–4/1988, pp. 137–144). On the other hand, Joachim Bronder, Tatjana G. Nefedova and Andrzej T. Jankowski published their “Badania degradacji środowiska naturalnego za pomocą serii map” (“Research into the natural environment degradation with a series of maps”)⁴ in Russian (issue no. 2/1991, pp. 163–172).

Since its first issue, the aim of *Archives of Environmental Protection* has been to propagate knowledge of the environmental engineering and protection in local, national and international terms. The number of foreign authors and articles written in English (Fig. 5) corroborate the fact that the journal has become an important international periodical. It is worth mentioning that the first article published in English was Emil Dratnal’s “The benthic fauna of the Prądnik stream below an inlet of dairy waste effluents” (issue no. 2/1976, pp. 235–242).

SUMMARY AND CONCLUSIONS

Archives of Environmental Protection is the oldest Polish scientific journal on the environmental engineering, which publishes original scientific articles. It has been indexed in a few bases by Thompson Scientific since 2006. It is also recorded in the ISI Master Journal List and has been given IF since 2010.

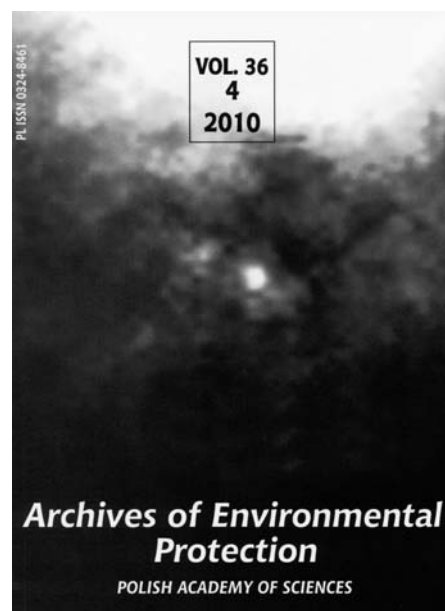
38 volumes which included 108 issues were published in the 37-year-old history of the journal. They contained 1,320 publications whose total page number was 17,810. The articles were authored by 1,361 people, both the Polish and foreigners. The fact that the journal obtained IF and has become more international is both typical for our times and necessary as the subjects related to the environmental engineering and protection have been globalized.

Within this time many aspects of the journal changed, including the discussed problems and authors. It is also worth reminding what the journal covers looked like when its titles were changed.

The role and importance of *Archives of Environmental Protection* is invaluable. From the historical point of view, the journal was the place in which environmental engineering was shaped as a science. It published the works of the most acknowledged experts in this discipline. As the databases usually embrace periodicals dating from ca. 1996, it is important to refer to the archival issues. They constitute an opportunity for discovering results of various research works, which are often unavailable on-line.

At present, *Archives of Environmental Protection* is one of many journals on the environmental engineering. Nonetheless, it is still one of the most important platforms for exchanging scientific ideas. The fact that the journal has been systematically developing and expanding (in terms of readers and authors) makes *Archives of Environmental Protection* one of the pillars of the modern science progress.

⁴ Translator’s note: The original Russian title has already been translated into Polish and for this reason it is also presented in English.



37 LAT CZASOPISMA *ARCHIVES OF ENVIRONMENTAL PROTECTION*

Archives of Environmental Protection to najstarsze polskie czasopismo naukowe z zakresu ochrony i inżynierii środowiska. Wydawane jest od 1975 roku przez Instytut Podstaw Inżynierii Środowiska PAN w Zabrze. W 2011 r. współwydawcą został Komitet Inżynierii Środowiska PAN. W kwartalniku publikowane są oryginalne artykuły (wcześniej także komunikaty) z zakresu szeroko rozumianej inżynierii i ochrony środowiska,

w szczególności dotyczące ochrony powietrza atmosferycznego, ochrony wód i powierzchni ziemi; technologii oczyszczania gazów odlotowych, ścieków oraz gleb; przemian i transportu zanieczyszczeń w środowisku; technik pomiarowych stosowanych w inżynierii i badaniach oraz monitoringu środowiska. Poruszane są również tematy rekultywacji i zagospodarowania terenów zdegradowanych; kształtowania środowiska oraz innych zagadnień związanych z inżynierią i ochroną środowiska.

Od roku 2006 wydawnictwo rejestruje Thomson Scientific w bazach: Science Citation Index Expanded, Biological Abstracts i BIOSIS Previews, a od 2010 kwartalnik ma przyznany wskaźnik Impact Factor obliczany za 2009 r. W niniejszej pracy przedstawiono wybrane dane statystyczne oraz krótką historię i charakterystykę czasopisma.

UTILIZATION OF ENVIRONMETRIC & INDEX METHODS AS WATER QUALITY COMPARATIVE ASSESSMENT TOOLS FOCUSING ON HEAVY METAL CONTENT

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Keywords: Cluster analysis, factor analysis, heavy metal, pollution fingerprint, water quality index.

Abstract: In the study suitability of water quality index approach and environmetric methods in fingerprinting heavy metal pollution as well as comparison of spatial variability of multiple contaminants in surface water were assessed in the case of The Gediz River Basin, Turkey. Water quality variables were categorized into two classes using factor and cluster analysis. Furthermore, soil contamination index was adapted to water pollution index and used to find out the relative relationship between the reference standards and the current situation of heavy metal contamination in water. Results revealed that surface water heavy metal content was mainly governed by metal processing, textile and tannery industries in the region. On the other hand, metal processing industry discharges mainly degraded quality of water in Kemalpaşa and Menemen. Furthermore, Kemalpaşa region has been heavily affected from tannery and textile industries effluents. Moreover, pollution parameters have not been influenced by changes in physical factors (discharge and temperature). This study indicated the effectiveness of water quality index approach and statistical tools in fingerprinting of pollution and comparative assessment of water quality. Both methods can assist decision makers to determine priorities in management practices.

INTRODUCTION

In the last few decades, there has been a tremendous increase in the demand for fresh water due to rapid growth of population and the accelerated pace of industrialization [19]. In parallel to an increasing demand, surface water bodies are prone to impacts from human activities, which may result in degradation of the resource. The best way to minimize adverse impacts on water quality is to plan basin development activities (including industrial, residential and agricultural) and manage protection measures by monitoring quality effectively [10]. However, water quality assessment is quite difficult due to the spatial variability of multiple contaminants and a wide range of indicators that could be measured.

Modern concepts of estimation of pollution impacts require not only careful organization of water quality monitoring of water bodies (surface waters, coastal sediments and benthic organisms, seawaters and plants) but also a reliable monitoring,

data treatment, classification and modeling. Since the analytical data from ecological systems possess a multivariate nature, environmetric methods, which are application of multivariate statistical techniques, are successful approach for their interpretation [15]. On the other hand, water quality index value makes the information more easily and rapidly understood by a) using measurements in a single metric, and b) facilitating comparison between different sampling sites and/or events [5, 7].

A lot of studies abound in the literature on pollution of water sources [e.g. 1, 2, 4, 11, 12, 18 and 20]. All these researchers used various methods (e.g. water quality indexing, statistical tools) to assess water quality focusing on heavy metal pollution. They indicated that the application of multivariate statistical methods and water quality index approach made it possible to interpret and model the complex data sets from river water monitoring sites in a more appropriate way.

The aim of the study is not only to assess the present water quality focusing on heavy metal content along the Gediz River and its tributaries but also to examine emissions from industrial sources and spatial differences between monitoring sites. The assessment was carried out by the use of factor analysis (FA), cluster analysis (CA), water quality index (WQI) method, correlation analysis and frequency histograms.

STUDY AREA

The Gediz River Basin is located in western Anatolia in the Aegean region neighboring the city of Izmir. The Gediz River, 401 km long, drains an area of 17 500 km² and flows from east to west into the Aegean Sea just north of Izmir (Fig. 1).

Annual average discharge of the river is about 60 m³/s. Agricultural lands and forest cover about 88% of the total area and residential and industrial area is almost 10% of the total land uses [16].

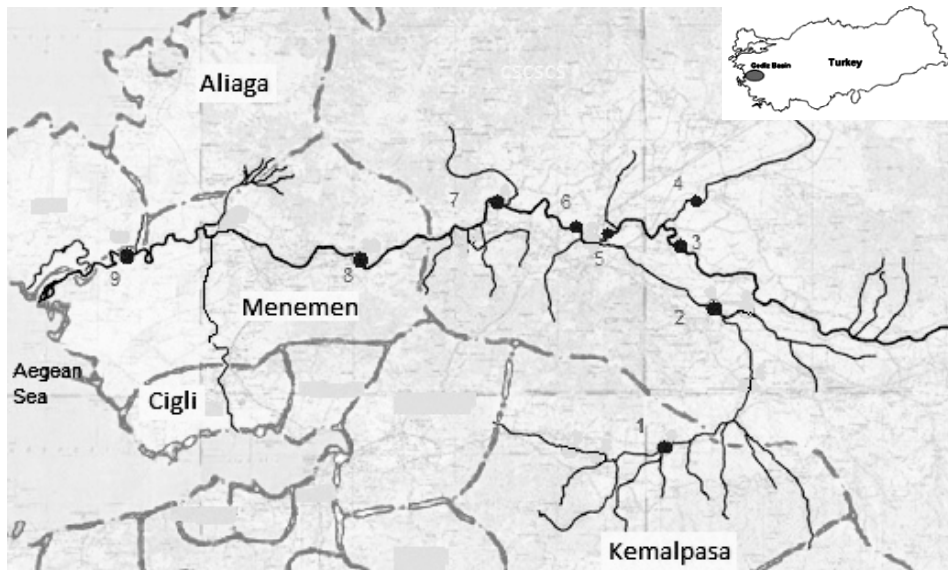


Fig. 1. Gediz River and monitoring stations

Wastewater discharges from urban areas and industries within the basin seriously degrade the quality of the surface water. There are several organized districts and individual companies along Nif Creek and downstream part of the river. The study focused on impacts of discharges on water quality focusing on heavy metal content in this region.

In the study area, Kemalpaşa Organized Industry Region, there are mainly metal processing, chemical, plastic and paper producing companies. On the other hand, there are leather and tannery processing companies in the organized district located in Menemen. İzmir Atatürk Organized Industry Region dominantly comprises textile, metal processing, electric and electronic, construction material, chemical and food industries, etc. In addition to these industrial regions, there are individual companies spread all over the region [16].

STUDY METHOD

In the study, the measured parameters of heavy metals – aluminum, boron, cadmium, iron, mercury, nickel, lead, total chromium and zinc were subject to examination by environmetric methods and water quality index calculation. Water samples were collected on a monthly basis from nine monitoring stations for two years and analyzed according to “Standard Methods for the Examination of Water and Wastewater [3]” at the laboratory. The determination of heavy metals was carried out by atomic absorption spectrophotometry (AAS). Overall objective of the study was water pollution fingerprinting, determination of spatial differences and also analyzing impact of physical factors on water quality.

Factor and cluster analysis were applied in order to explain the behavior and sources of water pollutants. Factor analysis was performed by examining the pattern of correlations (or covariances) between the observed measures. Measures that are highly correlated (either positively or negatively) are likely to be influenced by the same factors, while those that are relatively uncorrelated are likely to be influenced by different factors [9].

Cluster analysis encompasses a number of different algorithms and methods for grouping objects of similar kind into respective categories. In other words, the method is an exploratory data analysis tool which aims to sort different objects into groups in a way that the degree of association between two objects is maximal if they belong to the same group and minimal otherwise. The joining or tree clustering method uses the dissimilarities (similarities) or distances between objects when forming the clusters. Similarities (dissimilarities) can be based on a single dimension or multiple dimensions, with each dimension representing a rule or condition for grouping objects. A typical result of this type of clustering is the hierarchical tree [14].

Correlation is the mutual relationship between two variables. Direct correlation exists when increase or decrease in the value of one parameter is associated with a corresponding increase or decrease in the value of another parameter [8]. In the study the method was used to determine interdependence between particular variables.

Water quality index and frequency histograms were applied to assess present level of pollution by relating to standards and also to determine spatial differences in water quality. In this scope single contamination index used in the literature [12] to investigate heavy metal contamination in soils was adapted to water quality index by referencing Turkish Water Pollution Control Regulation. The objective was to find out a relative relationship between the national standards and the current situation of heavy metal contamination in water. In this method WQI_i was defined as the quality index of variable i and C_i as parameter

concentration (Tab. 1). Moreover, X_a , X_p , and X_c represented the limits for Class I, II and III waters defined by the regulation respectively (see Tab. 2). In this classification “Class I” water represented the best quality and “Class IV” heavily polluted waters.

Furthermore, frequency histograms were also plotted using combined data of each variable with size class interval of “1” to allow for distinctions for water quality classes.

RESULTS AND DISCUSSION

Water Pollution Fingerprinting and Investigation of Spatial Differences

In the study data set was analyzed using factor analysis-FA (extraction method – principal component analysis, rotation method – Varimax with Kaiser Normalization) with a view

Table 1. Water quality index [12]

Variable concentration			
$C_i \leq X_a$	Quality index formula	$WQI_i = C_i/X_a$	(1)
	Index range	$WQI_i \leq 1$	
	Water Quality Class represented	I	
$X_a < C_i \leq X_c$	Quality index formula	$WQI_i = 1 + (C_i - X_a)/(X_c - X_a)$	(2)
	Index range	$1 < WQI_i \leq 2$	
	Water Quality Class represented	II	
$X_c < C_i \leq X_p$	Quality index formula	$WQI_i = 2 + (C_i - X_c)/(X_p - X_c)$	(3)
	Index range	$2 < WQI_i \leq 3$	
	Water Quality Class represented	III	
$X_p < C_i$	Quality index formula	$WQI_i = 3 + (C_i - X_p)/(X_p - X_c)$	(4)
	Index range	$WQI_i > 3$ (max 4)	
	Water Quality Class represented	IV	

Table 2. Standart limits recommended by the Turkish Water Pollution Control Regulation ($\mu\text{g/L}$) [17]

Variable	Class I	Class II	Class III	Class IV
Al	300	300	1000	>1000
B	1000	1000	1000	>1000
Cd	3	5	10	>10
Fe	300	1000	5000	>5000
Hg	0.1	0.5	2	>2
Ni	20	50	200	>200
Pb	10	20	50	>50
T-Cr	20	50	200	>200
Zn	200	500	2000	>2000

to examine their correlations and influences. The objective was the identification of possible factors/sources that are responsible for variations in water quality and influence the water system. Combined data covering all sampling stations and study period was used for analysis.

Table 3 summarizes the FA results including the loadings, eigenvalue and variance explained by each factor. FA rendered two factors with eigenvalues >1 explaining 69.2% of the total variance of the data set. Factor 1 explained 40.3% of total variance and had strong positive loadings (> 0.90) on iron, aluminum, zinc and mercury. On the other hand, Factor 2, having strong positive loadings on total chromium, cadmium and nickel, explained 28.9% of the total variance.

Table 3. Rotated component matrix

Variable	Factor Component	
	1	2
Pb	1.536E-02	.353
TCr	.159	.902
Zn	.927	.241
Hg	.911	-2.936E-02
Cd	9.597E-02	.881
B	-.154	.282
Fe	.960	1.702E-02
Ni	.226	.861
Al	.952	7.282E-02
Total variance explained (%)	40.28	69.16

Cluster analysis is another data reduction method that is used to classify entities with similar properties. The method divides a large number of objects into a smaller number of homogeneous groups on the basis of their correlation structure [24].

In addition to factor analysis, classification of water quality variables was made by the use of cluster analysis (z-transformation of the input data, squared Euclidean distance as similarity measure and between groups method of linkage) and a dendrogram was generated. According to results shown in Figure 2 two associations were evident. The association between iron, aluminum, zinc and mercury were significant. Another group comprised variables – total chromium, nickel and cadmium. This result was in accordance with outcome of FA. Therefore, both FA and CA showed that water quality variables can be grouped into two main clusters (groups).

Pollution of surface water by industrial processes is a widespread and very serious environmental issue. Heavy metals are metallic elements (e.g., cadmium, chromium, copper, lead, mercury, nickel and zinc), many of which are toxic at relatively low concentrations and are found in industrial wastewaters [23]. The primary human-related

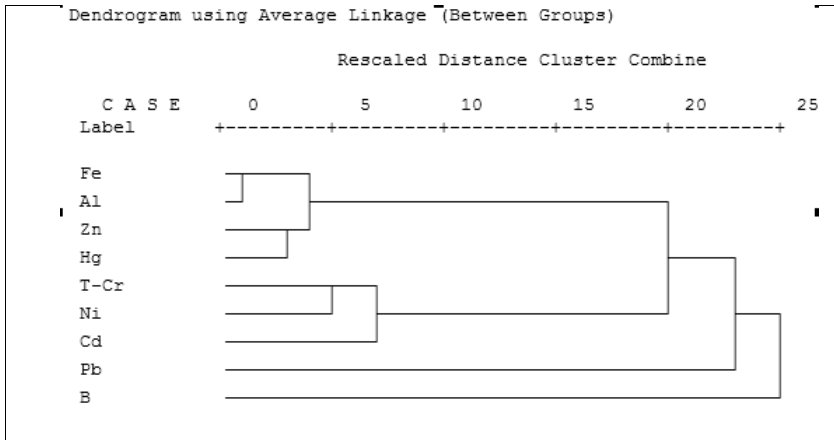


Fig. 2. Hierarchical dendrogram for variables clustering

mercury sources include coal combustion, chlorine alkali processing, waste incineration, and metal processing [21]. On the other hand, the main inorganic pollutants from metal molding and casting industry are copper, lead and zinc. Wastewater coming from non-ferrous metals manufacturing industry also includes aluminium, antimony, chromium, lead, magnesium, nickel, silver, tin, and zinc, as inorganic pollutants. [23].

Use of Cd, Cr and Pb in electroplating factory, plastic industry and in alloy preparation are quite common [22]. The tannery industry, which uses a variety of chemicals in the tanning process is recognized as a major contributor of heavy metals to the environment and poses serious environmental threats worldwide [4]. For example, chromium (Cr), when used in the productive cycle, is one of the most problematic pollutants discharged by the tanning industry [6]. The heavy metal constituents in wastewater from textile industry are chromium, copper and zinc [23]. Heavy metals such as lead, chromium, cadmium and copper are widely used for production of color pigments of textile dyes [13].

Based on these statements and considering the profile of production companies located in the region, it was concluded that Group I can represent impact of effluent dominated by metal processing industry. Besides Group II variables can be indicator of discharges from textile and tannery industries.

Accordingly, further analysis techniques have been carried out and results presented for two groups of variables representing “Group I-metal processing industry impact” and “Group II- textile and tannery industries impact” separately.

Water quality classification and spatial variability for the Group I

The simple linear correlation analysis has been carried out to find out a correlation between parameters classed under Group I. The correlation matrix was presented in Table 4.

The positive high correlations were found between zinc, mercury, iron and aluminum. The result was indicator of human induced changes in heavy metal content in surface water. In other words, high positive correlation between parameters can be explained by effect of industrial discharge containing these pollutants.

Table 4. Correlation coefficients between Group I variables

	Zn	Hg	Fe	Al
Zn	1.0	0.7	0.6	0.8
Hg		1.0	0.5	0.8
Fe			1.0	1.0
Al				1.0

Classification of water quality has also been made using WQI method. The unit indices that represent water quality class were determined from the values of individual parameters using formulas given in Table 1. Relative frequency histograms illustrating distribution of index scores of Group I variables are depicted in Figure 3.

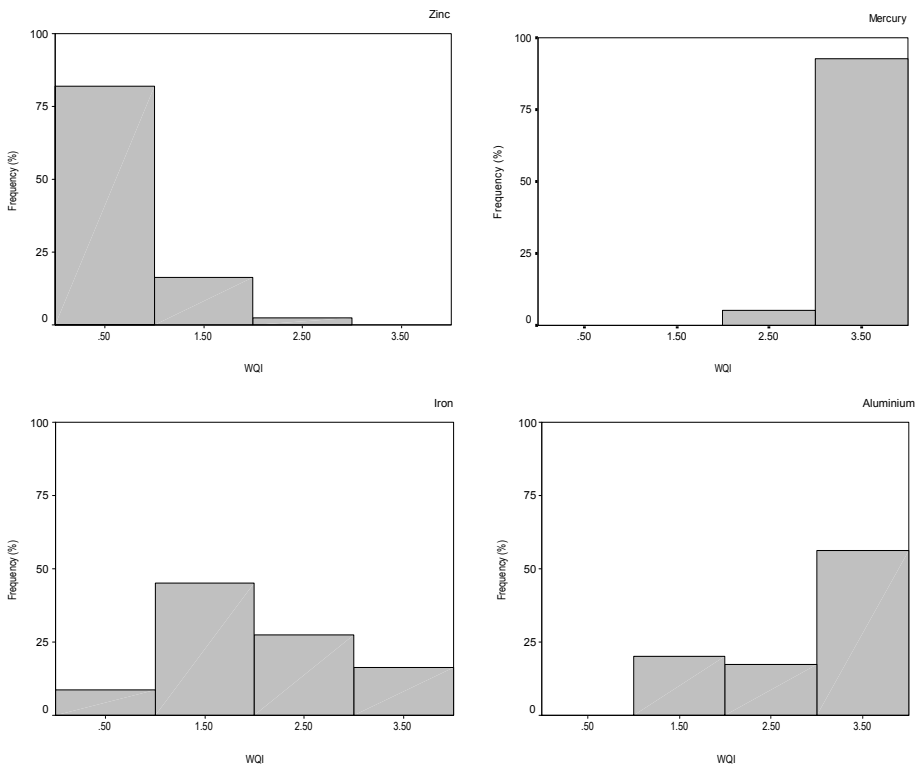


Fig. 3. Relative frequency histograms for Group I variables

The highest proportion of the samples represented “Class IV water” for mercury and aluminum, both of which were determined as the most serious threat among Group I parameters. In contrast, index score of samples analyzed for zinc were dominantly 1 and 2. Therefore, zinc was not a serious risk among Group I variables.

Furthermore, spatial differences among monitoring stations were analysed. In this scope, complying with Turkish Water Pollution Control Regulation, 90th percentile of

each data set was determined as the characteristic value. In addition to 90th percentile, median values were used for comparison and results are presented in Table 5.

Based on the median and 90th percentile values, it was concluded that the sites “1, 2, 6, 7, 8 and 9” appeared to be the most influenced parts from metal industry discharges. In contrast, Sites 3, 4 and 5 were the regions reflecting impact of discharges at minimum level.

As mentioned before, water quality classes were defined by assigning each sampling value to a number between 0 and 4. In this case, index scores greater than “4” were set to upper class limit value index score which is “4”. In the study, to give an idea about the extreme values (classified under Class IV and having index score greater than 4), the ratio of water quality parameters sampling values to Class IV reference values was analyzed. The range of exceedance rates is presented in Table 6.

Based on these values it was concluded that mercury was the most critical parameter with high ratios at the stations 1-3-4-5 and 7. The second critical variable was Al with relatively lower values.

Water quality classification and spatial variability for the Group II

Correlation analysis and WQI calculation have been performed for Group II variables. Correlation matrix is presented in Table 7. It is evident that Group II variables were significantly positively correlated. This could be explained by effect of “tannery-textile industrial discharges” on surface water.

Table 5. Median and 90th percentiles of data sets comprising index values for Group I variables at monitoring stations

Variable		Monitoring Sites								
		1	2	3	4	5	6	7	8	9
Zn	Median	1.0	0.6	0.3	0.3	0.3	0.3	0.4	0.4	0.4
	90 th percentile	1.9	1.8	1.0	0.6	1.0	1.3	0.8	1.0	1.2
Hg	Median	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
	90 th percentile	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Fe	Median	2.0	3.8	1.3	0.9	1.2	1.5	2.1	1.5	1.5
	90 th percentile	2.8	4.0	2.3	1.2	1.7	2.1	3.0	2.4	3.3
Al	Median	3.9	4.0	3.5	2.0	4.0	4.0	4.0	2.1	2.4
	90 th percentile	4.0	4.0	4.0	2.2	4.0	4.0	4.0	4.0	4.0

Table 6. Exceedance over the threshold values (Class IV waters) for Group I variables

Variable	Monitoring Sites								
	1	2	3	4	5	6	7	8	9
Zn	-	-	-	-	-	-	-	-	-
Hg	5-10	1-5	5-10	5-10	5-10	1-5	5-10	1-5	1-5
Fe	-	1-5	-	-	-	-	-	-	-
Al	1-5	5-10	1-5	-	1-5	1-5	1-5	1-5	1-5

Table 7. Correlation coefficients between Group II variables

	T-Cr	Cd	Ni
T-Cr	1.0	0.5	0.7
Cd		1.0	0.6
Ni			1.0

Frequency histograms plotted for three variables are depicted in Figure 4. In these histograms, while more than 75% of the samples analyzed for cadmium belonged to Class IV, water quality class for nickel was mainly Class III and Class IV with lower frequency. On the other hand, the variability of concentrations for chromium was higher than for the others. Samples represented Class II–IV waters with about 25% and Class III waters with 50% frequency.

Spatial differences among sites based on index scores of Group II variables were also analyzed (using the median and 90th percentile of each data set) and results are presented in Table 8. Based on these values it can be concluded that stations “1 and 2” were heavily affected from tannery and textile industry effluent. In contrast, other sites were influenced from discharges to a lesser extent.

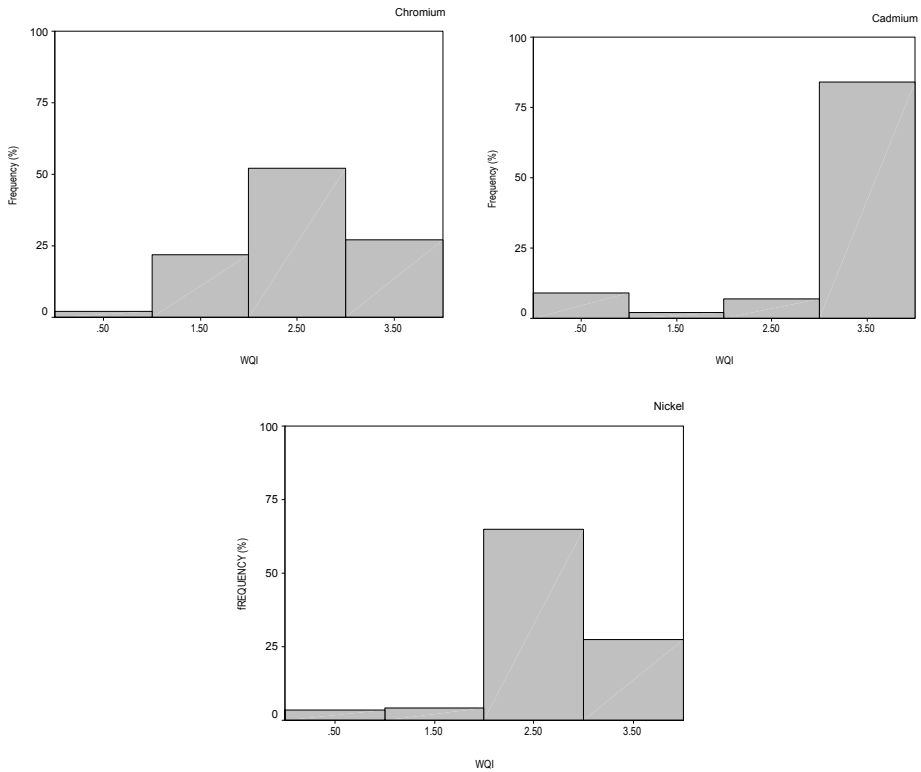


Fig. 4. Relative frequency histograms for Group 2 variables

What is more, exceedance ratios over the threshold values (Class IV waters) for Group II variables sampling results changed mainly between 1 and 5 (see Table 9). Sites 4 and 5 had no value exceeding threshold for total chromium and nickel.

Influence of Water Quality from Physical Parameters (Discharge and Temperature)

Although the variables analyzed for total chromium, zinc, mercury, cadmium, nickel and aluminum could be naturally found in surface water, their high level of concentrations in the study area was the evidence of industrial discharges to the river.

The correlation study was performed to measure strength of the relation between water quality variables and physical parameters. Results presented in Table 10 show that pollution parameters have not been influenced by changes in physical factors (discharge and temperature).

CONCLUSION

This study evaluated the applicability of the water quality index and also environmetric methods for the study area using heavy metal observations. Overall objective was water

Table 8. Median and 90th percentiles of data sets comprising index values for Group II variables at monitoring stations

Variable		Monitoring Sites								
		1	2	3	4	5	6	7	8	9
T-Cr	Median	3.1	2.4	2.4	2.4	2.3	2.7	2.5	2.3	2.3
	90 th percentile	4.0	3.4	3.1	2.7	3.3	2.9	3.7	3.2	3.7
Cd	Median	4.0	4.0	3.3	4.0	4.0	3.5	3.0	3.0	3.0
	90 th percentile	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Ni	Median	3.9	2.7	2.3	2.3	2.2	2.3	2.3	2.3	2.3
	90 th percentile	4.0	4.0	2.9	2.4	3.4	2.5	2.9	2.9	3.7

Table 9. Exceedance over the threshold values (Class IV waters) for Group II variables

Variable	Monitoring Sites								
	1	2	3	4	5	6	7	8	9
T-Cr	1-5	1-5	1-5	-	-	1-5	1-5	1-5	1-5
Cd	1-5	1-5	1-5	1-5	1-5	1-5	1-5	1-5	1-5
Ni	1-5	1-5	-	-	-	1-5	1-5	1-5	1-5

Table 10. Correlation coefficients between physical variables (Q; T) and water quality parameters

	T-Cr	Zn	Hg	Cd	Fe	Ni	Al
Q	-.03	-.07	-.06	-.05	.22	-.11	-.07
T	.06	-.04	-.06	-.06	-.11	-.01	.06

pollution fingerprinting, determination of spatial differences and also analyzing impact of physical factors on water quality.

Factor and cluster analysis offered a valuable tool for estimation of contaminant sources. Two groups were extracted and Group I included iron-aluminum-zinc and mercury variables which could be mainly found in metal industry discharge. On the other hand, the existence of total chromium, nickel and cadmium in Group II was explained by the influence of surface water quality from tannery and textile industry effluent. Therefore, it was concluded that heavy metal content of surface water in the region was mainly governed by metallic, tannery and textile industry discharges. Water quality analyzed for both groups mainly belonged to Class III and IV, which represented polluted and heavily polluted waters. Spatial differences were also examined and results revealed that although variability of level of impact from both groups of pollutants, Kemalpaşa and Menemen appeared to be the most effected region from metal industry discharges. In contrast, upstream part was influenced by pollution to a lesser extent. Similarly, textile and tannery industries effluents affected water quality dominantly at Kemalpaşa region. Correlation analysis examined the relation between quality variables and physical parameters (discharge and temperature). Results showed that pollution parameters were not affected from changes in discharge and temperature. The study showed that there was need to monitor water quality on a regular basis and extract information from data sets using environmetric methods and index approach for basin specific management decisions.

ACKNOWLEDGEMENTS

I wish to thank the members of the Izmir Water and Sewerage Authority (IZSU) and Dr. Vildan Gündoğdu for their support in providing necessary data for the study.

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PROCESS OPTIMIZATION OF NICKEL EXTRACTION FROM HAZARDOUS WASTE

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Keywords: Factorial design, hazardous waste, nickel extraction, optimization.

Abstract: Zinc plant residue is a hazardous waste which contains high quantity of nickel and other valuable metals. Process parameters such as reaction time, acid concentration, solid-liquid ratio, particle size, stirring speed and temperature for nickel extraction from this waste were optimized using factorial design. Main effects and their interactions were obtained by the analysis of variance ANOVA. Empirical regression model was obtained and used to predict nickel extraction with satisfactory results and to describe the relationship between the predicted results and the experiment results. The important parameters for maximizing nickel extraction were identified to be a leaching time solid-liquid ratio and acid concentration. It was found that above 90% of nickel could be extracted in optimum conditions.

INTRODUCTION

The industrial processing residues are the most important sources of environmental contaminations. Some of these wastes are recyclable and recycling the valuable part of these wastes instead of landfill depositing is an important issue from both environmental and economic point of views [1–3]. Zinc plant residue is a hazardous waste containing considerable amounts of metals, such as zinc, cadmium and nickel. It has been shown that the zinc plant residue poses potential environmental risks because it exhibits significant heavy metals solubilization [4–7].

Nickel is a strategic metal due to its extensive application in the production of stainless steel, alloy, battery, and catalyst [8, 9]. Recently, by depletion of primary nickel resources, a lot of researches have been done on the extraction of nickel from secondary resources, including spent catalyst [10–12], waste battery [13, 14] alloys and other waste nickel scraps [15–18] and tailings [19, 20]. In addition, the kinetics of nickel leaching from nickel alloys has been studied in some recent researches [12, 21–23].

In the state of our knowledge, there is not enough information about nickel extraction from zinc plant residue and only one study has been performed on this waste [24]. In

addition, there is not any detailed investigation about statistical optimization of nickel extraction from zinc plant residue.

Optimization of the process parameters in the leaching of zinc plant residue is of special importance. In classical experimental design, it is necessary to perform a large number of tests. Statistical design of experiments is a simple and systematic method to optimize a design for process performance, quality and cost of products. Statistics design of experiments can cover a larger area of experimental statistics and obtain unambiguous results at the minimum expense [25, 26]. Factorial design is a standard technique and widely used for studying a random response to a set of k possible factors [25, 26]. With the factorial design methodology, main effects, interaction effects and low-order interactions may be estimated [27, 28].

In this study, the most significant factors affecting the nickel extraction from zinc plant residue were studied. In order to obtain satisfactory nickel extraction at reasonable leaching times, parametric optimization and modeling of nickel extraction were investigated. A two-level factorial design was used to model the nickel extraction under different process conditions. In addition, the adequacy of the model was evaluated by analysis of variance.

MATERIALS AND METHODS

Material

The zinc plant residue used in the study came from Calcimin zinc plant in Iran. Table 1 shows the chemical composition of the sample. The chemical analysis was performed using X-ray diffractometer (Philips, Xunique II). As can be seen in Table 1, the concentration of nickel oxide was relatively high and the sample contained large amounts of cadmium and zinc. X-ray diffraction (XRD) analysis using Philips PW 1140 showed that the zinc-bearing minerals were the major components in the sample, and that cadmium, nickel and lead components were also present in the sample. Sulphuric acid (98%) was purchased from Merck (Germany) and used as leaching reagent. Leaching experiments were carried out in a 500 ml reactor equipped with a stirrer motor for mixing and a reflux condenser to prevent losses by evaporation.

Table 1. The chemical analysis of the sample

Component	ZnO	CdO	NiO	CuO	PbO	SO ₃	CaO	Fe ₂ O ₃	MgO	Al ₂ O ₃	LOI [*]
Amount (%)	38.92	16.56	4.21	1.99	1.38	12.10	2.61	0.44	0.20	0.34	20.54

Loss on ignition (LOI) is the sample weight reduction after being ignited.

Method

The representative sample was crushed and milled to collect the desired fraction for experiments. In the experiment, a 500 ml glass reactor fitted with an overhead stirrer was used. Temperature was controlled by water bath equipped with a thermostat. The reactor was fitted with a reflux condenser to prevent liquid loss by evaporation when the system was heated. In the experiments, after the desired temperature of the reactor content was reached, the reaction was initiated by adding the required volume of sample to 100 ml

leaching solution based on the required solid-liquid ratio. The concentrations of nickel in leach liquors were determined by using Unicom atomic absorption spectrometry (AAS).

Experimental design

Factorial design is a useful tool for characterizing multivariable processes. It gives the possibility to separate the important factors from those which are not, and identifying any possible interactions between them [29]. By factorial design, the optimum leaching conditions having satisfactory nickel extraction can be achieved with minimum number of experiments. The Design Expert Software (version 8.0) was used for the design of experiments and data analysis. In this investigation, factorial design was applied to optimize the most important operating factors. In the leaching experiments, based on preliminary tests, reaction time (t), temperature (T), acid concentration (c), particle size (p), solid-liquid ratio (s/l) and stirring speed (ss) were chosen as the six factors to be investigated. These variables may affect the response of the dissolution system, and it is practically impossible to identify and control the small contributions from each one. Statistical design was carried out to determine which of these variables, and their interactions presented more significant effects. Two-level factorial designs are efficient and economical for the screening of variables [30, 31]. In this study, factorial design was used in order to estimate main factors as well as interaction effects. The variables and levels of our factorial design are given in Table 2.

Table 2. Control factors and their levels in leaching experiments

Control factor	Unit	Levels	
		Low level	High level
Reaction time	min.	10	40
Reaction temperature	°C	25	75
Acid concentration	%	5	10
Particle size	µm	75	250
Solid/liquid	g/l	50	200
Stirring speed	rpm	300	600

After evaluation of the results by design Expert Software 8.0, the desirability function was used for the optimization of the process. The desirability function gives the possibility to predict the optimum levels for the independent variables [28, 32].

RESULTS AND DISCUSSION

Analysis of the effects of main factors and their interaction

The experimental tests were carried out randomly to avoid systematic errors during the collection of extraction data. In order to recognize effective parameters of the nickel extraction, the experiment results were entered into Design-Expert 8 software. We have chosen factorial design to fit the results. The test conditions and their results are shown in Table 3.

Table 3. Screening test conditions and their results

Run	A: Time Minutes	B: Temperature °C	C: Acid Concentration %	D: Particle Size Micron	E: Solid/ /Liquid (w/w)	F: Stirring speed RPM	Extraction (%)
1	40	75	5	75	5	300	92
2	10	25	5	75	5	300	69
3	10	75	10	75	5	300	89
4	40	25	5	75	20	300	36
5	25	50	7.50	75	12.50	450	79
6	10	25	5	250	20	300	30
7	10	75	10	250	5	600	89
8	10	75	5	75	5	600	81
9	10	25	5	75	20	600	33
10	10	25	10	250	20	600	53
11	10	75	10	75	20	600	57
12	25	50	7.50	75	12.50	450	77
13	40	75	10	250	20	600	64
14	10	25	10	75	20	300	46
15	25	50	7.50	250	12.50	450	76
16	25	50	7.50	250	12.50	450	75
17	40	75	10	250	5	300	99
18	25	50	7.50	250	12.50	450	74
19	40	75	5	250	5	600	99
20	10	75	10	250	20	300	50
21	25	50	7.50	75	12.50	450	75
22	40	25	10	75	20	600	70
23	10	75	5	250	20	600	34
24	40	25	10	75	5	300	95
25	40	25	10	250	20	300	64
26	10	75	5	75	20	300	30
27	40	75	10	75	5	600	99
28	10	25	10	250	5	300	78
29	40	75	10	75	20	300	65
30	25	50	7.50	75	12.50	450	78
31	40	25	5	75	5	600	97
32	40	75	5	250	20	300	37
33	40	25	10	250	5	600	99
34	40	25	5	250	20	600	36
35	10	75	5	250	5	300	69
36	25	50	7.50	250	12.50	450	77
37	10	25	10	75	5	600	89
38	40	25	5	250	5	300	83
39	10	25	5	250	5	600	78
40	40	75	5	75	20	600	47

The experimental results can be examined by the analysis of variance (ANOVA). Important factors and the significance of their effects and interactions of the operating factors on the investigated variables during the nickel leaching tests can be estimated using ANOVA [27, 28, 33]. ANOVA is based on the partitioning of the total variability of data (SS_T) into its component parts related to the principal effects of each factor (SS_A , SS_B , ...), to their interactions (SS_{AB} , SS_{BC} , ..., SS_{ABC} , ...) and to the experimental error (SS_{ERR}) [28, 33, 34]:

$$SS_T = \sum_{i=1}^{n_i} (x_i - \bar{x})^2 = SSA + SS_B + \dots + SS_{AB} + SS_{BC} + \dots + SS_{ABC} + \dots + SS_{ERR} \quad (1)$$

where i refers to different experiments conditions examined in the design, n_i is the number of tests in each design, x_i are the dependent variables observed during the leaching tests (i.e., c nickel extraction), \bar{x} is the average of x_i , the capital letters indicate the investigated factor, and SS_k is the generic sum of squares. The experimental error contribution (SS_{ERR}) was evaluated by the replicates of the central point of each factorial design as [28, 33, 34]:

$$SS_{ERR} = \sum_{j=1}^{n_j} (x_j - \bar{x})^2 \quad (2)$$

Where x_j are the values of the investigated variables (nickel extraction) in the replicates obtained under the conditions chosen for the central point, n_j is the number of replicates and \bar{x} is the average of x_j .

The sum of squares and the F test were used to estimate the effect of the factors. The experimental results were examined by the analysis of variance (ANOVA) to evaluate the significance of the main effects and interactions of the operating factors on the investigated parameters during the leaching tests (Table 4).

According to ANOVA analysis, solid liquid ratio, acid concentration and reaction time were the most significant factors affecting the nickel extraction in decreasing order under the investigated conditions. The predicted nickel extraction values against the actual values and normal plot of residual for nickel extraction are shown in Figure 1 (a and b). Figure 1a shows that the points follow a straight line, therefore the residuals follow a normal distribution. Figure 1b does not show significant differences between actual and predicted extraction.

The effects of important variables and their interactions are shown in Figure 2. In this section, our aim was as to maximize the nickel extraction and also to determine the most significant factors affecting the response. The results revealed that the reaction temperature, stirring speed and particle sizes did not significantly influence nickel extraction under the investigated conditions. It was also obvious that the reaction time, acid concentration and solid-liquid ratio influenced remarkably the nickel leaching. Reaction time and acid concentration positively affected nickel dissolution while nickel extraction decreased by increasing solid-liquid ratio. This conclusion is also proven by the ANOVA analysis shown in Table 4.

Temperature had a little positive effect on nickel extraction and the nickel extraction increased only a little when reaction temperature increased from 25 to 75°C. Nickel

Table 4. ANOVA for the nickel extraction

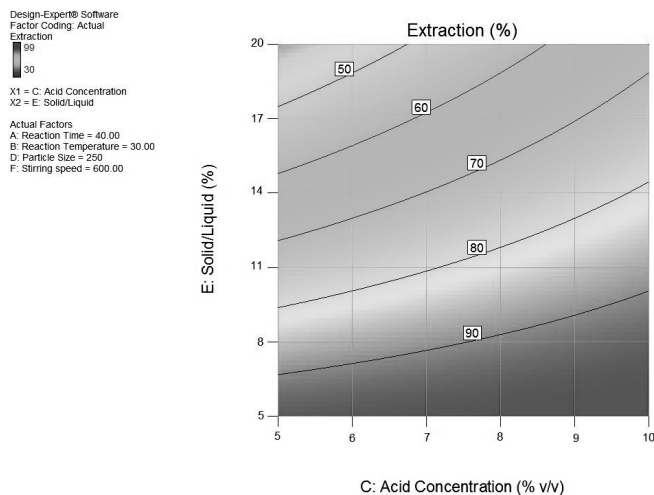
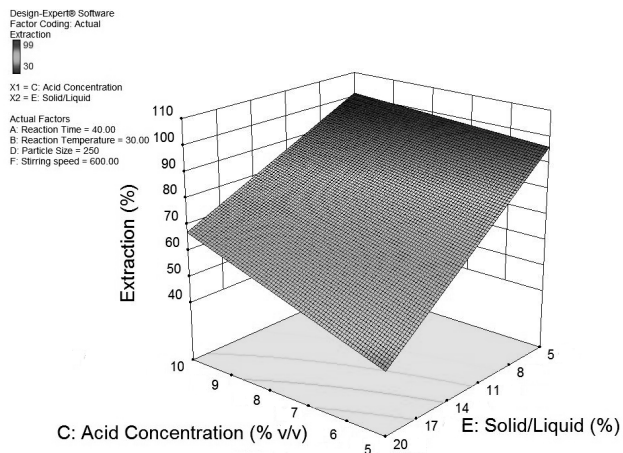
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	17656.81	11	1605.16	233.64	< 0.0001
A-Reaction Time	1339.03	1	1339.03	194.90	< 0.0001
B-Reaction Temperature	63.28	1	63.28	9.21	0.0054
C-Acid Concentration	2032.03	1	2032.03	295.78	< 0.0001
D-Particle Size	34.03	1	34.03	4.95	0.0349
E-Solid/Liquid	13325.28	1	13325.28	1939.58	< 0.0001
F-Stirring speed	270.28	1	270.28	39.34	< 0.0001
AC	0.031	1	0.031	4.549E-003	0.9467
AE	38.28	1	38.28	5.57	0.0260
CE	427.78	1	427.78	62.27	< 0.0001
ACE	94.53	1	94.53	13.76	0.0010
ADE	26.28	1	26.28	3.83	0.0613
Residual	178.62	26	6.87	-	-
Pure Error	13.75	6	2.29	-	-
Cor Total	18350.40	39		-	-

extraction efficiency was not affected so much by a change in particle size, although the extraction increased slightly using smaller particle size. Under the experimental conditions, extracted nickel increased a little by increasing stirring speed from 300 to 600 rpm. Stirring speed positively affects nickel leaching rate but this effect is not one of the most important ones in relation to nickel extraction.

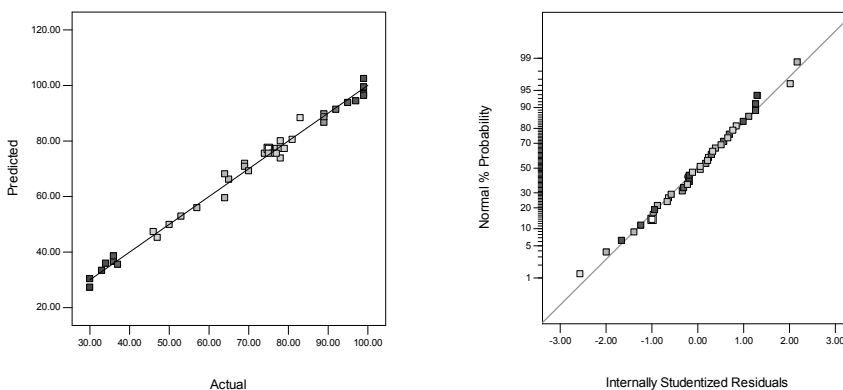
Reaction time positively influenced nickel extraction. Reaction time was significant in the first 20 minutes of extraction and then its importance decreased. Acid concentration was one of the most significant factors in nickel dissolution rate at each time. Solid-liquid ratio had a negative effect on nickel dissolution rate, and it was the most important factor which influenced nickel extraction yield. This effect was higher as compared to other factors such as acid concentrations and reaction time.

Process optimization

The goal of the optimization of nickel extraction was to find the levels of parameters, where nickel leaching rate could be maximized. In the optimization procedure, it is necessary to consider all the responses that may affect the nickel leaching yield. The optimization of nickel leaching was carried out by a multiple response method (desirability function) to optimize different combinations of the process parameters such as reaction time, acid concentration, solid-liquid ratio, particle size, temperature and stirring speed. The desirability function equation that describes the influence of the factors on the overall desirability was as follows:



a



b

Fig. 1. a: Predicted vs. actual values of nickel extraction %, b: Normal plot of residual for nickel extraction

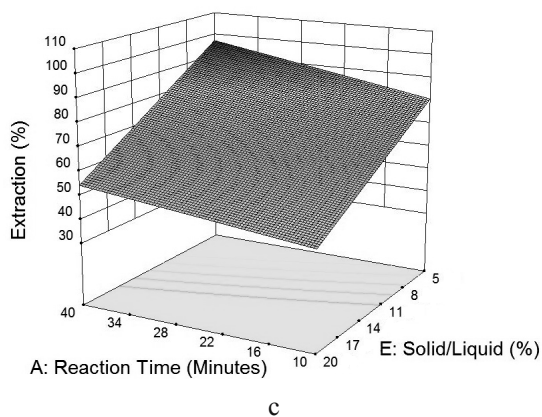
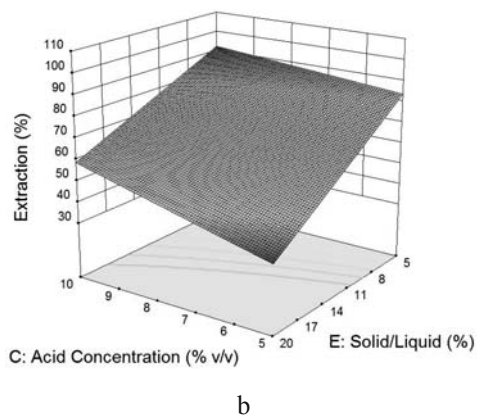
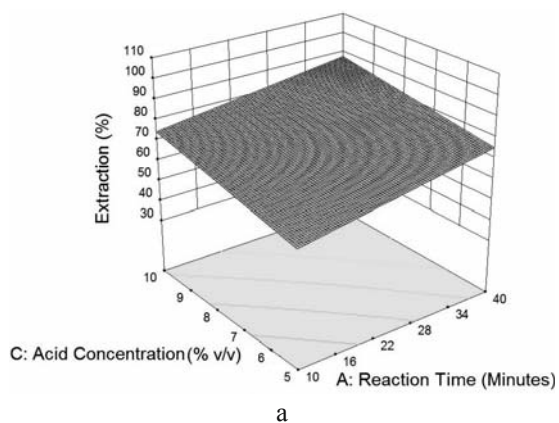
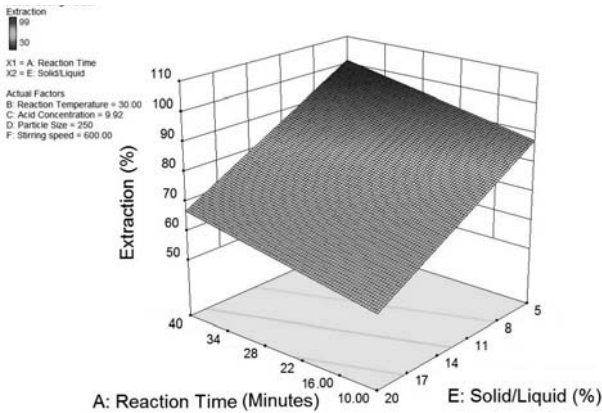
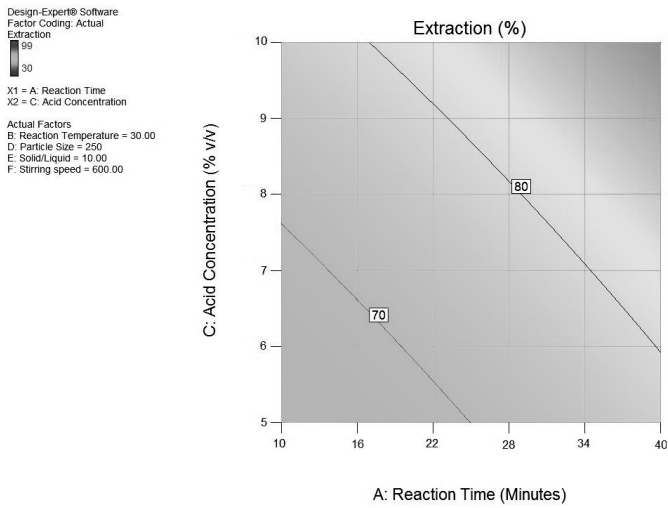
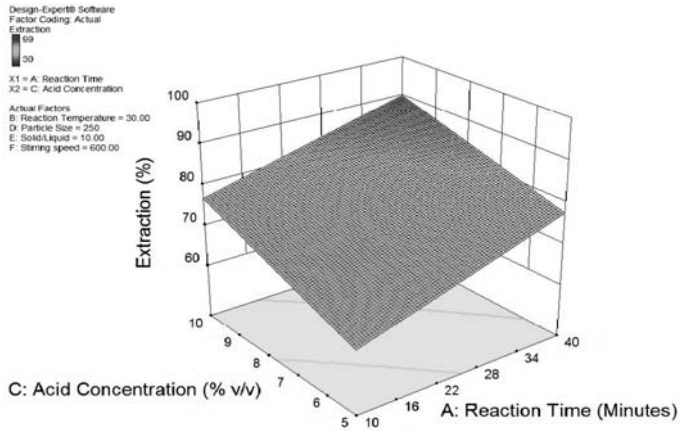
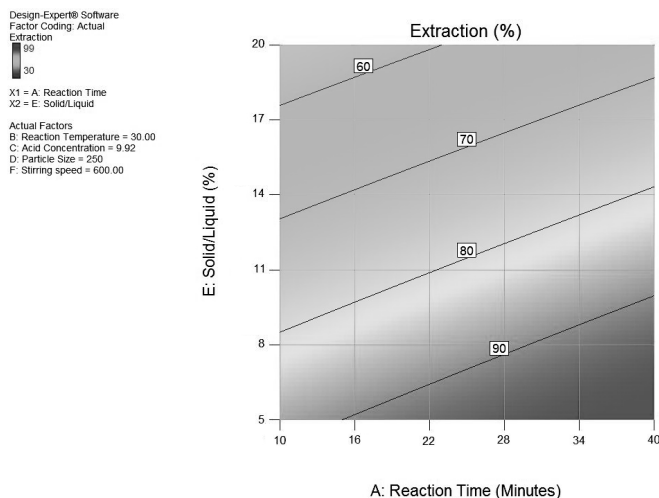


Fig. 2. The effects of Main variable interaction on the nickel extraction, a: acid concentration and reaction time, b: acid concentration and Solid/liquid ratio, c: Solid/liquid ratio and reaction time





b

Fig. 3. 3D surface and contour plot for nickel extraction. (a) Influence of the acid concentration and solid-liquid ratio on the overall nickel extraction, (b) Influence of the acid concentration and reaction time on the overall nickel extraction, (c) Influence of the reaction time and solid-liquid ratio overall nickel extraction

$$\begin{aligned} \text{Extraction} = & +57.58 + 1.119 \times \text{Reaction Time} + 0.0562 \times \text{Reaction Temperature} \\ & + 2.639 \times \text{Acid Concentration} - 2.794 \times \text{Solid/Liquid} + 0.019 \times \text{Stirring speed} - 0.075 \quad (3) \\ & \times \text{Reaction Time} \times \text{Acid Concentration} - 0.057 \times \text{Reaction Time} \times \text{Solid/Liquid} \\ & + 0.042 \times \text{Acid Concentration} \times \text{Solid/Liquid} \end{aligned}$$

Table 5 shows several optimum conditions, and the expected results for nickel extraction. It is possible to extract 90% of the content by 9.9% (v/v) acid concentration at solid-liquid ratio of 0.10. Figure 3 shows the influence of the factors on the overall nickel extraction at optimum conditions. The study of these plots showed that higher than 90% nickel could be extracted at high amounts of acid concentration and low values of solid-liquid ratios.

In order to check the reliability of the results suggested by the model, four additional tests were conducted applying the optimum conditions to confirm the

Table 5. Optimum process conditions and their results

Number	Reaction Time (min)	Reaction Temperature (C)	Acid Concentration (V/V)%	Particle Size (micron)	Solid/Liquid	Stirring speed (RPM)	Extraction (%)
1	40.00	31.5	9.90	250	10.00	600	90
2	40.00	33.5	10	250	10.10	600	90
3	40.00	37.0	9.85	250	10.00	590	90

Table 6. Verification experiments at optimum conditions

Number	Reaction Time (min)	Reaction Temperature (C)	Acid Concentration (V/V)%	Particle Size (micron)	Solid/Liquid	Stirring speed (RPM)	Extraction (%)
Model							90
Experiment	40.00	31.5	9.90	250	10.00	600	91.5
Model							90
Experiment	40.00	33.5	10.00	250	10.10	600	93
Model							90
Experiment	40.00	37.0	9.85	250	10.00	590	92

agreement between model results and experiment results. As can be seen from Table 6, there was a good agreement between the predicted and the experimental values, so it we concluded that the effects of important variables on nickel extraction can be predicted properly by equation 3.

CONCLUSION

The results of this study showed that more than 90% of nickel can be extracted from hazardous waste. The effects of operating parameters such as reaction time, temperature, acid concentration, solid-liquid ratio, stirring speed and particle size on the nickel leaching were studied using factorial design. The results showed that the time, acid concentration and solid-liquid ratio were the main factors, and the interactions between these variables were found to be statistically significant. A model was developed by designing expert 8 software to predict nickel extraction. The process optimization was performed, and the experimental results were found to agree satisfactorily with the predicted values.

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EVALUATION OF ANTHROPOGENIC POLLUTION IN RIVER WATER BASED ON THE GENETIC DIVERSITY OF *AEROMONAS HYDROPHILA*

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Keywords: *Aeromonas*, river water, aquaculture, DNA marker, genetic diversity.

Abstract: *Aeromonas hydrophila* is a valuable indicator of the quality of water polluted by sewage and pathogens that pose a risk for humans and cold-blooded animals, including fish. The main aim of this research was to evaluate anthropogenic pollution of river water based on genetic diversity of 82 *A. hydrophila* strains by means of RAPD, semi-random AP-PCR (ISJ) and the rep-BOX conservative repeats test. Genetic diversity of *A. hydrophila* was $HT = 0.28$ ($SD = 0.02$) for all DNA markers (RAPD, semi random and rep-BOX). None of the analyzed electrophoretic patterns was identical, implying that there were many sources of strain transmission. The presence of genes for aerolysin (*aerA*), hemolysin (*ahh1*) and the cytotoxic enzyme complex (AHCYTOGEN) was verified for all tested strains, and drug resistance patterns for tetracycline, enrofloxacin and erythromycin were determined. The most diverse *A. hydrophila* strains isolated from river water were susceptible to enrofloxacin ($HS = 0.27$), whereas less diverse strains were susceptible to erythromycin ($HS = 0.24$). The presence of the multidrug resistance marker (ISJ4-25; 1100 bp locus) in the examined strains (resistant to three analyzed drugs) indicates that intensive fish cultivation affects the microbiological quality of river water.

INTRODUCTION

Aeromonas hydrophila Gram-negative heterotrophic and nonsporulating bacterium is an important etiological factor of disease in fish and humans [2, 11], and together with *Escherichia coli*, it is an indicator of water quality [29]. *A. hydrophila* as well as *Pseudomonas* spp. and *Vibrio* spp. are the predominant microorganisms in surface waters such as rivers, lakes and ponds [16]. The ecology, biochemistry and the genome of *A. hydrophila* has been very well researched [7, 24]. In their efforts to analyze the genetic diversity of *A. hydrophila*, most researchers have focused on taxonomic aspects of identification [10], mutations in drug resistance genes [12], selected sequences responsible for virulence [5], transposable genetic elements [6] and repeated sequences [19, 25, 30]. There is a general scarcity of information

about the diversity of the *A. hydrophila* genome, with the exception of selected, non-representative and well-researched regions [26]. Although the structure of the discussed genome has been well documented, little is known about the genetic variability of the entire *A. hydrophila* genome. The use of randomly amplified and semi-random DNA markers could support a comparison of genetic diversity between *A. hydrophila* and *E. coli*. A higher level of genetic diversity points to various sources of origin (pollution) and high genetic potential for multidirectional phenotypic differentiation, in particular varied resistance to drugs (single drug, multi-drug and extended resistance) [15]. The aim of this paper was to evaluate the anthropogenic pollution of river water based on genetic diversity and similarity of drug-resistant and virulent strains of *A. hydrophila*.

MATERIALS AND METHODS

Genetic variation in arbitrary regions of the *A. hydrophila* genome was analyzed based on 82 strains that had been isolated during a previous study of the upper section of the Drwęca River. The process of phenotypic and molecular identification of *A. hydrophila* has been described in detail by Gołaś *et al.* [2009]. The selected strains were Gram-negative, motile, oxidase and catalase positive and β -hemolytic positive with confirmed presence of *aer* and *ahh1* genes. Their resistance to tetracycline (TE), enrofloxacin (ENR) and erythromycin (E) was tested on Oxoid discs. The tested strains were described as resistant (R), moderately resistant (MR), susceptible (S) as well as multidrug resistant to TE+ENR+E (MDR). Only moderately resistant and susceptible strains were tested to determine the enrofloxacin resistance pattern.

Nucleic acids of the studied *A. hydrophila* strains were extracted by the modified [17] CTAB method [4]. The quality and quantity of DNA were analyzed photometrically. Long RAPD and short semi-random primers were applied with the following respective sequences: OPB06-5'TGCTCTGCCC3', OPA11-5'CAATCGCCGT3', ISJ2-5'ACTTACCTGAGGCGC-CAC3', ISJ4-5'GTCGGCGGACAG-GTAAGT3'. Primer A1R-5'CTACGGCAAGGCGACGCTG-ACG3' was used to amplify the rep-boxA sequence for 15 randomly selected strains. The thermal profile and the chemical conditions for PCR were consistent with previous recommendations [8, 27, 28]. Each amplification was performed in three replications to compare results and test the reproducibility of electrophoretic patterns. Visible bands on gel were scored as loci (allele 1). The A1R primer indicated sites compatible with the region of the boxA repeat sequence. The absence of a compatibility site in the same locus was marked as allele 0 or a place of incompatibility (PI) in the boxA sequence. *A. hydrophila* is a haploid, therefore, it was assumed that the obtained molecular phenotypes corresponded to genotypes. Alleles "1" or "0" were observed in every locus. Allele frequencies were calculated using POPGENE 1.32 software [31]. Genetic diversity coefficients (H , h) were determined by Nei's method based on allele frequencies in a locus [22]. The genetic similarity coefficient (I) was calculated based on shareable bands between strains. *A. hydrophila* populations were grouped by minimum evolution (ME), neighbor joining (NJ) and unweighted pair grouping with arithmetic mean (UPGMA) [22]. Dendrograms were developed using POPGENE 1.32 and MEGA v 3.1 software [31]. Clustering results were validated by principal component analysis.

RESULTS

All primers revealed 82 different molecular phenotypes ($G = 1$ or $G = 100\%$). A total of 168 loci were scanned, and all of them were found to be polymorphic ($P = 100\%$). Short primers (10 nt) revealed 1 to 24 amplification products (amplicons), including 1–13 for OPB and 1–15 for OPA. In 42 strains, “allele 1” was observed predominantly in locus OPB-33 as a band with molecular weight of around 2.5 kbp. Long primers (18 nt) generated 1 to 31 amplicons. Allele 1 was most frequently determined in locus ISJ2-30 (46 strains) and ISJ4-23 (36 strains) as a band with molecular weight of 1.6 kbp and 1 kbp, respectively (Fig. 1).

An analysis of 0–1 patterns produced after amplification with RAPD and AP-PCR primers revealed that the strains were not grouped as resistant (R), moderately resistant (MR) or susceptible (S) in line with TE, ENR and E patterns. Minimum evolution (ME) changes in 82 strains grouped based on their resistance to tetracycline (TE) revealed two main clusters of 11 and 71 strains each (Fig. 2). Strain grouping by the neighbor joining (NJ) method revealed 9 clusters containing strains with different TE resistance patterns. UPGMA revealed 5 clusters, one of which contained 20 out of the 30 strains susceptible to TE.

The results were analyzed by the ME method in view of the enrofloxacin resistance pattern to reveal two clusters and a similar number of strains in each cluster (12 and 70). In cluster I, all strains were resistant with one exception, and in cluster II, nine different groups of strains were identified. The neighbor joining (NJ) method was used to divide the strains into 11 clusters of strains with various ENR resistance patterns. Cluster ENR contained 11 out of the 12 strains characterized by moderate resistance to enrofloxacin (Fig. 2). The UPGMA algorithm was used to divide strains into 5 main clusters, including one with 29 strains that were mostly resistant to ENR.

The clustering of 82 *A. hydrophila* strains by the ME method based on the erythromycin resistance pattern revealed two main clusters of 11 and 71 strains, respectively. The first cluster contained erythromycin resistant strains, whereas the second cluster was divided into 10 groups of mostly erythromycin-resistant strains (66 out of 71). Grouping by the NJ method produced 9 clusters without a clear E resistance pattern, with the exception of cluster E^R where 9 out of 11 strains were resistant to E. The UPGMA

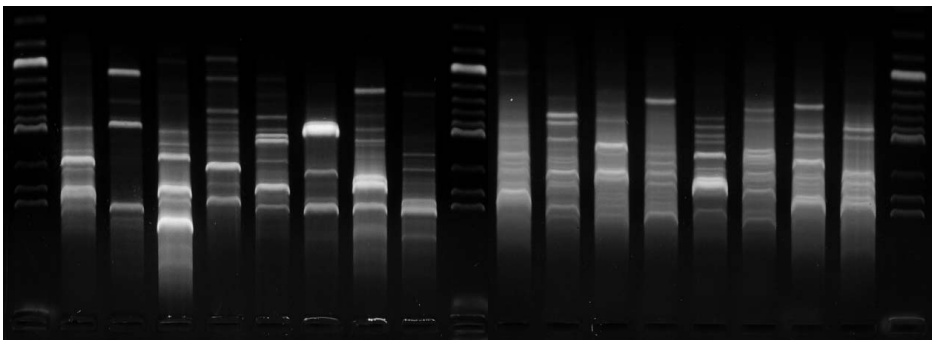


Fig. 1. Electrophoretic patterns of *A. hydrophila* strains obtained with the use of OPB (A) and ISJ4 (B) primers; M – perfect 100bp DNA ladder, AKOR Laboratories

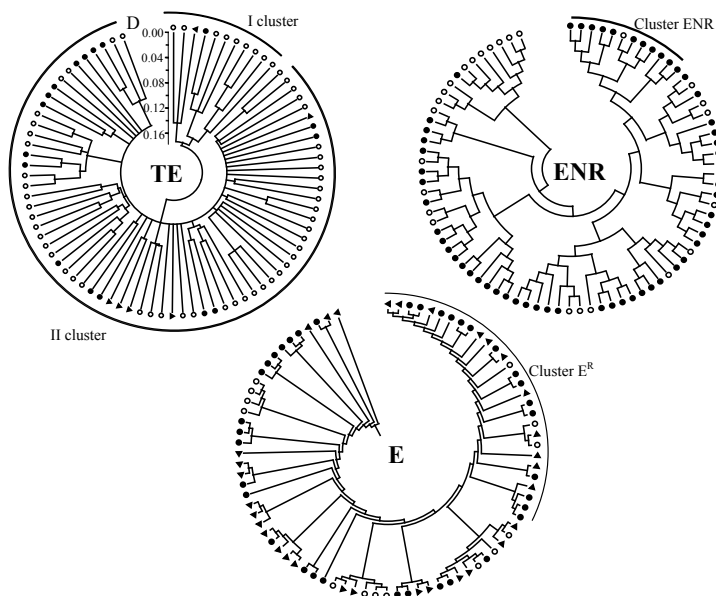


Fig. 2. Grouping of 82 strains after an analysis of arbitrarily primed regions of *A. hydrophila* genome in view of tetracycline (TE), enrofloxacin (ENR) and erythromycin (E) resistance patterns; D – genetic distance, ○ – susceptible strains, ● – moderately resistant strains, ▲ – resistant strains; clustering TE, ENR and E strains by ME, NJ and UPGMA methods, respectively

method was applied to group 82 strains into 5 main clusters, one of which contained 26 out of 29 erythromycin-resistant strains (Fig. 2).

The clustering of 28 multidrug resistant *A. hydrophila* strains revealed 6 groups of strains that were mostly resistant to three drugs. Clusters RI, RII and SI, SII contained only strains that were resistant and susceptible to three drugs, respectively (Fig. 3).

The frequency of allele 1 in locus (A) was determined in a wide range of 0.01 to 0.50, with an average of 0.19 (Table 1). The mean and effective number of alleles in locus (n_a and n_e) was 2 and 1.44, respectively. Mean genetic diversity over a representative locus within species (H_T) was 0.27 with Shannon's index of 0.43. Genetic diversity over locus (h) ranged from 0.02 to 0.50. Nei's coefficient of genetic identity (I_N) for strains was determined in the range of 0.56–0.93, and mean genetic distance (D_N) reached 0.33. The mean genetic distance between populations with similar TE patterns was 0.05 at $I_N = 0.95$ (Fig. 4). Genetic diversity and population structure of TE-susceptible strains were similar to the mean values representative of the *Aeromonas hydrophila* species. Genetic variation between three populations grouped in view of their TE patterns, measured by parameter GST, reached 0.08. The theoretical gene flow between those populations was estimated at $N_m(G_{ST}) = 5.6$. In strains with varied patterns of resistance to ENR, the mean genetic distance was 0.02 and the genetic identity coefficient was determined at $I_N = 0.98$. Similarly to TE-susceptible strains, genetic diversity and population structure of ENR-sensitive strains approximated the average values for the entire *Aeromonas hydrophila* species.

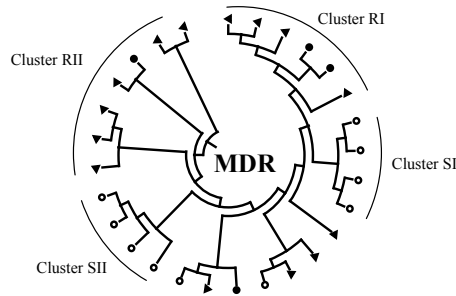


Fig. 3. Grouping of 28 multidrug resistant (MDR) strains based on an analysis of arbitrarily primed regions of *A. hydrophila*. ○ – susceptible strains, ● – moderately resistant strains, ▲ – resistant strains, SI, SII – susceptible clusters, RI, RII – resistant clusters; clustering by the UPGMA method

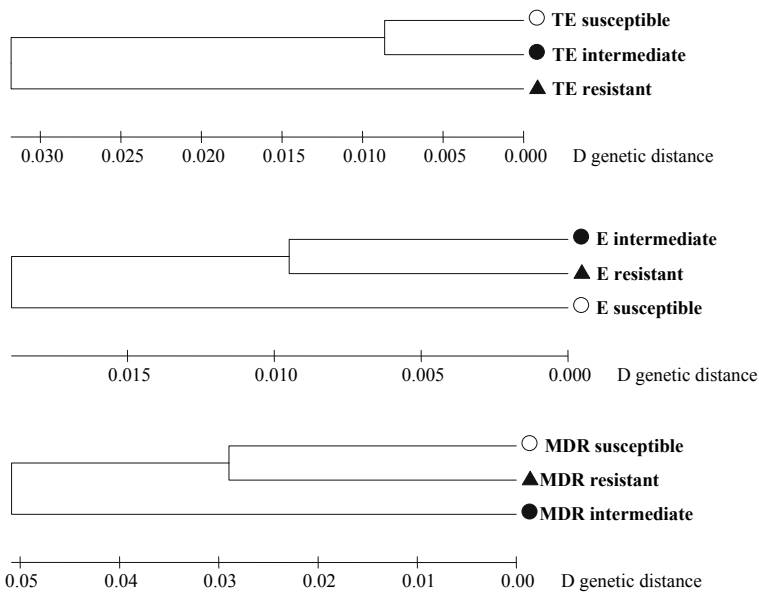


Fig. 4. Genetic distance between *A. hydrophila* strains with various TE, E and MDR resistance patterns; ○ – susceptible strains, ● – moderately resistant strains, ▲ – resistant strains

Genetic diversity between two populations with varied ENR patterns (G_{ST}) was 0.02, and theoretical gene flow was observed at $N_m(G_{ST}) = 21.7$. The mean genetic distance between strains with different erythromycin resistance patterns was 0.03, and genetic identity was determined in the range of 0.96 to 0.98 with an average of 0.97 (Fig. 4). Similarly to TE and ENR patterns, the values indicative of genetic diversity and population structure of erythromycin-susceptible strains approximated the average values representative of the *Aeromonas hydrophila* species. Genetic diversity between three populations with varied

E patterns (G_{ST}) was 0.02, and theoretical gene flow was determined at $N_m(G_{ST}) = 8.4$. For multidrug-resistant *A. hydrophila* strains (MDR), the mean genetic distance D was 0.09, and the genetic identity coefficient I_N reached 0.92 (Fig 4). G_{ST} and gene flow parameter were determined at 0.16 and 2.6, respectively.

The amplification of regions characterized by structural similarities with boxA conserved repeat sequences revealed 15 different phenotypes ($G = 100\%$) and 39 compatible amplification sites (CAS) with $P = 100\%$. In a given CAS, the amplification product was observed with the frequency of 0.21. Genetic diversity for the entire species (H_T) was determined in the range of 0.1 and 0.5 with an average of 0.28. In reference to boxA repeats, genetic identity between 15 strains was 0.77 within the 0.43 and 0.95 range of values. A preliminary clustering analysis revealed two main clusters and a branched pseudocluster (data not shown) of seven strains.

The selection of loci with various drug resistance patterns revealed 7 marker bands of resistance and susceptibility to TE, ENR and E and 6 bands specific for MDR strains (Table 1).

DISCUSSION

In the literature [1, 3], the values of genetic diversity among enzymatic loci (HS) of *Aeromonas* spp. vary extensively between 0.09 and 0.88. In our study, *A. hydrophila* strains sampled from the Drwęca River were characterized by moderate genetic diversity of $H_T = 0.27$. Both types of primers were easy to use, and they produced repeatable, high resolution results in genetic analyses of the studied populations. The grouping of 28 MDR

Table 1. Nei's genetic identity coefficients for *A. hydrophila* strains with various TE, ENR and E resistance patterns

Drug	Pattern	A_{max} (frequency of allele 1)	Resistance marker	Susceptibility marker	Mass [bp]
TE	S	0.56	OPA11-15; ISJ2-29; ISJ4-25; ISJ4-30	none	800; 1500; 1100; 1450
	I	0.59			
	R	0.83			
ENR	S	0.63	none	IS4-21	900
	I	0.56			
E	S	0.79	OPA11-29	ISJ2-33	1600 / 1900
	I	0.64			
	R	0.59			
MDR	S	0.80	OPB6-20	OPB6-25; OPA11-14; ISJ2-33; ISJ4-23	1500; 750; 1900; 1000
	I	1.00			
	R	0.79			

S – susceptible; I – intermediate; R – resistant;

strains revealed clusters of strains resistant to three drugs. A preliminary grouping analysis, performed separately for TE, ENR and E patterns, did not classify the strains according to their drug resistance profiles. In view of the above, all loci were reviewed to identify the resistance marker among RAPD and ISJ amplification products. This is an interesting consideration because there are few simple methods for screening bacterial resistance that can effectively determine a given strain's resistance to a specific drug and the degree of that resistance. In addition, the presented genetic diversity parameters should be correlated with resistance markers (relevant band on gel), and the resulting information should be combined with the degree of anthropogenic pollution in intensive fish farms. The values illustrating *A. hydrophila*'s qualitative and quantitative impacts on the environment can be used as bioindicators of anthropogenic pollution in fish farms.

In 2005, DNA markers were used for the first time to determine the genetic variation of *A. hydrophila*. Most papers do not present or vaguely discuss the parameters describing the genetic diversity of *A. hydrophila*, including the number of loci and amplification sites, types of polymorphism within loci, allele frequency, h parameters, genetic identity and distance. Enzymatic markers and DNA markers obtained in the bacterial population analyses are difficult to compare because very little is known about the dissonance between those molecular markers in bacterial domains. The value of HS reported by Feizabadi *et al.* [9] in an enzymatic analysis of the *M. tuberculosis* complex was lower than that noted by other researchers who relied on DNA markers [17, 26]. Many enzymatic analyses of bacteria, plants and animals produced genetic diversity values that were two- to three-fold lower in comparison with DNA marker tests [13, 21]. Based on the level of genetic diversity reported in this paper, *A. hydrophila* can be classified near the tubercle bacillus (*M. tuberculosis*) [17, 26]. In *A. hydrophila*, the value of H was less than half that reported in *E. coli* (0.85) and other clonal species. Some authors [17] argue that the level of genetic diversity produced by DNA markers should be regarded as acceptable when it is up to 3–4-fold higher than genetic variation values obtained in enzymatic analyses.

The genetic diversity analysis of *A. hydrophila* based on the boxA sequence revealed that this marker is an effective molecular tool in population studies. A box element is dispersed in several copies throughout the *Escherichia coli* genome as a complex of three sectors (boxA, boxB, boxC) [18]. Eight scored bands per strain may be equal to the number of boxA sequences with the length of 59 nt. From among 39 sites compatible with boxA, BOX-6 (450 bp) can be regarded as a selection marker capable of identifying MDR strains of *A. hydrophila* which are potentially harmful for the environment.

The majority of TE-susceptible *A. hydrophila* strains were closely related to moderately resistant strains (Fig. 3). At the same time, the degree of genetic correlation between TE-susceptible strains and highly resistant strains was higher than that between strains characterized by high resistance and moderate resistance to TE (Fig. 3). The above could point to intense selective antibiotic pressure on bacterial cells. Lower genetic similarity between TE-sensitive and moderately TE-resistant bacteria in comparison with TE-resistant strains could result from a higher number of genetic changes in genomic regions complementary to the applied DNA markers. Further studies investigating variations in *tet* and *otr* genes that condition TE resistance in *A. hydrophila* strains are needed to verify the above hypothesis [5, 20].

A high level of genetic identity ($I_N = 0.98$) was also observed between strains that were susceptible and moderately resistant to E. A change from a pattern of moderate

resistance to one of high resistance to E could result from a higher number of minor changes in the studied bacterial genome. Minor changes in DNA could be accumulated due to long-term chemical pressure on the Drwęca River resulting from erythromycin use. The patterns of erythromycin resistance in *A. hydrophila* strains sampled from the Drwęca River should be additionally validated by analyzing the diversity of *mel* and *mph* genes and other pRSB105 plasmid sequences [23]. A statistical analysis of multidrug resistance patterns revealed the presence of the closest genetic relations between strains that were susceptible and highly resistant to three drugs. These results could indicate a small number of genetic changes in the genome of highly MDR strains in comparison with moderately resistant and completely susceptible strains of *A. hydrophila*.

CONCLUSIONS

The evolution of *A. hydrophila* strains which were highly resistant to the tested drugs probably took place faster than the process of acquiring many mechanisms of moderate resistance. In the ecosystem of the Drwęca River, drugs exerted chemical selection pressure on bacterial strains. The regions of the *A. hydrophila* genome tested by arbitrary DNA markers revealed fewer genetic changes in highly resistant than in moderately resistant strains. The above could point to inadequate drug dosage during fish treatment. On the other hand, long-term administration of drugs poses an environmental threat by increasing the dilution of toxic chemicals in the river. The *A. hydrophila* genome was scanned with regard to different resistance patterns to reveal that genetic diversity was related to the tested strains' resistance or susceptibility to drugs. The above is validated by the presence of amplification products such as OPA11-15, ISJ2-29, ISJ4-25 or OPB6-20. Resistance marker ISJ4-25 could serve as an effective molecular tool for monitoring the environmental effects of multidrug (TE+ENR+E) resistant strains. The discussed marker supplies information about the effects of intensive fish farming on the microbiological quality of river water. The results of this study could support evaluations of aquatic habitats subjected to human pressure.

ACKNOWLEDGMENTS

This study was co-funded by grant No. N305 110 31/3667 from the Ministry of Science and Higher Education (Poland).

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OCENA ZANIECZYSZCZENIA ANTROPOGENICZNEGO WODY RZECZNEJ NA PODSTAWIE ZRÓŻNICOWANIA GENETYCZNEGO AEROMONAS HYDROPHILA

Aeromonas hydrophila jest cennym wskaźnikiem jakości wody w przypadku zanieczyszczeń ściekami oraz mikroorganizmami względnie patogennymi dla człowieka i zwierząt zimnokrwistych, w tym ryb. Celem niniejszych badań była ocena zanieczyszczenia antropogenicznego na podstawie zróżnicowania genetycznego 82 szczepów *A. hydrophila* poprzez analizy RAPD, pół-przypadkowo amplifikowanej klasy AP-PCR (ISJ) i konserwatywnego powtórzenia rep-BOX. Zróżnicowanie genetyczne *A. hydrophila* wyniosło $H_T = 0,28$ ($SD = 0,02$) dla wszystkich markerów DNA (RAPD, pół-przypadkowe i rep-BOX). Wszystkie szczepy dla wszystkich markerów ujawniły indywidualny wzór elektroforetyczny, nie ujawniono jednego źródła rozprzestrzeniania się szczepów. U szczepów potwierdzono obecność genów aerolizyny (*aerA*), hemolizyny (*ahh1*) i kompleksu enzymów cytotoksycznych (AHCYTOGEN), jak również określono wzorzec oporności na tetracyklinę, enrofloksacynę i erytromycynę. Najbardziej zróżnicowane okazały się szczepy *A. hydrophila* wrażliwe na enrofloksacynę ($H_S = 0,27$) a najmniej zróżnicowane były szczepy wrażliwe na erytromycynę ($H_S = 0,24$). Wyselekcjonowany marker wielolekooporności (locus ISJ4-25, 1100 pz) obecny u szczepów (opornych na 3 rozpatrywane leki) świadczy o wpływie intensywnej hodowli ryb na jakość mikrobiologiczną wody rzecznej.

REMOVAL OF INDIGO CARMINE FROM AN AQUEOUS
SOLUTION BY FUNGUS *PLEUROTUS OSTREATUS*SIBEL KAHRAMAN^{1*}, FILIZ KURU², DEMET DOGAN³, OZFER YESILADA²¹Inonu Univ. Faculty of Education. Department of Science. 44280, Malatya, Turkey²Inonu Univ. Art and Science Faculty. Department of Biology. 44280, Malatya, Turkey³Inonu Univ. Institute of Science, Department of Biology. 44280, Malatya, Turkey

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Keywords: Indigo Carmine, decolorization, *Pleurotus ostreatus*, dead biomass, fungus.

Abstract: The role of fungi in the treatment of wastewater has been extensively researched. Many genera of fungi have been employed for the dye decolorization either in living or dead form. In this study, the removal of an acidic dye, Indigo Carmine (IC), from an aqueous solution by biosorption on dead fungus, *Pleurotus ostreatus*, was investigated. The effects of contact time, initial dye concentration, amount of dead biomass, agitation rate and initial pH on dye removal have been determined. Experimental results show that an increase in the amount of dead biomass positively affected the dye removal. The highest removal was obtained at 150–200 rpm. Slightly lower removing activities were found at lower agitation rates. The dye adsorption efficiency was not affected by pH except minor variation in the pH of 2–8. Color removal was observed to occur rapidly within 60 minutes. The removal of dye by dead biomass of *P. ostreatus* was clearly dependent on the initial dye concentration of the solution. Dye removal was reduced from 93% to 64% as concentration was increased from 50 to 500 mg/L Indigo Carmine. This study showed that it was possible to remove textile dyes by dead biomass of *P. ostreatus*.

INTRODUCTION

Textile industries generate large volumes of wastewater. The removal of dye from textile effluents is one of the most significant environmental problems. Color is one of the greatest contaminants in wastewater, as it is highly visible and undesirable and also reduces light penetration and photosynthesis. In general, dyes have complex chemical structures and are resistant to biological degradation. There are various methods available for the removal of dyes, including membrane-separation, electrochemical, flocculation-coagulation, reverse osmosis, ozone oxidation, biological treatments, sorption, etc. [12, 20].

Due to low biodegradability of dyes, a conventional biological wastewater treatment process is not very efficient in treating a dye wastewater. It is usually treated by physical – or chemical – treatment processes [3]. Adsorption on activated carbon has been found to be an effective process for dye removal from dye wastewater, but it is too expensive. Low-cost adsorbents developed to replace activated carbon generally have low adsorption

capacities [8]. Therefore, there is a need to find new, economical, easily available and highly effective adsorbents and techniques.

Biosorption can be defined as sequestering of organic and inorganic species including metals, dyes and odor causing substances using live or dead biomass or their derivatives. This biomass may be bacteria, fungi, algae, sludge from biological wastewater treatment plants, byproducts from fermentation industries or seaweeds. In this process, adsorbents are biological materials, and the removal mechanism is mainly sorption [18]. Most of the studies concentrated on living fungi for biodegradation and biosorption of the dyes. There are a few studies on dye removal using dead fungal biomass. Both living and dead fungi have been shown to be capable of removing dyes due to the presence of various functional groups on the biomass [6, 7]. However, dead cells offer several advantages over living cells. Firstly, for efficient dye removal using living fungal cells, the growth conditions (nutrients requirements, pH and temperature) of the fungi are extremely important. Use of dead fungal cells obviates the need for nutrients requirements as well as eliminates the problem of waste toxicity. In addition, dead fungal biomass can be stored easily and kept for prolonged periods [17]. Apart from these factors, researchers have also reported that dead biomass is more effective in adsorbing various pollutants than live biomass [2, 13, 21].

Indigo is one of the oldest and most important dyes, mainly used in the dyeing of clothes (blue jeans) and other blue denim. This dye in water is transformed into more soluble products before industrial application. Its reaction with sulfuric acid yields indigo carmine (Acid Blue 74, Fig. 1), a common dye also used as food coloring, as indicator in analytical chemistry, and as a microscopic stain in biology [1]. However, indigo carmine is considered a highly toxic indigoid class of dye and its touch can cause skin and eye irritations to human beings. It can also cause permanent injury to cornea and conjunctiva [12].

In this study, dead biomass of *Pleurotus ostreatus* was used as a biosorbent to remove the Indigo Carmine (IC). The aim of this research was to develop effective adsorbents for dye-removal technology. So, the effect of various operating parameters on dye removal such as initial pH, dye concentration and adsorbent amount were studied.

MATERIALS AND METHODS

Dye solution

The dye stock solution was prepared by dissolving accurately weighed dye in distilled water to the concentration of 500 mg/L. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

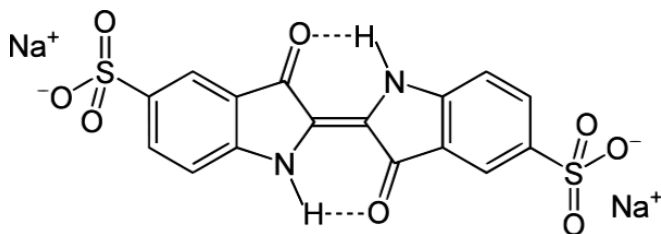


Fig. 1. Chemical structure of Indigo Carmine

Fungal biomass preparation

The white rot fungus *Pleurotus ostreatus* was cultured at 30°C on slant Sabouraud Dextrose Agar (SDA). After 1 week, mycelial suspensions were prepared and used for the cultivation of inoculum. Mycelial suspensions were transferred into 250-mL flasks with 100 mL Sabouraud Dextrose Broth (SDB). Conidial suspension was transferred into a 250-ml flask with 100 mL Stock basal medium (SBM). Growth medium consisted of (in g/L of distilled water); KH_2PO_4 , 0.2; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.1; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.05; $\text{NH}_4\text{H}_2\text{PO}_4$, 0.5; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.035; Glucose, 2; Yeast Extract, 1; Sabouraud dextrose broth, 5. Fungal pellets were formed after 2–5 days under 30°C and 150 rpm agitation. When pellet diameters became 3 to 5 mm, the pellets were harvested. After washing, the pellets were dried at 30°C for 24 h and powdered in a pestle and blender. The powdered biomass (particle size less than 100 μm) referred as “dead biomass”. Dead biomass was used in dye removal studies.

Assay

Different amounts of dead biomass were transferred to 100 mL flask containing 20 mg/L of dye containing distilled water. The effect of agitation was investigated at different agitation rates, namely 0, 50, 100, 150, 200 and 250 rpm. The effect of the amount of dead biomass was investigated at different amounts, namely 0.1, 0.2 and 0.5 g/20 mL and the effect of contact time was tested at 30, 60, 90, 120, 180 minute. In order to study the effect of pH on dye removal, the pH of the solutions was varied from 2 to 8, by adding 0.1M NaOH or 0.1M HCl solutions. The effect of the initial dye concentration on the removal was studied between 50–500 mg/L at 30°C. Samples were taken at different time intervals. Dye concentration was determined with an UV visible spectrophotometer at their visible maxima (610 nm). The absorbance of the supernatant was estimated to determine the residual concentration. Residual dye concentration was determined using absorbance values measured before and after the treatment with spectrophotometer at their visible maxima. All the biosorption experiments were run in triplicate. Controls without the adsorbent were also run.

RESULTS AND DISCUSSION

Effect of adsorbent amount on decolorization

The dye removal of Indigo Carmine (IC) by dead biomass of *P. ostreatus* was studied by changing the quantity of dead biomass (0.1, 0.2, and 0.5 g/20 mL) in test solution. The initial dye concentration, temperature and time were 50 mg/L, 30°C, 60 and 120 minutes, respectively. Unless otherwise stated, experiments were conducted without adjusting the pH of the dye solution (Figure 2). As shown in Fig. 2, the percent decolorization was increased with adsorbent dose. 0.2 g/20 mL of dead biomass was selected as the sorbent dose in the further experiments. The removal efficiency of different amount of biomass was in order 0.2 g = 0.5 g > 0.1 g. The use of a smaller sorbent dose may be a more economically viable option.

Increase in the dye removal with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption site [4]. Similar results were reported by Asma *et al.* [2] for decolorization of Astrazone Blue by dead biomass of *Phanerochaete chrysosporium*. It was possible to increase the decolorization of Malachite

Green by increasing the adsorbent dose of the agro-industry waste [9]. Similar results were reported by Gong *et al.* [10] and Gupta *et al.* [11] for decolorization of Quinoline yellow and three anionic dyes, respectively. Also, the similar study by Kahraman and Yalcin [14] demonstrated that removal of Astrazone Blue and Red was dependent on the agro-industrial waste adsorbent dose.

Effect of initial pH on decolorization

The effect of initial pH on the dye removal capacity of dead biomass (*P. ostreatus*) was investigated in the pH range 2.0–8.0 To study the effect of pH on decolorization capacity of dead biomass, the experiments were carried out at 50 mg/L initial dye concentration with 0.2 g 20/ mL adsorbent mass (100 mesh) at 30°C for 60 and 120 minute time and 150 rpm (Figure 3). As shown in Fig. 3 the dye adsorption efficiency was not affected by pH except minor variations in pH of 2–8.

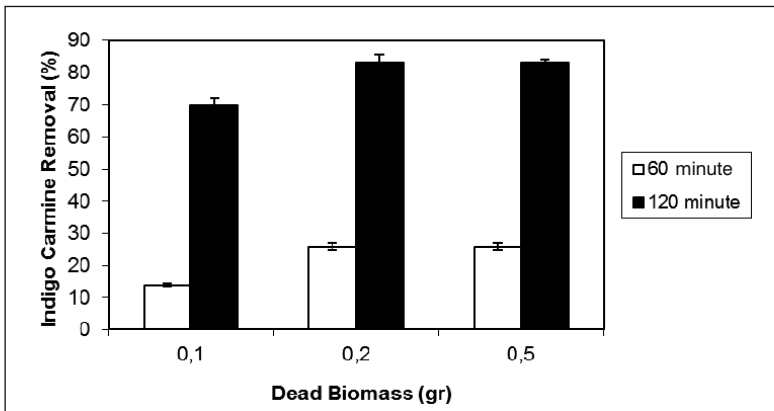


Fig. 2. The effect of dead biomass amount of *Pleurotus ostreatus* on the Indigo Carmine dye removal. (The initial dye concentration and temperature – 50 mg/L, 30°C, respectively)

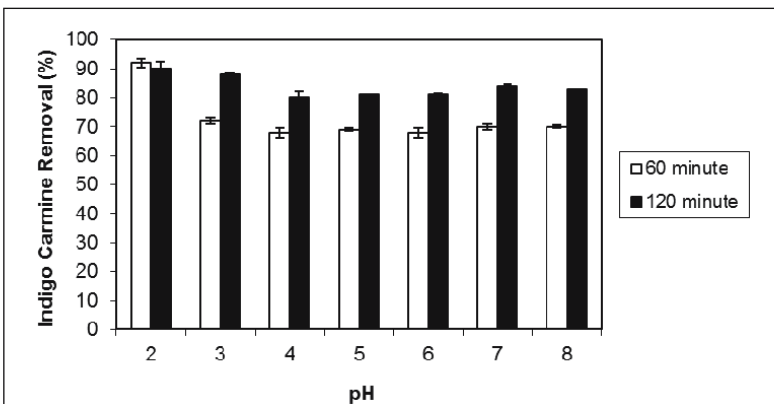


Fig. 3. The effect of pH on the Indigo Carmine dye removal. (The experiments were carried out at 50 mg/L initial dye concentration with 0.2 g 20/mL adsorbent mass (100 mesh) at 30°C and 150 rpm)

There are two possible mechanisms for the effect of pH on adsorption of dyes on any adsorbent: (a) electrostatic interaction between the protonated groups of carbon and acidic dye, and (b) the chemical reaction between the adsorbate and the adsorbent [19]. Dye molecules may interact with the functional groups on dead biomass via extremely complicated pathways. Also, there may be weak electrostatic interaction between the dye molecules and the electron-deficient sites on the surface of the dead biomass. However, for this study, the extent of IC adsorption onto dead biomass remained constant in the pH range of 4.0–8.0. This may be attributed to a second mechanism of weak electrostatic interaction [5, 16].

Removal of indigo carmine by dead biomass at different time intervals

In this part of study, dead biomass of *P. ostreatus* was tested for Indigo Carmine removal capacity at different time intervals. To study the effect of time on decolorization capacity of dead biomass, the experiments were carried out at 50 mg/L initial dye concentration with 0.2 g/20 mL adsorbent mass (100 mesh) at 30°C, pH 2.0 and 150 rpm. Color removal was observed to occur rapidly within 60 min (Table 1). Dye decolorization was high at the beginning of adsorption (within the initial 60 min) and after this period, the concentration of adsorbed dyes did not significantly change.

Effect of agitation on the removal of Indigo Carmine by dead biomass of *P. ostreatus*

The effect of agitation rate on Indigo Carmine removing was studied in the range of 0–250 rpm. To study the effect of the agitation rate on decolorization capacity of dead biomass, the experiments were carried out at 50 mg/L initial dye concentration with 0.2 g/20 mL adsorbent mass (100 mesh) at 30°C for 60 minute time and pH 2.0. Dead biomass showed high dye removal at all of the agitation rates (Table 1). As shown in Table 1, the optimal agitation values for decolorization were around 150–250 rpm. Slightly lower activities were found at lower agitation rates. At lower agitation speeds, the biomass particle agglomerated. Knapp *et al.* [15] reported that the decolorization of Orange II was 45% after 23-h incubation in static conditions and 98% in agitated conditions. High decolorization yield in agitated conditions offers many advantages over static cultivation for development of practical processes [22].

Table 1. Effect of Time and Agitation rate on the Removal (%) of Indigo Carmine by Dead Biomass of *Pleurotus ostreatus*

Time (Minute)	Indigo Carmine Removal (%) \pm Sd	Agitation Rate (rpm)	Indigo Carmine Removal (%) \pm Sd
30	88 \pm 0,57	Static	92 \pm 0,57
60	93 \pm 0,57	50	93 \pm 0,57
90	94 \pm 0,00	100	94 \pm 1,00
120	94 \pm 0,57	150	95 \pm 0,57
180	95 \pm 1,00	200	93 \pm 2,51
		250	95 \pm 2,08

Sd: Standard deviation

Effect of initial dye concentration on decolorization

The influence of the initial concentration of dye in solutions on removal of Indigo Carmine was studied. The experiments were carried out at fixed adsorbent dose (0.2 g/20 mL) in the test solution, 30°C temperature, pH 2.0, fixed agitation (150 rpm) for 60 minute time at different initial concentrations of dye (50, 100, 200, 300, 400, 500 mg/L). The removal of dye by dead biomass of *P. ostreatus* was clearly dependent on the initial dye concentration of the solution (Figure 4). Dye removal was reduced from 93% to 64% as concentration was increased from 50 to 500 mg/L Indigo Carmine. Generally, the amount of dye in the industrial textile wastewaters is lower than 500 mg/L (approximately 10–50 mg/L). Therefore, these results are quite significant in terms of prevention of environmental pollution.

CONCLUSIONS

During the last decade, more attention has been focused on the development of new treatment technologies that lead to complete decomposition of dye molecules. In the present study, dead biomass of *P. ostreatus* was applied successfully for the sorption of Indigo Carmine. Operating conditions (dye concentration, pH and temperature) may negatively affect the decolorization potential of living cells. However, when compared with live biomass, dead biomass has many advantages. Dead biomass may be stored or used for extended periods and operation is easy and regeneration is simple. Dead biomass can be obtained from industrial sources as a waste product. Therefore, it can be used as cheap and effective biosorbent. The results obtained in this paper for the mechanisms involved in dye removal can be considered as a fundamental step for the representation of the experimental behavior and for development of process design.

ACKNOWLEDGEMENTS

This work was supported by Inonu University Research Fund (2011/42).

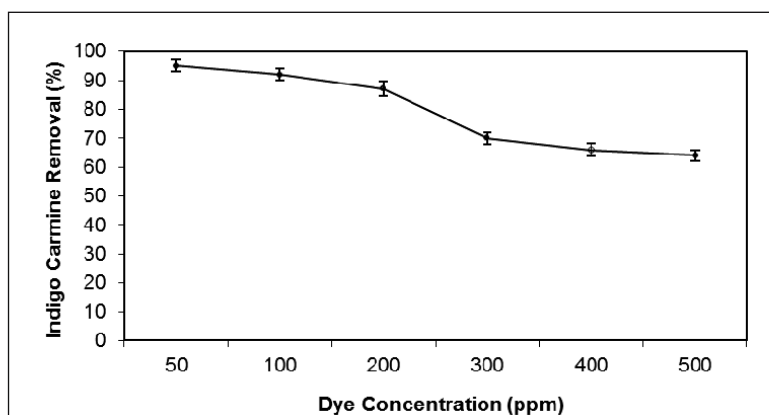


Fig. 4. The effect of initial dye concentration (mg/L) on the removal of Indigo Carmine by dead biomass of *Pleurotus ostreatus*. The experiments were carried out at fixed adsorbent dose (0.2 g/20 mL) in the test solution, 30°C temperature, pH 2.0, fixed agitation (150 rpm) for 60 minute time

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PROGNOSIS OF ENVIRONMENTAL IMPACT OF TRACE
ELEMENTS FROM BROWN COAL-FIRED POWER PLANT
“BEŁCHATÓW”

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Keywords: Environment protection, brown coal, traceelements, combustion products, flue gas desulphurization (FGD) gypsum, forecast of trace elements emission, forecast of trace elements transfer.

Abstract: A forecast of the negative impact exerted on the environment by selected trace elements in “Bełchatów” Power Plant has been prepared on the basis of the results of investigations into these elements’ distribution carried out as part of earlier research on coal from “Bełchatów” Field and the data on updated analyses of the content of these elements in 55 brown coal samples from test boreholes.

Work in “Bełchatów” Power Plant, which is supplied with coal from “Szczerców” Field, will be accompanied by trace elements transfer. On the basis of the conducted investigations it has been found that the biosphere is most threatened by mercury emissions. As shown by the presented results of analyses and calculations, the emissions of mercury in “Bełchatów” Power Plant are low. Mercury is accumulated chiefly in gypsum produced in the FGD plant. The content of mercury in slag and ash is low.

INTRODUCTION

There is a growing interest in hazardous substances emitted to the environment from power and industrial plants. Although introduced in relatively small amounts, these substances create a threat due to their dangerous properties. Their harmful effect is reflected in the destruction of immunological system, various toxic effects and a negative impact on the development of young organisms. The substances are known for their carcinogenic, mutagenic, teratogenic and genotoxic properties or there is a justified fear that they may have such properties. They penetrate into the human organism mainly via respiratory tracks, but also through the digestive track, participating in particular links of the food chain. Among numerous dangerous substances which contaminate the environment one should mention metals: beryllium, chromium, cadmium, cobalt, nickel, lead and mercury, as well as their compounds and semi-metals such as arsenic, boron and selenium as well as their compounds.

In Poland an inventory of emissions of this group of elements (under the name of heavy metals) from particularly arduous plants is taken, and the data is published in statistical yearbooks [5]. In 2011 the emissions of heavy metals from these plants (in kg/a) were determined as follows: arsenic – 1857, chromium – 5990, tin – 307, zinc – 81971, cadmium – 959, cobalt – 84, manganese – 7314, molybdenum – 8, nickel – 6218, lead – 40517 and mercury – 1220.

Being trace components of brown and hard coal, after the coal is burned, they escape with flue gas into the air and move towards other components of the environment with by-products captured in dust collectors and flue gas desulphurisation (FGD) plants. In Poland this problem is particularly important given the dominance of hard and brown coal in the domestic power industry and heat engineering. Therefore, selected power plants launched investigations into the distribution of trace elements in coal and slag as well as dedusting and flue gas desulphurization by-products: ash fly captured in dust collectors, gypsum produced in the desulphurization process and semi-dry scrubbing FGD products [9]. “Bełchatów” was one of the investigated power plants. The studies revealed that as a result of distribution in the coal combustion and flue gas desulphurization process, a dominant part of the stream of particular trace elements moves with waste and solid products, and emissions into the air are low [9].

“Bełchatów” Power Plant, which is the biggest in Poland and burns more than 30 Tg of brown coal annually, in the nearest 30 years will be supplied with coal from new “Szczerców” Field. This is taking place gradually due to exhaustion of previously exploited “Bełchatów” Field. Therefore, the power plant will influence the environment for the nearest several dozen years. This impact remains huge despite the fact that modern protective equipment is used.

The EEA technical report No. 15/2011 [3] published in 2011 presents an estimate in EUR of damage done to the environment due to emissions of air-contaminating substances as well as a ranking of the examined facilities. It was found that 191, i.e. ca 2% from among approximately 10,000 evaluated industrial plants cause as much as 50% of the estimated damage, which in the year 2009 ranged from 102 to 169 billion euros.

The list of the first 20 plants includes three Polish power plants: “Bełchatów” (1), “Turów” (10) and “Kozienice” (13). Bearing in mind the present and future significance of “Bełchatów” Power Plant, the change of coal burned and the authors’ own results of previous studies [9], a decision was taken to start works aimed at evaluating the future emissions of selected trace elements into the air as well as their transfer to dedusting and flue gas desulphurization products, which may create a threat to other segments of the environment.

RESEARCH PART: BROWN COAL IN POLISH POWER INDUSTRY. “BEŁCHATÓW” POWER PLANT

Characteristics and resources of brown coal in Poland

Poland belongs to European countries having the largest resources of brown coal. In Poland there are more than 150 coal beds and coal-bearing areas. Over 24.5 Pg of resources have been documented, including 14 Pg in guaranteed deposits, over 60 Pg in estimated deposits and more than 140 Pg in potential deposits [8]. The economic usefulness is determined by the overburden thickness to coal deposit ratio.

In recent years the role of brown coal as a fuel has increased. Other energy sources in the previously discovered deposits are depleting, and new deposits are characterized by worse mining-geological conditions. Brown coal occurs in abundance and its deposits are relatively easily accessible.

The most important is power coal characterised by ash content below 40%, expressed as dry coal A^{db} , and calorific value Q_i^{ar} above 6.7 MJ/kg, expressed as coal with total moisture content TM_T^{ar} reaching 50%. Power coal, containing more than 0.5% of alkalis ($Na_2O + K_2O$) expressed as dry coal, is included in the so-called saline coal.

In Poland, brown coal deposits are exploited solely by the open pit mining method, the oldest and most profitable system of obtaining resources from natural deposits [10]. Currently, electrical energy produced from brown coal is the cheapest and brown coal has been playing the role of a strategic fuel for many years.

“Belchatów” Brown Coal Mine

“Belchatów” brown coal deposit (Fig. 1) lies in the rift valley of Kleszczów, having the length of ca 40 km, the width ranging from 1.5 to 3.5 km and the depth of 150–350 m, within Szczecin–Łódź–Miechów synclinorium [6].

Within “Belchatów” deposit, which is the subject of this study, three brown coal fields have been separated [1]:

„Belchatów” Field – situated in the middle part of Kleszczów rift valley; its western part is Dębina salt dome. At present, „Belchatów” field is being exploited – more than half of its resources have been already mined. The current state of the deposit reaches more than 400 Tg, and the end of exploitation is projected for the year 2019 [6].

„Szczerców” Field – is a western extension of „Belchatów” Field, from which it is separated with a salt dome. Its western boundary is marked by natural dwindling of the coal bed. We can already talk about “Szczerców” Strip Mine, as since the year 2002 works making the bed available have been carried out, and the coal overburden is stored at an external dumping ground. Coal mining in this field, which began in 2007, will be continued until 2038.

There are plans to reclaim the post-mining heading in more distant future by building a water reservoir [12].



Fig. 1. Brown coal deposit – Belchatów [6]

The geological structure of „Szczerców” Field is similar to that of “Bełchatów” Field, as it is a part of the same deposit.

Brown coal deposit in „Szczerców” Field:

- overburden thickness: 129.1 m
- seam thickness: 55.3 m
- floor depth: 179.5 m
- overburden to coal deposit ratio: 2.3:1
- geological resources: 891 Tg
- balance resources: 877 Tg
 - off-balance resources: 14 Tg
 - industrial resources: 620 Tg

Average parameters of coal from the open pit in „Szczerców” Field:

- calorific value: $Q^{\text{ar}} - 7.42 \text{ MJ/kg}$
- moisture content: $TM_{\text{T}}^{\text{ar}} - 51.16\%$
- ash: $A^{\text{ar}} - 11.56\%$
- total sulphur: $S_{\text{T}}^{\text{ar}} - 1.05\%$

[6, 12]

„Kamieńsk” Field is an eastern extension of „Bełchatów” Field. Currently there are no plans for its economic use due to the unfavourable overburden to coal ratio.

From „Bełchatów” and „Szczerców” Fields which have been made available a total of 39 Tg of brown coal can be mined annually until the year 2038. Resources in these fields reach 898 Tg, while in “Kamieńsk” Field – 402 Tg. The mined coal is delivered by belt conveyers to “Bełchatów” Power Plant where it is burned [4]. The participation of “Bełchatów” Field is decreasing, whereas that of “Szczerców” Field keeps growing, which has been presented in Table 1.

„Bełchatów” Power Plant

„Bełchatów” Power Plant is the biggest brown coal-fired powerhouse in Poland and Europe. The power of its power units reaches 4440 MW, which accounts for ca 15% of power installed in Polish professional power industry. The annual production of energy reaches an average of 27–28 TWh and accounts for ca 20% of the domestic production [11]. As a result of modernisation and the use of effective gas treatment technologies and low emission technologies, the emission of air-polluting substances has been significantly reduced in “Bełchatów” Power Plant.

Table 1. Output of brown coal for the needs of “Bełchatów” in Tg [7]

Years	„Bełchatów” Field	„Szczerców” Field
2010	25.1	7.0
2013	22.0	15.0
2017	12.1	23.2
2020	5.0	33.0
2025	–	36.5
2030	–	35.0

Dedusting and flue gas desulphurisation versus trace elements

Thanks to the advances in flue gas dedusting, the emissions of dust from coal-fired boiler furnaces fired with hard or brown coal have been reduced a few times. Additionally, the wide use of flue gas desulphurization units improved the situation. A flue gas desulphurization (FGD) plant, usually based on the wet limestone method, located behind the electrofilter also plays the role of second-stage dust containment with total filtration efficiency reaching 80%. Fly ash and slag captured in the boiler and dedusting equipment is utilized or stored at dumping grounds, and only 0.1% of the mineral substance contained in coal penetrates into the air.

Trace elements contained in coal escape into the air with flue gas from power sources or move towards other elements of the environment through by-products captured in dust containment equipment and flue gas desulphurisation plants. The existing knowledge of the distribution of frequently dangerous trace elements in these products is insufficient.

After analysing the research material (Tab. 2) from previous investigations [9] into coal from „Belchatów” Field and combustion and gas desulphurisation products from „Belchatów” Power Plant, the authors evaluated the distribution of selected trace elements: Cr, Cu, Hg, Mn, Ni, Pb and Zn, which penetrate into slag, ash captured in an electrofilter and gypsum, which is a flue gas desulphurization product (Tab. 3).

The effect of brown coal quality on the consumption of fuel and the amount of combustion and flue gas desulphurisation products

The use of coal from „Szczerców” Field, characterised by a higher content of mineral substance, and in consequence a lower calorific value and a higher content of sulphur

Table 2. Concentrations of selected trace elements in coal, slag, ash and flue gas desulphurisation products [9]

Type of sample	Cr, mg/kg	Cu, mg/kg	Hg, µg/kg	Mn, mg/kg	Ni, mg/kg	Pb, mg/kg	Zn, mg/kg
brown coal	13.2	9.7	516	38.8	6.4	13.7	8.3
slag	91.5	46.6	32	115.1	30.1	20.9	65.9
ash	105.8	56.1	125	179.2	41.4	22.5	70.1
gypsum	3.1	3.0	2411	5.5	3.5	4.1	2.2
limestone	0.1	4.7	7	0.1	8.7	9.7	0.2

Table 3. Distribution of selected trace elements in slag, ash and gypsum from the FGD unit in „Belchatów” Power Plant (K5–K8 boilers) [9]

Waste/product	Distribution of trace elements, %						
	Cr	Cu	Hg	Mn	Ni	Pb	Zn
slag	4.9	4.6	0.1	3.7	3.9	4.5	5.3
ash	92.0	90.0	4.4	93.1	87.7	79.2	91.5
gypsum	3.0	5.4	95.5	3.2	8.3	16.2	3.2

compounds will result in an increased consumption of coal and a bigger amount of slag, ash and gypsum produced in the flue gas desulphurisation process. This is presented in a table with data computed for the basic type of boiler BB-1150 (Tab. 4).

RESEARCH GOAL

The investigations are aimed at evaluating the size of harmful streams of selected trace elements from brown coal, penetrating into the air as a result of work in „Bełchatów” Power Plant in the years 2013–2030, which causes emission of dust and production of slag, ash and gypsum in the process of flue gas desulphurization. The results will be useful for an inventory of trace elements’ emissions in the national, regional and global scale. The evaluation covers the period when the power plant will burn brown coal some properties of which are different compared to coal burned in the first period of the plant’s activity.

CONCEPT AND SCOPE OF RESEARCH

In the years 2011–2030 ca 550 Tg of brown coal from „Szczerców” Field is planned to be burned in the power blocks of „Bełchatów” Power Plant. In the light of the conducted investigations [9], trace elements: Cr, Cu, Hg, Mn, Ni, Pb and Zn contained in coal transfer into slag, ash captured by an electrofilter and gypsum, which is a flue gas desulphurization product. Penetration into the air with the desulphurised flue gas, which is currently marginal, may also decrease after using the CCS technology. Given the fact that “Szczerców” and “Bełchatów” Fields are parts of the same coal bed, it may be assumed that the properties of chemical compounds in which trace elements in coal from both Fields occur are similar.

Such an assumption allows to evaluate the future impact of selected trace elements on the environment on the basis of the results of investigations into the distribution of these elements in previous studies [9] and the data obtained in current analyses of these elements’ content in brown coal samples from 3 test boreholes. In the prognostic calculations as a content of mercury was assumed the arithmetic mean of the analysis of mercury in the three samples, which were created after averaging samples from all layer depth ranges taken from the three above-mentioned holes.

For the remaining elements there was established an upper and lower level content of the elements in coal, found in 80% of the tested samples. Using the lower and upper

Table 4. Consumption of coal, solid combustion and flue gas desulphurisation products in BB-1150 boiler in “Bełchatów” Power Plant, Mg/h

BB-1150	Coal	Slag*	Ash*	Dust emitted to the air	Gypsum from FGD
Coal from „Szczerców” Field	502	3.37	48.86	$48.86 \cdot 10^{-3}$	26.92
Coal from „Bełchatów” Field	423	2.16	31.34	$31.34 \cdot 10^{-3}$	16.98

* assuming that the fraction of slag and ash is the same

levels of the element in the calculation, the ranges, which include forecasted emissions and transfer were determined.

RESEARCH-ANALYTICAL PART

Research material

Table 5 presents a list of coal samples taken from “Bełchatów” Coal Brown Mine (“Szczerców” Field).

Methodology

Coal analysis

Coal from the western part of „Szczerców” Field is highly sulfated ($S_T^{db} = 2.61\%$). The average ash content (A^{db}) is high, reaching 29.3%. The calorific value $Q_i^{ar} = 7.42$ MJ/kg is low compared to „Bełchatów” Field and the eastern area of „Szczerców” Field, where it is 8.8 MJ/kg.

Manner of sample taking and sample preparation for tests and analyses

The research material was taken, separated or processed in a proper way, by using appropriate methods and procedures so as to prepare samples for further tests and analyses [13]. As required, by averaging and grinding the original samples of brown coal, 52 analytical samples from particular depth ranges of the layer taken from the holes were prepared for analysis. Moreover, 3 averaged samples of coal from all depth ranges of the layer taken from the holes were prepared.

Table 5. A list of coal samples from „Bełchatów” Brown Coal Mine (“Szczerców” Field)

Type of hole	Sample No.	Number of samples	Layer depth range [m]
observation	PS 173/1 ÷ PS 173/11	11	113.7 – 140.0
observation	PS 52–2/1 ÷ PS 52–2/10	10	23.5 – 55.0
pilot	K46P/1 ÷ K46P/31	31	140.8 – 237.2

Table 6. Selected data of brown coal characteristics

Field	Total sulphur content	Ash content	Total moisture content
	S_T^{ar}	A^{ar}	TM_T^{ar}
	% mass		
Szczerców	1.05*	11.56	51
Szczerców – western part	1.27*	14.3	51
Bełchatów	0.50–0.83**	8.80	53

* [6], ** [2]

*Analytical methods***Determination of mercury in coal**

Mercury in the tested samples was determined with a MA-2 mercury analyser produced by Nippon Instruments Corporation [9]. Table 8 presents average values from three analyses.

Determination of As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V and Zn in coal

Solid samples were dissolved under high pressure (max. pressure 60 bar) and at high temperature (max. temperature 260°C) in a Multiwave 3000 microwave mineralization unit produced by Anton Paar, in an appropriate mixture of acids which allowed to obtain a clear solution. A mixture of 65% nitric acid – 6 ml, 70% perchloric acid (VII) – 1 ml and 40% hydrofluoric acid – 1 ml was used. After dissolving, the whole amount of the solution was poured into a 50 ml measuring flask and filled up with deionised water to nominal volume.

In so obtained solutions the concentrations of selected trace elements were determined using the ICP MS method, by means of an Elan DRC-e 6100 spectrometer produced by Perkin-Elmer. The reagents for trace analysis produced by Sigma-Aldrich were used to prepare the samples and reference samples.

Each sample was mineralised and analysed three times.

The extended uncertainty of the determined analytes using ICP-MS technique, composed of the uncertainty of the reference sample, the uncertainty of weighing, the uncertainty of calibration, the uncertainty of intermediate precision and the limits of detectability and determinability, (Table 7) was established.

Analysis results

Table 8 presents the results of determinations of mercury concentrations in averaged coal samples from the examined observation and pilot holes from „Szczerców” Field, as well as upper and lower levels of the analyzed elements in coal. The results of the analyzes were developed as described in “Concept and scope of research” above.

Table 7. The extended uncertainty as well as the limits of detectability and determinability of analytes

Isotope	Uncertainty [%]	Detectability limit (LOD) [µg/l]	Determinability limit (LOQ) [g/l]
⁷⁵ As	14.5	0.20	0.60
⁹ Be	15.5	0.09	0.27
¹¹⁴ Cd	5.1	0.03	0.09
⁵⁹ Co	4.1	0.01	0.03
⁵⁵ Mn	4.5	0.03	0.09
⁶⁰ Ni	10.5	0.05	0.15
⁶⁶ Zn	15.4	0.18	0.54
⁶⁵ Cu	5.1	0.06	0.18
⁵¹ V	5.7	0.03	0.09
²⁰⁸ Pb	6.0	0.02	0.06
⁵³ Cr	11.5	0.04	0.16

Table 8. The upper and lower levels of the examined elements' concentration in coal from „Szczerców” Field

Level	Component [mg/kg]											
	As*	Be*	Cd*	Co*	Cr	Cu	Hg	Mn	Ni	Pb	V*	Zn
Lower	4.74	0.59	0.30	4.56	25.79	6.57	0.39	64.60	11.73	4.18	31.27	52.05
Upper	12.40	1.90	1.60	14.85	79.47	23.48		143.08	48.84	20.02	83.79	182.62

* elements were determined in coal samples, but their emissions and transfer into the environment segments were not analysed

RESEARCH-PROGNOSTIC PART

Methodology of forecasting the emissions and transfer

On the basis of data from Table 1, calculations of emissions and transfer for five timespans, namely for the years 2013, 2017, 2020, 2025 and 2030, were made. Coal from “Bełchatów” and “Szczerców” Fields is projected to be burned until 2020, with an increasing stream from the latter. After 2020 “Bełchatów” Power Plant will burn coal from “Szczerców” Field. Calculations were based on the assumption that the whole coal mined at “Bełchatów” Coal Mine will be burned in “Bełchatów” Power Plant. The results have been given in Table 10.

Calculations of combustion and flue gas desulphurisation products mass streams as well as emissions and transfer of trace elements into the environment segments

Calculations were based on the projected masses of fuels and products in figures rounded up to 1 Mg/a. Basing on the data on the content of ash A^{ar} , the amount of solid combustion products and next the amounts of slag and fly ash were calculated by using mass fractions of slag (0.058) and fly ash (0.942). As a result of containment in an electrofilter, 99.6% of fly ash is arrested in the form of ash. 0.4% of fly ash penetrates through the electrofilter and with the dedusted flue gas moves to an FGD absorber, in which 75% of residual fly ash is captured. Hence, the total flue gas dedusting efficiency reaches 0.999%.

The amount of produced gypsum was calculated on the basis of the amount of burned coal, the content of total sulphur $S_T^{ar} = 1.05\%$ (wt%), desulphurisation efficiency η_{FGD} (0.95) and F_G coefficient (5.375) – yield of gypsum $CaSO_4 \cdot 2H_2O$ from a unit of SO_2 mass in the SO_2 and $CaCO_3$ reaction in the flue gas desulphurization process by the wet limestone method.

Table 9 presents the calculated combustion and flue gas desulphurisation products' mass streams.

The calculations of the emissions and transfer of element i into the air, gypsum, ash and slag were made on the basis of data on the amount of combustion and flue gas desulphurization products obtained in the combustion of 1 Tg/a of coal from “Szczerców” Field, the content of element i in the burned coal from “Szczerców” Field (Table 8), the fractions* of element i in slag, ash and gypsum from the FGD plant in the process of

* As fractions of element the values of distribution were assumed.

Table 9. Combustion and flue gas desulphurisation products' mass streams obtained in the combustion of 1 Tg/a of brown coal from „Szczerców” Field in Mg/a

Product	„Szczerców” Field
ash	108459
emitted dust	109
slag	6705
flue gas desulphurisation gypsum	53616

Table 10. Emissions and transfer of trace elements in the years 2013–2030 as a result of burning coal from „Szczerców” Field

547.9	59424916	59721	29376206	3673670			Cr	Cu	Hg	Mn	Ni	Pb	Zn
							[Mg]	[Mg]	[kg]	[Mg]	[Mg]	[Mg]	[Mg]
					ash	min.	1410	333	958	3391	580	187	2686
						max.	4345	1192		7512	2415	894	9423
					emitted dust	min.	1	below 1	1	3	1	below 1	3
						max.	4	1		8	2	1	9
					gypsum	min.	23	10	10831	61	29	20	49
						max.	70	37		135	119	95	172
					slag	min.	5	1	1	9	2	1	10
						max.	14	4		19	7	3	36

burning coal from “Szczerców” Field (Table 3) and on the amount of brown coal from “Szczerców” Field burned in particular years (according to Table 1).

Forecast emissions and transfer of selected trace elements as a result of simultaneous burning of coal from „Szczerców” and „Bełchatów” Fields in the years 2013–2030

On the basis of the presented assumptions and the method of calculation, prognostic calculations were made, which are presented in Table 10.

DISCUSSION OF RESULTS

After comparing basic properties of coal from „Szczerców” and „Bełchatów” Fields, it was found that coal from “Szczerców” Field contains more mineral substance and sulphur compounds. This observation is concurrent with previous publications. It should

be emphasized that the comparison is only an estimate, as in the case of “Szczerców” Field averaged samples from the above mentioned pilot holes were investigated, whereas in the case of “Bełchatów” Field the authors had access to the results of previous analyses of coal taken by an automatic sample taker from the system of three boilers carburizing in 24-h cycles – the coal was averaged and prepared for analysis.

In coal from „Szczerców” Field the following were determined: As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V and Zn.

In coal from „Bełchatów” Field in previous studies there were determined: Cr, Cu, Hg, Mn, Ni, Pb i Zn.

The evaluation of the results of 55 samples analysis reveals a high differentiation of the level of particular trace elements’ concentrations: the level of mercury concentration is the lowest – below 0.5 mg/kg, beryllium and cadmium – below 2 mg/kg, arsenic, cobalt, copper and lead – below 30 mg/kg, chromium, nickel and vanadium – below 100 mg/kg, whereas manganese and zinc – below 200 mg/kg. A comparison of the levels of selected trace elements’ concentrations in coal from “Szczerców” and “Bełchatów” Fields shows a close similarity in the case of copper and lead, a certain similarity but with higher concentrations in coal from “Szczerców” Field in the case of chromium, mercury and nickel and a considerable difference in the case of zinc, the concentration of which is higher in coal from “Szczerców” Field.

The level of selected trace elements’ concentrations is considerably different in a vertical distribution.

Due to the use of coal from „Szczerców” Field, characterised by a higher content of mineral substance, and in consequence a lower calorific value as well as a higher content of sulphur compounds, the consumption of coal and the amount of slag, fly ash and gypsum produced in the flue gas desulphurisation process will increase. It is assumed that by the year 2030 a basic boiler in the power blocks of “Bełchatów” Power Plant will be BB-1150 boiler, probably modernized. For prognostic purposes basic data were calculated, namely the streams of coal used, produced slag, fly ash, emitted dust and gypsum produced in the FGD unit. Throughout the whole evaluated period the same values $A^{ar} = 11.56\%$ and $1.05\% S_T^{ar}$ and the same calorific value were applied for coal from „Szczerców” Field, resulting in the same burned coal mass stream. *Solid combustion products: slag*, carried off directly from the boiler furnace and *flue dust*, carried away from the boiler in a flue gas stream, which are produced from mineral substance in coal in the coal combustion process have mass fractions: 0.058 and 0.942 respectively. Analyzing action of EF and FGD it may be assumed that 0.1% of fly ash is introduced into the air with the desulphurised flue gas as emitted dust, and 0.3% of fly ash mixes with gypsum from the FGD unit and becomes its contamination. Calculations of the amount of gypsum were based on the assumption that the content of sulphur compounds in coal was total sulphur and flue gas desulphurization efficiency reached 95%. A coefficient according to a stoichiometric equation of the reaction of sulphur dioxide and calcium carbonate with the production of calcium sulphate dihydrate was applied. The calculated mass of *gypsum* is pure $CaSO_4 \cdot 2H_2O$, without admixtures in a form of excess calcium carbonate, calcium sulphate and residual fly ash.

Calculations of the mass of combustion and flue gas desulphurization products carried out in relation to 1 Tg of burned coal from “Szczerców” Field gave the following results (in Mg): ash – 108459, slag – 6705, gypsum – 53616 and emitted dust – 109.

For the needs of investigations, a distinction was made between emission and transfer. Emission refers to the introduction of contaminating substances which occur in the solid phase into the air along with waste gas. Transfer is the moving and penetration of contaminating substances into solid products of coal combustion, dedusting and flue gas desulphurization.

It was assumed that the properties and contents of selected trace elements in coal from two observation holes and one pilot hole are representative for whole „Szczerców” Field. The obtained results make it possible to conduct a preliminary evaluation of the emission of selected trace elements into the air and refer the results to the data on estimated emissions of heavy metals in Poland quoted in GUS (Central Statistical Office) yearbooks.

The projected emissions of selected trace elements with dust will reach a peak in the year 2005, in which „Bełchatów” Power Plant will use 36.5 Tg of coal from „Szczerców” Field, reaching the following probable values in kg/a: chromium – up to 291 (4.86), copper – up to 84 (no data available), mercury – up to 0.07 (0.006), manganese – up to 529 (7.23), nickel – up to 170 (2.73), lead – up to 63 (0.16) and zinc – up to 664 (0.81). In relation to the reported emissions of heavy metals, in “Bełchatów” Power Plant the highest emission is forecast for manganese, chromium and nickel. However, it does not exceed 7.3%. The forecast emission is a percentage value in relation to the national emission of heavy metals in 2011 reported by GUS, which has been given in brackets next to the previously quoted values.

Among the investigated trace elements the greatest threat to the biosphere is posed by mercury emitted into the air. As shown by the presented data, mercury emissions in “Bełchatów” Power Plant are marginal. Prognostic calculations for the products of combustion and flue gas desulphurization which are not emitted into the air should not give cause for concern, as it was found [9] that mercury accumulates chiefly in gypsum produced in the FGD plant. The content of mercury in slag and fly ash is low. This results from the properties of mercury compounds, which in the process of coal combustion escape with flue gas in a gaseous form as mercury vapours or its volatile compounds. In an FGD absorber the sorption of mercury in the gaseous phase as well as mercury and its compounds adsorbed on the surface of fly ash particles takes place. In the desulphurization process, mercury present in flue gas transfers into gypsum and leaves the FGD absorber as gypsum contamination or a component of sewage from the process of gypsum dehydration and washing in a vacuum filter. The probability of dangerous mercury amounts being present in desulphurised flue gas is minimal. However, due to the lack of measurement data, gypsum and sewage should be subjected to analysis, including speciation analysis, and the release of mercury from gypsum by washing out and evaporating at an increased temperature should be examined. Such investigations should also be conducted for fly ashes and slag.

The output reaching ca 550 Tg of coal from „Szczerców” Field in the years 2013–2030 and its burning in the power blocks of “Bełchatów” Power Plant, which will be accompanied by the presence of combustion and flue gas desulphurization products, is a rare enterprise. The projected amounts of ash produced with such consumption of coal reach 59.4 Tg, slag – 3.7 Tg, gypsum – 29.4 Tg and the forecast emission of fly ash is 59721 Mg. The work of “Bełchatów” Power Plant, supplied with coal from “Szczerców” Field, will be accompanied by a transfer of trace elements. The transfer of Cr, Cu, Hg,

Mn, Ni, Pb and Zn into ash is of considerable importance. The transfer of mercury into ash will reach ca 1 Mg, copper and lead – ca 1000 Mg, nickel – over 2000 Mg, chromium – above 4000 Mg, manganese – 7500 Mg, and zinc – nearly 10000 Mg. The transfer of these elements into gypsum, excluding mercury, is several dozen times lower. The most important is the transfer of mercury into gypsum, which in the evaluated period will reach 11 Mg.

Special attention should be paid to the transfer of trace elements. Microcomponents will move from coal, where they existed in stable forms in the organic and inorganic substance of brown coal, to the above mentioned products, from which they may migrate at particular conditions. It is impossible to evaluate these processes without knowing the speciation of these elements' compounds in products and their behaviour in the process of using the products. These investigations are extremely significant for the selection of proper solutions. It is not certain whether gypsum from the FGD plant will in the future be used for the production of building materials due to changes in the construction technology and demand for gypsum products, or in what way and in what quantities solid products of coal combustion will be utilized. Ash and slag should not be stored in the headings after coal has been mined, if there are plans to flood these headings and create artificial reservoirs the scale of which will resemble that of the Solina Lagoon (Zalew Soliński). Neither should it be stored at dangerous dumping grounds.

Emissions to the air are reduced to the extent allowed by the best currently available technology. However, it should be emphasized that the conducted calculations of dust emissions, based on the assumption that the total (EF and FGD) dedusting efficiency reaches $\eta = 99.9\%$, are higher compared to the data of "Bełchatów" Power Plant, based on the dust emission indicator 0.06 kg/MWh. Further reduction of dust emissions is possible after introducing basic technological changes, such as CCS or coal gasification. Given a minimum double increase in the cost of produced electrical energy, it is difficult to evaluate the plausibility of such technological changes.

CONCLUSIONS

- The output of ca 550 Tg of coal from „Szczerców” Field and its burning in the power blocks of „Bełchatów” Power Plant in the years 2013–2030 is a rare enterprise. It will be accompanied by a transfer of trace elements into ash, slag and gypsum from the FGD unit and emissions with the emitted dust into the air. The evaluation of the influence of these processes on the biosphere requires research into the speciation and migration of harmful trace elements in the conditions of work of “Bełchatów” Brown Coal Mine and “Bełchatów” Power Plant.
- The emissions of trace elements into the air are effectively limited due to the use of electrofilters and the wet limestone method of flue gas desulphurisation.
- Mercury emissions into the air are low due to the transfer to gypsum in the flue gas desulphurisation process.
- Potential susceptibility to the washing out and volatilization of mercury contained in gypsum which is currently processed into building materials should be investigated.
- It is necessary to assess the prospects of the previously applied methods of slag, ash and FGD gypsum utilization, taking into consideration the accumulation of trace elements from the burned brown coal.

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