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CHEMICALLY MODIFIED EXCESSIVE SLUDGE AS AN ADSORBENT OF DYES

CHEMICZNIE MODYFIKOWANY OSAD NADMIERNY JAKO SORBENT BARWNIKÓW

Abstract: In the municipal wastewater treatment technology, the biological method based on the activated sludge process is most commonly used. The activated sludge consists of small flocs, which mainly include bacteria. During the purification process, the growth of microorganisms and their multiplication occurs. Whereby it is necessary to discharge the excess sludge outside the technological system to maintain the concentration of the activated sludge in bioreactor at the appropriate level. Currently, the excess sludge is subjected to the stabilization process (usually biologically) and then it is directed to e.g. agricultural use as fertilizer. In recent years, research is conducted on the use of excessive sludge in the sorption process as a waste sorbent. During the studies, experiments on the use of a chemically modified excess sludge (as an sorbent) to remove two dyes from aqueous solutions (Acid Red 18 and Acid Green 16) were conducted. Excessive activated sludge was thickened, dried at 105 °C and ground to a grain size < 0.49 mm. The sludge was then chemically treated using Fenton's reagent. Next, the adsorption process was carried out. The effect of pH, the effect of reaction time and sorption isotherm was determined. Parameters of three models of isotherms were calculated: Freundlich, Langmuir and Dubinin-Radushkevich.

Keywords: excessive sludge, waste sorbents, sorption process, dyes removal, sorption isotherm

Introduction

Synthetic dyes have been used in numerous industries, such as: textile, paper, cosmetic, dyestaff, carpet, wool, plastic and leather. Their characteristic enable effective covering the surfaces, on which they are applied, giving them required colour. For this reason, dyes are resistant to action of e.g. detergents [1, 2]. Production processes generate wastewater, which to a smaller or larger extent contains dyes used in the production. Most synthetic dyes are complex organic compounds, which contain aromatic rings. Therefore, dyes often are of toxic, carcinogenic and mutagenic properties [3]. The symptoms of harmful effect of dyes on humans include: dysfunction of kidneys, reproductive system, liver, brain and central nervous system [4]. Moreover, dyes discharged into the water ecosystems affect unfavourably on the photosynthesis process through decreasing the light penetration into water reservoirs and rivers.

To protect aqueous ecosystems and human health, effective treatment of dye-containing wastewater is necessary. Various purifying methods are implemented, including biological processes [5], chemical oxidation [6-8], precipitation and coagulation [9, 10], membrane techniques [5], or adsorption processes [3, 11, 12].

The phenomenon of adsorption occurs when surface forces, located on the interface, contribute to changes in the number of molecules. Adsorption then occurs on the boundary

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surface. The number of surface contacts that cause adsorption is defined as the probability of adhesion. This process occurs in two ways: physical or chemical. In the case of physical adsorption, van der Waals bonds as well as hydrogen bonds occur. However, chemical adsorption, also called chemisorption, can take place at high temperatures different from the critical temperature of the adsorbate.

Methodology

Dyes

In the study two acid dyes were used: Acid Red 18 (referred as AR 18) and Acid Green 16 (referred as AG 16).

The Acid Red 18 dye belongs to the azo dyes group, which contain one or more azo bonds in their structure. This is an example of sulfonated dye and is used in many food product and textile products. It is also characterized by relatively high resistance to light and oxidant reagents, which results in less effective purification using biological methods and conventional treatment processes [13, 14].

The Acid Green 16 dye is an example of triphenylmethane group. This dye is characterized by genotoxic and mutagenic effects in mice [15]. In its structure such functional groups as aryl-amino-dimethyl and sulfonic groups and also naphthalene ring [16]. Acid Green 16 is mainly used in industries such as: textile industry, especially for the dyeing of wool and silk [17].

Sorbent

Excessive activated sludge from a municipal sewage treatment plant adapted to remove nutrients (using aerobic activated sludge) was used in the research. The sludge was initially dried at 105 °C, ground to grain size < 0.49 mm and then chemically modified by Fenton reaction. For this purpose, the following doses of reagents were used: reaction pH equal to 3, 0.4 g H_2O_2/g_{sludge}, 0.5 g $FeSO_4/g_{sludge}$, contact time of 24 hours. After this time, the sludge was separated from the reagent solution, washed with distilled water (to remove residual Fenton reagents), dried at 105 °C and ground once again to a grain size < 0.49 mm.

Experiments procedure

The experiments were conducted in three phases:

- the effect of pH value,
- the effect of contact time of dye solution with adsorbent surface,
- the estimation of sorption isotherm.

To determine the influence of pH on the effectiveness of the adsorption process, five different pH values were used: 2, 4, 6, 8 and 10. For this purpose, 50 cm^3 of dyes at an initial concentration of 700 mg/dm^3 were introduced into 250 cm^3 Erlenmeyer flasks. Sludge (sorbent) was added in the amount of 0.1 g (concentration of sludge was 2 g/dm^3) and the pH adjusted to the appropriate value using 10 % H_2SO_4 or 5 % NaOH. The samples, prepared according to the described procedure, were shaken for 60 minutes. After this time, the sludge was separated from the dye solutions by centrifugation. In the dye solutions obtained in this way, the remaining dye concentration was determined by spectrophotometry method using calibration curves at the appropriate wavelength (λ = 506 nm for AR 18 and λ = 631 nm for AG 16). The amount of dye adsorbed was then calculated using equation:

$$q_e = \frac{(C_0 - C_e)}{m_{sl}} \tag{1}$$

where: q_e - the amount of dye adsorbed at equilibrium [mg/g], C_e - the dye concentration at equilibrium [mg/dm^3], C_0 - the initial dye concentration [mg/dm^3], m_{sl} - amount of sludge [g/dm^3].

In the case of determining the effect of adsorbent contact time with dye solutions on the efficiency of the adsorption process, the process was carried out at the most favourable pH value obtained in the first stage of study and using an initial concentration of dyes of 700 mg/dm^3. The concentrations of sludge in the samples were 2 g/dm^3. Increasing contact times from 5 minutes up to 180 minutes were applied. After an appropriate contact time, the samples were subjected to an analogical procedure to determine the final concentration of dyes in the solutions, as described in the first stage of the study. The amount of dye adsorbed was also calculated according to eq. (1).

The final stage of the study served to determine the adsorption isotherm $q_e = f(C_e)$. To this end, for the designated contact time (determined on the basis of the second stage of testing) and the pH of the solutions (obtained in the first stage of testing), the adsorption process was carried out using increasing values of the initial concentration of dyes (from 100 to 1600 mg/dm^3) for the sludge concentration (adsorbent) equal to 2 g/dm^3.

Based on the results obtained in the third stage, calculations were carried out to determine the parameters of adsorption processes such as: mean adsorption energy, adsorption capacity, adsorption type. Three linear forms of two-parameter isotherm models were used: Freundlich, Langmuir and Dubinin-Radushkevich (equations (2)-(7)).

Freundlich model:

$$\log q_e = \log K_F \cdot \frac{1}{n} \log C_e \tag{2}$$

Langmuir model:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L \cdot q_m} \tag{3}$$

$$\frac{1}{q_e} = \frac{1}{K_L \cdot q_m} \cdot \frac{1}{C_e} + \frac{1}{q_m} \tag{4}$$

Dubinin-Radushkevich model:

$$\ln q_e = \ln Q_s - K_{DR} \cdot \varepsilon^2 \tag{5}$$

$$\varepsilon = \mathrm{R}T \cdot \ln\left(1 + \frac{1}{C_e}\right) \tag{6}$$

$$E = \frac{1}{\sqrt{2 \cdot K_{DR}}} \tag{7}$$

where: q_e - the amount of dye adsorbed at equilibrium [mg/g], C_e - the dye concentration at equilibrium [mg/dm^3], m_{sl} - amount of sludge [g/dm^3], K_L - Langmuir constant related to the free energy of adsorption [dm^3/mg], q_m - maximum adsorption capacity in Langmuir model [mg/g], n - Freundlich equation exponents [-], K_F - Freundlich constant indicative of the relative adsorption capacity of the adsorbent [mg$^{(1-1/n)}$dm$^{3(1/n)}$/g], Q_s - theoretical monolayer saturation capacity in Dubinin-Radushkevich model [mg/g], K_{DR} - Dubinin-Radushkevich model constant [mol^2/kJ^2], E - mean energy of sorption [kJ/mol], ε - Polanyi potential [-], R - gas constant [8.314 J/mol·K], T - the absolute temperature [K].

Results and discussion

Effect of pH

The conducted experiments showed a significant impact of the pH value of solutions on the efficiency of the adsorption process. Much higher adsorbed charge values were obtained at a pH of 2 for both dyes. The use of higher pH values contributed to a significant reduction in the efficiency of adsorption (Fig. 1). This phenomenon is associated with the nature of the molecules of the dyes used. Both AR 18 and AG 16 belong to the group of acid dyes. Therefore, the charge of dye molecules in their aqueous solutions is negative.

The use of low pH contributes to the presence of large amounts of positive hydrogen ions in the solution, which cover the adsorbent surface thus causing the attraction and binding of dye molecules on the surface of the sludge (adsorbent).

a) b)

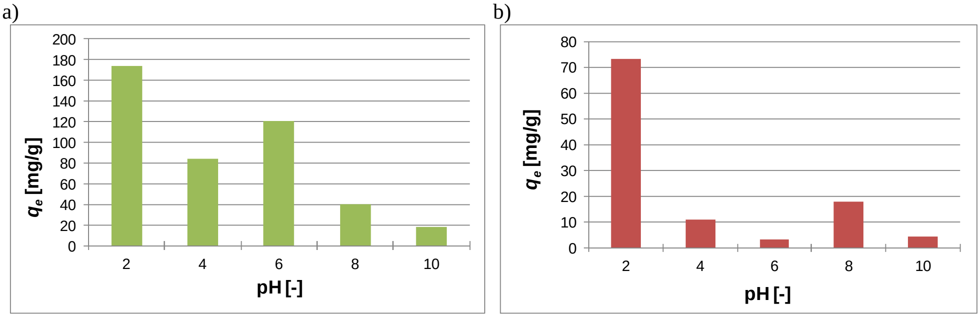

Fig. 1. Effect of pH for dye: a) AG 16, b) AR 18

Effect of contact time

During the study, the impact of contact time on the adsorption efficiency was checked. Based on the results of this stage, the most favourable value of contact time was determined. The experiments showed that for both dyes the adsorption process was the fastest in the first minutes of the process. In the case of AG 16, the largest increase in adsorbed charge took place in the first 5 minutes of the process, while extending the contact time to 45 minutes contributed to an increase in the efficiency of the adsorption process (Fig. 2). However, in the case of the AR 18 dye, the largest increase in q_e was noted in the first 30 minutes of the reaction, after which the process efficiency remained relatively stable. Therefore, in the case of AG 16, contact time of 45 minutes was considered as the time after which the adsorption equilibrium occurred, and in the case of AR 18 - the time of 30 minutes.

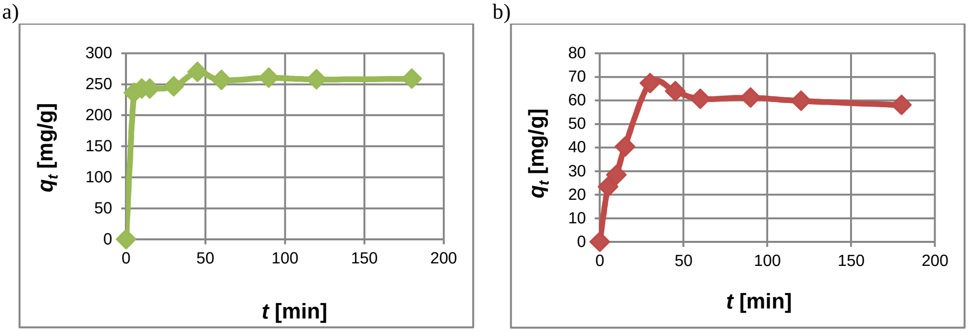

Fig. 2. Effect of contact time on sorption efficiency: a) AG 16, b) AR 18

Sorption isotherm

The final stage of the study was to determine the dye adsorption isotherm on chemically modified excessive sludge. For both dyes, the shape of the adsorption isotherm graph ($q_e = f(C_e)$) suggests that multilayer adsorption occurred or the maximum capacity of the monolayer was not been achieved. For both dyes, AR 18 and AG 16, in the range of dye initial concentration values applied, the plot of the adsorbed amount of dye *vs* the equilibrium concentration shows an almost linear relationship (Fig. 3).

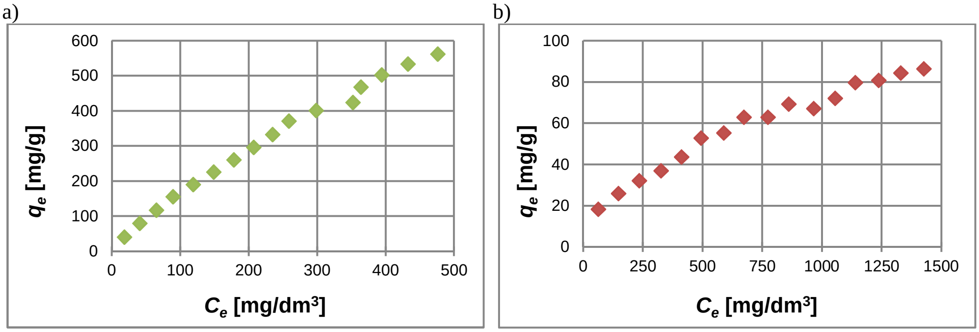

Fig. 3. Sorption isotherm for dye: a) AG 16, b) AR 18

Freundlich model

Based on the results obtained in the third stage of the tests (associated with the determination of adsorption isotherms), the parameters of the Freundlich isotherm model were determined based on the linear form described by equation (2). For this purpose, a graph of $\log q_e = f(\log C_e)$ was made and, based on linear estimation, values of parameters K_F and $1/n$ were calculated (Fig. 4). For both dyes, the value of $1/n$ was obtained lower than 1. This indicates that physical and not chemical sorption occurred. The correlation coefficient value was also determined. For both dyes, its value was 0.99 and above, while better matching of results to the Freundlich model was obtained for dye AG 16 (higher R^2 value was achieved).

a) b)

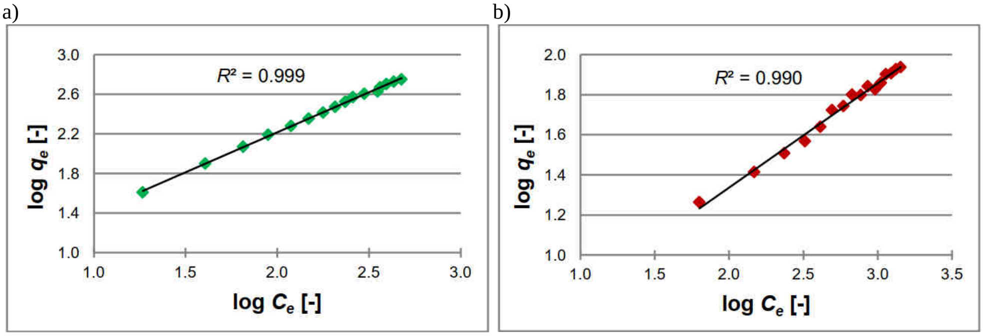

Fig. 4. Linear form of Freundlich isotherm model for: a) AG 16 and b) AR 18

Langmuir model

a) b)

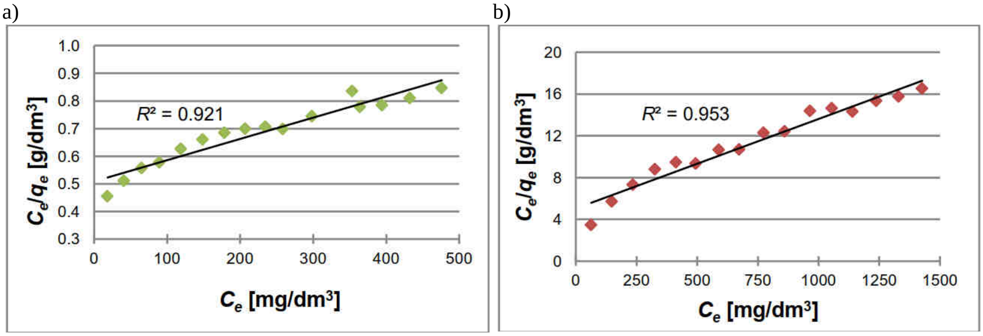

Fig. 5. The first linear form of Langmuir isotherm model according to eq. (3) for: a) AG 16 and b) AR 18

a) b)

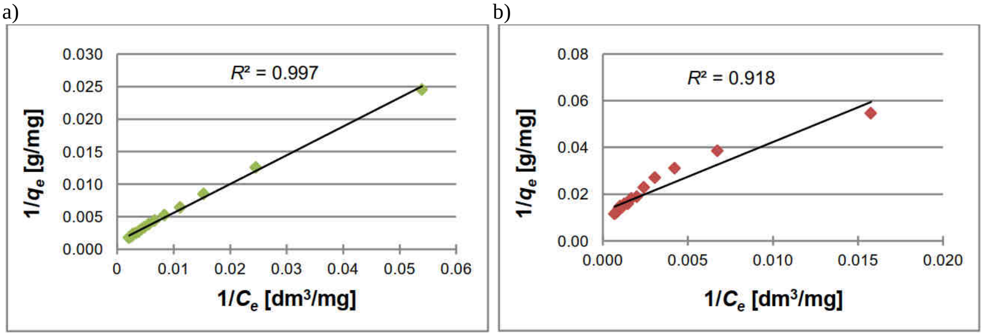

Fig. 6. The second linear form of Langmuir isotherm model according to eq. (4) for: a) AG 16 and b) AR 18

The parameters of the Langmuir model were also calculated using the test results obtained in the last phase of the experiments. Two different linear forms of this model were used, described by equations (3) and (4). The results showed that better matching of the test results to this isotherm model was obtained for dye AG 16 than AR 18. The values of R^2 were equal to 0.997 and 0.953 for AG 16 (Fig. 6a) and AR 18 (Fig. 5b) respectively.

The maximum sorption capacities for both dyes were also calculated. Much higher values of this parameter were obtained for the AG 16 (q_m = 833.3 mg/g) than for the AR 18 (q_m = 116.3 mg/g).

Dubinin-Radushkevich model

In the case of the Dubinin-Radushkevich model, both dyes showed a slight match. The correlation coefficient R^2 values reached small levels, 0.599 and 0.541 for Ag 16 and AR 18, respectively (Fig. 7). Adsorption energy E was calculated (based on K_{DR} parameter), its value for both dyes being lower than 8 kJ/mol (Table 1). This indicates that physical sorption occurred. The sorption capacities of the monolayer Q_s were also calculated. The results showed that much higher capacity was noted for the dye AG 16 (Q_s = 345.4 mg/g) than for AR 18 (Q_s = 60.2 mg/g), similar to the q_m values calculated from the Langmuir model.

Table 1

The parameters of sorption isotherm models

Isotherm model	Dye	Parameter	Unit	Value
Freundlich	AR 18	$1/n$	[-]	0.521
		K_F	[mg$^{(1-1/n)}$dm$^{3(1/n)}$/g]	1.970
		R^2	[-]	0.990
	AG 16	$1/n$	[-]	0.807
		K_F	[mg$^{(1-1/n)}$dm$^{3(1/n)}$/g]	3.991
		R^2	[-]	0.999
Langmuir	AR 18	q_m	[mg/g]	116.3
		K_L	[dm^3/mg]	0.00171
		R^2	[-]	0.953
	AG 16	q_m	[mg/g]	833.3
		K_L	[dm^3/mg]	0.00271
		R^2	[-]	0.997
Dubinin-Radushkevich	AR 18	Q_s	[mg/g]	60.2
		K_{DR}	[mol^2/kJ^2]	933.9
		E	[kJ/mol]	0.0231
		R^2	[-]	0.541
	AG 16	Q_s	[mg/g]	345.4
		K_{DR}	[mol^2/kJ^2]	144.3
		E	[kJ/mol]	0.0594
		R^2	[-]	0.599

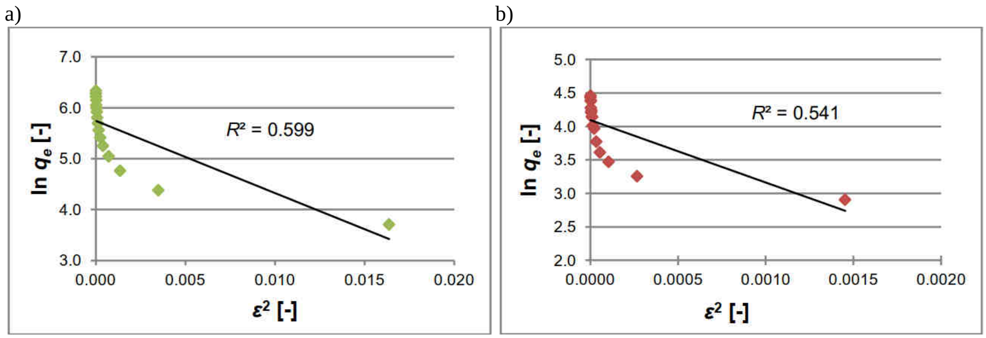

Fig. 7. Linear form of Dubinin-Radushkevich isotherm model for: a) AG 16 and b) AR 18

Conclusion

Based on the results of the studies including the determination of effect of pH, contact time and the estimation of sorption isotherm, the following may be concluded:

1. The most favourable pH value of adsorption was 2 for both dyes; when pH was greater than 2, the effectiveness decreased significantly.
2. In the case of dye AG 16, much higher amounts of adsorbed dyes were observed in comparison with dye AR 18.
3. In the case of AR 18, the most favourable contact time of the sorbent and the dye equalled 30 min. And in the case of AG 16, it was 45 min.
4. The highest value of correlation coefficient was obtained for Freundlich model for both dyes.
5. Both dyes were subject to physical sorption - the values of mean energy of sorption (E) were lower than 8 kJ/mol. Moreover, for both dyes, values of Freundlich parameter $1/n$ were lower than 1, which also indicates that physical sorption process occurred.
6. Much higher value of maximum sorption capacity (q_m) was obtained for AG 16 in comparison with AR 18.

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CHEMICZNIE MODYFIKOWANY OSAD NADMIERNY JAKO SORBENT BARWNIKÓW

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Abstrakt: W technologii oczyszczania ścieków komunalnych najczęściej stosowana jest metoda biologiczna wykorzystująca osad czynny. Osad czynny składa się z małych kłaczków, które głównie zawierają bakterie. Podczas procesu oczyszczania ma miejsce wzrost mikroorganizmów i ich namnażanie. W związku z tym konieczne jest odprowadzenie nadmiaru osadu poza układ technologiczny w celu utrzymania na odpowiednim poziomie stężenia osadu czynnego w bioreaktorze. Obecnie osad nadmierny poddawany jest procesowi stabilizacji (zwykle biologicznej), a następnie kierowany np. do wykorzystania rolniczego jako nawóz. W ostatnich latach prowadzone są badania nad możliwością wykorzystania osadu nadmiernego jako sorbentu odpadowego w procesie sorpcji. Podczas badań przeprowadzono eksperymenty z użyciem chemicznie modyfikowanego osadu nadmiernego (jako sorbentu) do usuwania dwóch barwników z roztworów wodnych (Acid Red 18 oraz Acid Green 16). Nadmierny osad czynny zagęszczono, wysuszono w 105 °C i zmielono do wielkości ziarna < 0,49 mm. Następnie osad poddano obróbce chemicznej z użyciem odczynnika Fentona, po czym przeprowadzono proces adsorpcji. Określono wpływ pH, czas reakcji i wyznaczono izotermę sorpcji. Ponadto obliczono parametry trzech modeli izoterm: Freundlicha, Langmuira i Dubinina-Radushkevicha.

Słowa kluczowe: osad nadmierny, sorbenty odpadowe, proces sorpcji, usuwanie barwników, izoterma adsorpcji