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OPTIMALIZATION OF METALS IONS EXTRACTION FROM INDUSTRIAL WASTEWATER SLUDGE WITH CHELATING AGENTS

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Abstract: The report presents the results of selected heavy metals (Zn, Cu, Cd, Ni, Pb) removal from industrial wastewater sludge collected from metallurgy industry. As washing solutions two chelating agents were used: EDTA and citric acid. The study was focused on 0.000 (deionized water), 0.010, 0.050, 0.075, 0.100 M and 0.000, 0.050, 0.100, 0.500, 1.000 M, EDTA and citric acid solutions, respectively.

Efficiency of EDTA and citric acid solutions for metal removal was studied by extraction of sludge samples with chelators. Chemical extraction of selected metals was effective for both types of solution. Optimal concentration of EDTA was 0.100M for Zn, Ni and Cd, 0.075 M for Cu and Pb. Optimal concentration of citric acid was 0.500 M for all analyzed metals.

INTRODUCTION

Rapid industrialization, urbanization and modern agricultural activities have resulted in increased release of toxic heavy metals entering the biosphere. Especially electroplating, metallurgical, semiconductors production and printed circuit bard industry generates toxic metal ions-containing wastewaters. Simple, effective and economic classical treatment of these wastewaters, involving chemical precipitation under alkaline conditions, results in hazardous solid waste generation. High concentration of metals in sludge is one of the most important environmental problems. Unlike organic compounds, that can be biodegraded with time or can be combusted, metals are not degradable, they accumulate in living organisms and remain a real potential threat to the environment and human health [12]. Therefore, direct disposal of hazardous metals containing sludge may cause serious soil and ground water pollution problems. Protection of the environment from metal containing sludge impact has put pressure to research into adequate application of these materials.

Heavy metals in wastewater sludge are present in different forms and their mobility and bioavailability is dependent on fraction of solid matrix. Moreover, the form of metal changes during digestion processes [3]. The named metals are toxic for humans, animals and plants. They can accumulate to phytotoxic levels which results in reduced grow of plants and after consumption by animals they enter the food chain [19]. The metals of great concern are Zn, Cu, Cd, Pb and Ni. Zinc, copper, cadmium and lead are especially interesting because of their phytotoxicity. Nickel accumulates generally in kidneys and causes allergic reactions as well as disorders of kidneys, lungs or liver.

Heavy metals' content in wastewater sludge is a general limitation for their practical application, but disposal of sludge is in practice significantly reduced according to European Union Directive 99/31/EC. An effective approach to reduce the toxicity of metals in sludge is the metals removal from sludge. In recent years, several attempts have been made for different technologies of metals ions removal, e.g. ion exchange, adsorption, electrochemical, chemical extraction, bioleaching or supercritical extraction [1, 2, 11, 14, 16, 20]. By using an adequate approach, a selective removal of heavy metals, to make sludge non-hazardous, is possible. Such methods can also result in concentration, recycling and reuse of the heavy metals [5].

Various methods used for the extraction of heavy metals from sludge have previously been used for the removal of metals from soils. Recently different chemicals have been reported as an effective agents for extraction of metals from sewage sludge, e.g. nitric acid [4], sulfuric acid [10], ferric sulfate [8]. But chelating agents such as EDTA (ethylenediaminetetraacetic acid) and citric acid seem to be very promising. In comparison with other chelating agents, they present some advantages, mainly a high level of complexing capacity with respect to heavy metals [18] and a large stability as complexing agents [15]. Due to their high extraction efficiency for most metals and high stability, EDTA and citric acid have been extensively investigated for applications in contaminated sediment remediation [9, 13, 15].

The purpose of this study was optimalization of experimental conditions for selected heavy metals (Zn, Cu, Cd, Ni and Pb) extraction from industrial wastewater sludge using aqueous solutions of EDTA (ethylenediaminetetraacetic acid) and citric acid at different concentration.

EXPERIMENTAL PROCEDURE

Material

The analyzed wastewater sludge was collected from metallurgic industry treatment plant in central Poland. The samples were air-dried under laboratory condition (temperature about 20ºC), homogenized in an agate mortar and passed through a stainless sieve with 2 mm diameter meshes and dried at 105ºC in dryer. Then sludge samples were homogenized and kept in plastic container for further analyses.

The material was analyzed for water content, dry mass, pH, ignition residual and ignition losses as well as selected heavy metals (Zn, Cu, Cd, Ni, Pb) content. All analyses were carried out in triplicate and results given are mean values.

Water content, dry mass, ignition residual, ignition losses and pH were measured according to standard methods [7, 17]. A total content of the analysed heavy metals (Zn, Cu, Cd, Ni, Pb) in sewage sludge was determined after digestion with mixture of concentrated mineral acids: HNO_3 and HCl (1 + 3 – aqua regia). Content of heavy metals was detected by atomic absorption spectrometry (novAA 400 Analytik Jena spectrometer).

Extraction procedure

Efficiency of EDTA and citric acid solutions for selected heavy metals removal was determined using single step washing tests. Extraction of 5 g samples of dried and homogenized sludge was carried out with 50 cm^3 EDTA solution at concentration 0.00 (deionized water), 0.010, 0.050, 0.100 M and citric acid solution with concentration 0.000 (deionized water), 0.050, 0.100, 0.500, 1.000 M. Samples were shaken for 6 hours, then the extracts were filtered through a filter paper and finally extracts were analyzed for heavy metals content by atomic absorption spectrophotometry. Results given are mean values from triplicate analysis.

RESULTS AND DISCUSSION

The studied wastewater sludge was characterized by pH equal to 9.1, small content of organic matter given as ignition losses 36 g/kg of sludge and high mineral matter content (ignition residual 425 g/kg of sludge). Water content was at the level of 54%. Analyzed industrial wastewater sludge was practically in inorganic form, organic compounds content was negligible.

The total content of heavy metals in wastewater sludge was relatively high: 3665.0, 112.5, 3.2, 85.0 and 120.3 mg/kg d.m. for zinc, copper, cadmium, nickel and lead, respectively. The order of metal content in sludge was Zn > Pb > Cu > Ni > Cd. Especially large concentration of zinc and copper, classified the analyzed sludge as potentially hazardous material.

Single step extraction procedures indicated different behavior of metals in solutions of EDTA and citric acid. Wide variations in metal removal efficiency were depending on both the considered metal and the agent used for extraction. Figure 1 summarizes plots obtained for metal concentration in eluates in dependency on concentration of chelating agent used.

The amount of Zn in wastewater sludge was the highest among investigated metals and concentrations obtained in particular extractants were the highest, too. The lowest concentration of zinc, after 6 hours' extraction, was observed in pure deionized water (0.50 $mgZn/dm^3$). As concentration of EDTA increased, the concentration of Zn in eluate increased reaching the highest value 249.20 mg/dm^3 in 0.100 M EDTA. Relationship between zinc concentration changes and EDTA concentration (Figure 1A) is almost linear and the further increase of Zn content is stopped only by limited solubility of EDTA in water. Thus optimal concentration of EDTA for removal of zinc from the studied wastewater sludge was determined at the level of 0.100 M. Efficiency of 0.100 M EDTA for zinc extraction (calculated assuming Zn concentration in eluate and total metal content in dry mass of sewage sludge) was equal to 68%.

The plot of Zn concentration in eluate versus concentration of citric acid (Figure 1B) was similar at the initial part of experiment. For citric acid solutions from 0.000 up to 0.100 M the relationship is nearly linear and the concentration of zinc changes from 0.50 to 315.00 mg/dm^3. For higher concentration of citric acid, the process of metal extraction reached equilibrium and the concentration of zinc was equal 360.00 and 372.00 mg/dm^3 in 0.500 and 1.000 M citric acid, respectively. Optimal concentration of citric acid for zinc extraction was 0.500 M, and related efficiency of citric acid was 98%.

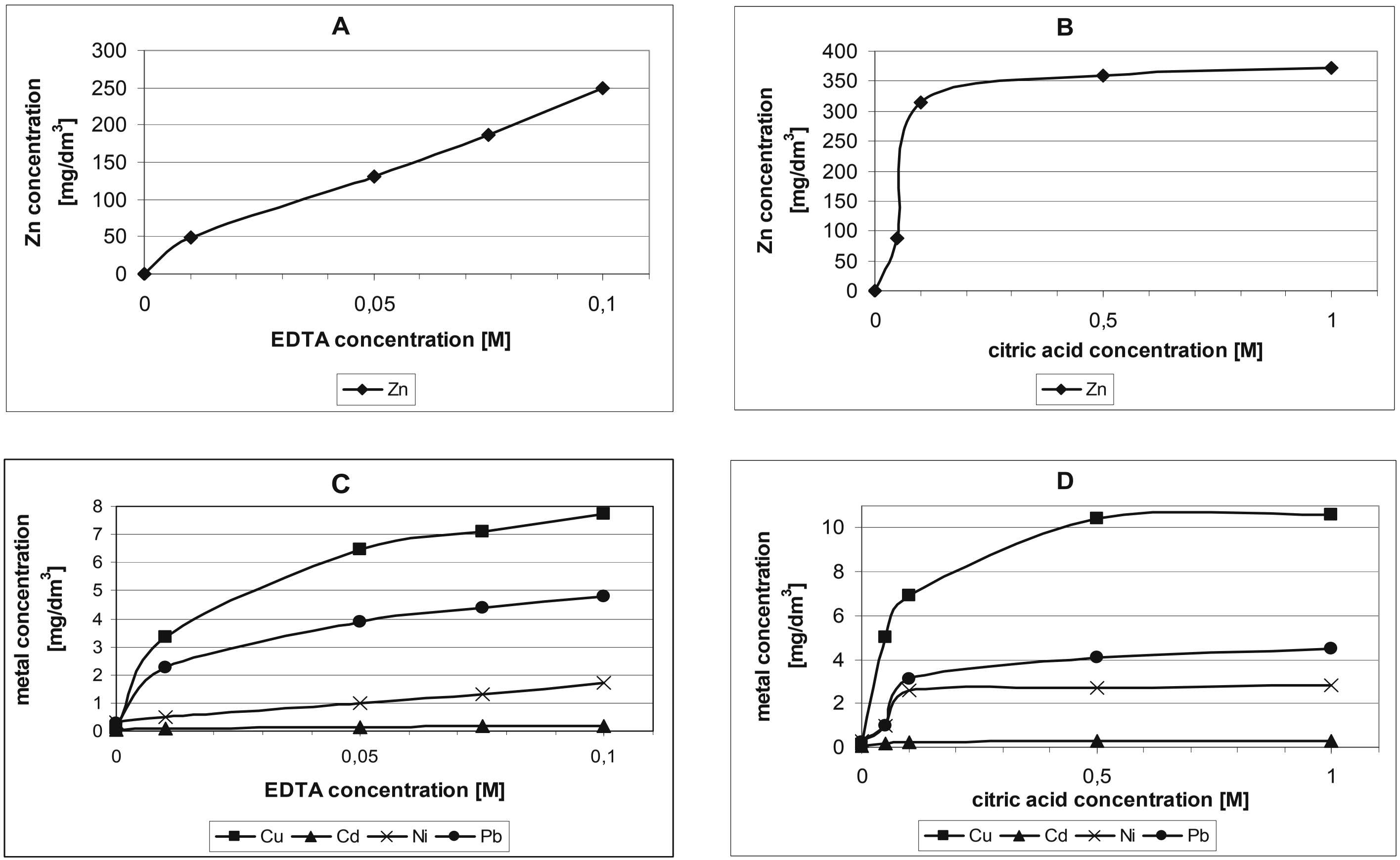

Fig. 1. Concentration of metals (Zn, Cu, Cd, Ni, Pb) obtained in chelating agents: EDTA (A, C) and citric acid (B, D), after 6 hours extraction of 5 g sample of industrial wastewater sludge

The relationships for nickel and cadmium extracted with EDTA are presented on Figure 1C. The concentration of metal in eluate was the lowest in deionized water (0.00 M EDTA): 0.3 and 0.05 mg/dm^3 for Ni and Cd respectively. Increased concentration yielded raising in metals concentration in eluates and the dependences were almost linear. For 0.100 M EDTA the measured values of concentration were 1.72 and 0.20 mg/dm^3 for Ni and Cd, respectively. Efficiencies of extraction processes with optimal concentration of EDTA (0.100 M) were 62 and 20%.

Different plots were obtained for copper and lead (Figure 1C). The increase in EDTA concentration resulted in raising of metal concentration in eluate, but the relationship was similar to that for zinc concentration in citric acid. Initial change was significantly higher, but further changes were lower and the plot was not linear. The concentrations of copper and lead in 0.075 M EDTA (7.10 mg /dm^3 for Cu and 4.40 mg /dm^3 for Pb) were practically the same as the concentrations in 0.100 M EDTA (7.70 mg Cu/dm^3 and 4.80 mg Pb/dm^3). Thus for Cu and Pb the optimal concentration of EDTA was 0.075 M with efficiencies 50 and 37% for Cu and Pb, respectively.

Figure 1D presents changes in Cu, Cd, Ni and Pb concentration after extraction of wastewater sludge with citric acid. Citric acid was the efficient washing solution in the case of all analyzed metals. Similarly to the behavior described for zinc, the lowest values of concentration were obtained in deionized water (0.10, 0.05, 0.30, and 0.20 mg/dm^3 for Cu, Cd, Ni and Pb respectively) and increase in citric acid concentration resulted in increase of metals content in extracts. At optimal concentration of citric acid (0.500 M) the obtained concentrations of Cu, Cd, Ni and Pd were 10.4, 0.3, 2.7, 4.1 mg/dm^3, respectively. For further increase of citric acid concentration, the studied heavy metals content in liquid was practically at the same level. Calculated efficiencies for optimal concentration of citric acid solution were 92, 88, 32 and 34% for Cu, Cd, Ni and Pb, respectively.

Studied metals removal from industrial wastewater sludge was in the order: Cu > Zn > Cd > Pb > Ni using 0.100 M EDTA. For the same concentration of citric acid the obtained order was: Zn > Cd > Cu > Pb > Ni. The highest efficiencies were observed for 1.000 M citric acid and reached about 100% for Zn, 95% for Cd, 94% for Cu, 37% for Pb and 33% for Ni. The mobility of zinc, cadmium and copper was higher than the mobility of lead and nickel. Extraction efficiencies of various metals, presented in the literature, are different [10, 14] independently of an extractant type.

EDTA and citric acid efficiencies for metals removal, determined previously by Nair *et al*. for electroplating industry wastewater sludge, were significantly lower [13]. That behavior suggested that metals ions bounding with matrix strictly determined the mobility of metal and optimization of extraction process conditions, especially extractant concentration, have to be considered as a first step of experiment.

Generally EDTA, citric acid and other chelators were reported as useful agents for metals ions removal from industrial [10, 13] and municipal sewage sludge [1], water sediments [6] as well as soil [18].

Chemical extraction of metals from wastewater sludge generated new waste material – liquid with relatively high content of hazardous heavy metals. The concentration of Zn, Cu, Cd, Ni, Pb reached 249.2, 7.7, 0.2, 4.8 mg/dm^3 in EDTA eluates and 372.0, 10.6, 0.3, 2.8 and 4.5 mg/dm^3 in citric acid eluates, respectively. Heavy metals should be recovered from extracts by precipitation under alkaline condition or by electrochemical reduction to obtain metallic form for further practical application.

CONCLUSIONS

The studied material contained a relatively high concentration of zinc, copper and lead and could be classified as environmentally hazardous. Both analyzed chelators: EDTA and citric acid were efficient for selected heavy metals removal from industrial sewage sludge. Further experiments should be developed for metals removal from municipal sewage sludge before their natural and agricultural application of sludge. Removal of analyzed metals was dependent on the concentration of extracting agent and raised with increasing concentration of chelators.

The results of experimental tests performed at different chelators concentrations show that EDTA was more effective with respect to citric acid in removing copper and lead but citric acid was more effective for zinc, cadmium and nickel removal from the studied material.

The optimal concentration of chelators for particular heavy metals washing was determined: 0.100 M EDTA for Zn, Ni and Cd, 0.075M EDTA for Cu and Pb and 0.500 M citric acid for all analyzed metals.

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OPTYMALIZACJA PROCESU EKSTRAKCJI JONÓW METALI Z PRZEMYSŁOWYCH OSADÓW ŚCIEKOWYCH ZA POMOCĄ ROZTWORÓW ZWIĄZKÓW CHELATUJĄCYCH

W skali roku generowane są na oczyszczalniach ścieków ogromne ilości osadów, które kumulują wiele szkodliwych substancji zarówno organicznych, jak i nieorganicznych. Pośród nich szczególne zagrożenie dla środowiska stanowią jony metali ciężkich. Podstawowe kierunki zagospodarowania osadów ustalają limity zawartości metali ciężkich. Z kolei przetrzymywanie osadów na składowiskach innych niż składowisko odpadów niebezpiecznych jest w znacznym stopniu ograniczone przez wymogi Dyrektywy Unii Europejskiej 99/31/EC.

Celem badań było określenie optymalnych warunków prowadzenia ekstrakcji metali ciężkich (Zn, Cu, Cd, Ni, Pb) z osadów ściekowych przy użyciu wybranych ekstrahentów jak EDTA (kwas etylenodiaminotetraoctowy) i kwas cytrynowy. Osady ściekowe pochodziły z oczyszczalni ścieków przemysłowych zakładu metalurgicznego. W osadach całkowitą zawartość metali ciężkich oznaczono, po mineralizacji wodą królewską, metodą ASA.

Efektywność wodnych roztworów EDTA i kwasu cytrynowego w wymywaniu badanych metali ciężkich określano poprzez ekstrakcję próbek wodą demineralizowaną, roztworem EDTA o stężeniach: 0.010, 0.050, 0.075, 0.100 M oraz kwasu cytrynowego o stężeniach: 0.050, 0.100, 0.500 oraz 1.000 M. Ekstrakcję prowadzono przez 6 godzin w temperaturze pokojowej. W uzyskanych ekstraktach oznaczono zawartość metali ciężkich metodą ASA.

Badane osady były znacznie zanieczyszczone metalami. Oznaczone całkowite zawartości cynku, miedzi, kadmu, niklu i ołowiu wynosiły odpowiednio: 3665.0, 112.5, 3.2, 85.0 oraz 120.3 mg/kg s.m.o.

Zarówno EDTA, jak i kwas cytrynowy okazały się efektywnymi ekstrahentami badanych metali, przy czym optymalne stężenia dla prowadzenia procesu wyniosły odpowiednio 0.075 oraz 0.500 M. Porównując stopień usunięcia metali z badanych osadów ściekowych przez roztwory o takim samym stężeniu (0.100 M) stwierdzono, że efektywniejszym ekstrahentem dla miedzi i ołowiu okazał się roztwór EDTA, a dla cynku kadmu i niklu roztwór kwasu cytrynowego.