

COMPOST AS BIOSORBENT FOR REMOVAL OF ACID DYES FROM THE WASTEWATER GENERATED BY THE TEXTILE INDUSTRY

JOANNA KYZIOŁ-KOMOSIŃSKA, CZESŁAWA ROSIK-DULEWSKA,
AGNIESZKA DZIENISZEWSKA, MAGDALENA PAJĄK

Institute of Environmental Engineering, Polish Academy of Sciences, ul. M. Skłodowskiej Curie 34, 41-819 Zabrze, Poland,
Corresponding author e-mail: joasia@ipis.zabrze.pl

Keywords: Acid dyes, compost derived from cellulosic material, sorption isotherms.

Abstract: The compost derived from cellulosic material coming from the Public Utility Company in Zabrze (Poland) was investigated for its capability for adsorbing acid dyes from aqueous solution at various concentrations of the dyes and the compost dosages. Four acid dyes were investigated: Acid Red 18 (AR-18), Acid Blue 9 (AB-9), Acid Green 16 (AG-16) and Acid Black 1 (ABk-1). The adsorption isotherms were determined by comparing the experimental data with the isotherm models (Freundlich, Langmuir and Dubinin–Radushkevich models). The sorption capacity of the compost depended on the initial concentrations of dyes in the solution, compost dosage, and on the structure of dyes. The maximum sorption capacities of the compost for adsorbing particular dyes may be ordered as follows: ABk-1 > AG-16 > AB-9 > AR-18. The amounts of bound and the percentages of removed acid dyes from effluent depended on the adsorbent dosage. The growth of the dye removal percentages with growing adsorbent mass may be attributed to the growth of the adsorbent uptake surface with growth of the adsorbent mass. The dyes were bound onto the surface of compost through the electrostatic interaction between the surface (negatively charged at $\text{pH} > \text{pH}_{\text{pzc}}$) and the dye cations (AG-16), and/or through the hydrogen bond between the functional groups of the humic matter in compost (–OH, –COOH) and the functional surface groups of AR-18, AB-9 and ABk-1 dyes (–OH, –NH₂). At the experiment conditions, the Freundlich and Dubinin–Radushkevich adsorption isotherm models fitted the equilibrium data very well (much better than the Langmuir one). The values of $1/n$ in the Freundlich equation and E in the Dubinin–Radushkevich one indicate the favourable adsorption. The studied compost may be used as a low-cost sorbent for the removal of acid dyes from wastewater released by textile industries. However, elevated values of chemical oxygen demand (COD) in the final solutions may enhance the solubility of humic compounds.

INTRODUCTION

Dyes are among the most hazardous organic compounds occurring in industrial wastewater. They are applied in many modern industries (textile, paper, printing, cosmetics, pharmaceutical, food) to color products. At present, over 100000 dyes are commercially used. Their yearly production is above 7×10^5 Mg [29] and about 10–15% of their commercially used amounts are discharged into the environment as pollutants [7]. Dyes, present in water, disable photosynthesis in aqueous flora. The chemical oxygen demand (COD) of wastewater containing dyes exceeds the limits established for wastewaters allowed to be discharged into waters, soil [27] and sewage systems [26]. Some dyes can cause allergies, dermatitis, cancers and are mutagenous to humans [8]. Therefore, industrial dye-containing effluents have to be treated before releasing into the environment.

Dyes are synthetic aromatic compounds and they can be classified according to their application (Direct, Acid, Basic, Disperse, Reactive, Vat, etc.) and chemical structure (Azo, Anthraquinone, Phthalocyanine, Xanthene, Nitroso, Nitro, etc.).

Many physical, physicochemical, chemical and biological processes have been investigated for their efficiency in dye removal from effluents. The biological processes are inefficient because, in general, dyes are not biodegradable [1, 19, 20]. The physical and physicochemical processes, such as flocculation, flotation, membrane filtration, chemical precipitation and ozonation are costly and cause the problem of the secondary sludge disposal.

The most efficient method for removal of dyes from textile effluents is adsorption. The most popular adsorbent for dye removal from aqueous solutions is activated carbon. However, activated carbon is expensive and must be regenerated. Therefore, there is a growing interest in finding alternative low-cost and efficient adsorbents for dye removal from solutions. The natural humic substances, rich in organic functional groups such as carboxyl, hydroxyl and others, may be used as adsorbents to remove heavy metals and organic pollutants from wastewater. They may be natural organogenic materials, such as peat, lignite, oxihumulite [13, 15, 16, 17, 24, 25] or biosorbents and wastes from agriculture, such as sawdust, leaf powder, fruit peel, compost, etc. [4, 11, 12, 14, 21, 23, 31]. The sorption properties of the carbonaceous material depend strongly on their origin [3].

Composting is widely employed in treatment of organic waste. Universality of recycling and/or neutralizing of organic waste by composting makes composts commonly available. Compost contains large amounts of organic carbon and may be used to remove the same pollutants from water and wastewater. Although some waste-derived composts do not meet the requirements for fertilizers, they can still be used as adsorbents.

In the paper, an application of the cellulosic material-derived compost as biosorbent in removal of four acid dyes (Acid Red 18 – AR-18, Acid Blue 9 – AB-9, Acid Green 16 – AG-16 and Acid Black 1 – AB-1) from single-dye solutions by using the batch method is discussed. The isotherms of the sorption of the dyes were studied as well.

MATERIALS AND METHODS

Dye solutions

Four textile dyes:

- C.I. Acid Red 18 (AR-18) – CI 16255, CAS 2611-82-7, $C_{20}H_{11}N_2O_{10}S_3 \cdot 3Na$, 604 g mol⁻¹,
 - C.I. Acid Blue 9 (AB-9) – CI 42090, CAS 2650-18-2, $C_{37}H_{36}N_2O_9S_3 \cdot 2H_3N$, 782 g mol⁻¹,
 - C.I. Acid Green 16 (AG-16) – CI 44025, CAS 12768-78-4, $C_{27}H_{27}N_2O_6S_2$, 539 g mol⁻¹,
 - C.I. Acid Black 1 (ABk-1) – CI 20470, CAS 1064-48-8, $C_{22}H_{14}N_6O_9S_2 \cdot 2Na$, 616.6 g mol⁻¹
- were examined without pre-treatment. Their molecular structures are shown in Figure 1.

They are produced by Boruta ZACHEM-KOLOR Ltd. (Poland), a leading Polish producer of synthetic organic dyes.

The stock solutions were prepared by dissolving the dyes in distilled water to the concentration of 1000 mg L⁻¹. The working solutions were obtained by diluting the stock solutions to the following concentrations: 1, 10, 25, 50, 100, 250, 500 and 750 mg L⁻¹. The values of the solution pH were 7.65 for AR-18, 6.09 for AB-9, 5.67 for AG-16 and 7.95 for ABk-1. They were the natural pH values of the working solutions, no pH adjustments were done.

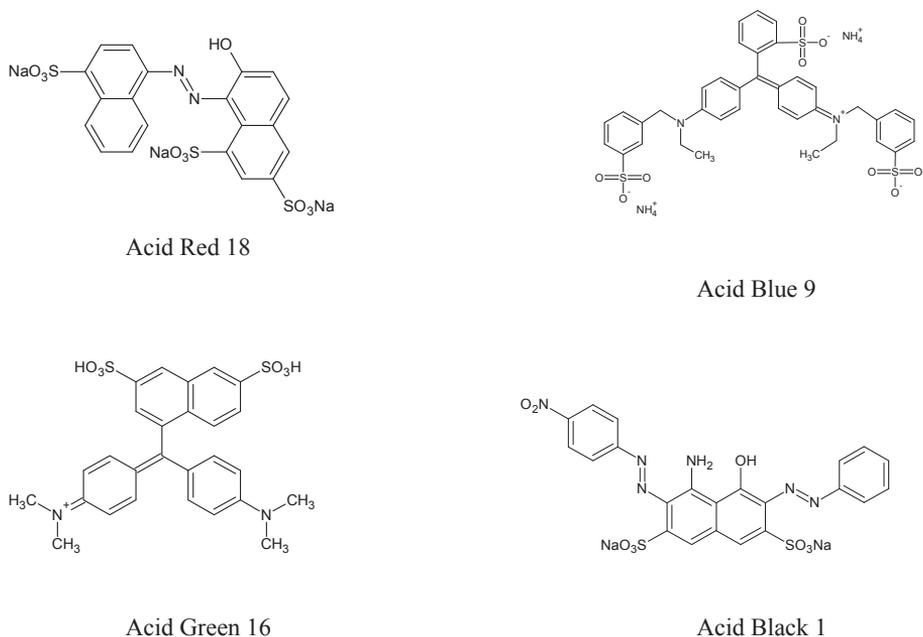


Fig.1. The molecular structure of the studied acid dyes

Characterization of adsorbent

The compost derived from cellulosic material (crushed tree branches, wood, leaves and grasses) from the Public Utility Company in Zabrze (Poland) was used as biosorbent. The compost was not chemically pre-treated. Raw compost was dried at 328K for 8 h, then ground and sieved to particles < 1000 μm .

The major physical and physicochemical properties of the compost were determined. Its specific surface area (SSA) – by using the standard BET procedure with N₂ sorption/desorption at the liquid nitrogen boiling point (Fisons, Sorptomatic 1990), its total porosity – with the use of a mercury porosimeter (Carlo Erba model 2000). The point of zero charge was determined according to the procedure described by Calvete *et al.* [5] and Cardoso *et al.* [6]. A Perkin Elmer infrared spectrometer was used to determine the main functional surface groups of organic matter in the compost and energy dispersive X-ray spectrometry (EDXRF) to determine the chemical composition and heavy metal content. The leachability of these elements was measured using the standard leaching tests (EN 12457-2). Also, the values of pH and chemical oxygen demand (COD) in the water extracts were determined.

Conditions of sorption

AR-18, AB-9, AG-16 and ABK-1 were adsorbed onto compost from the aqueous solutions in the batch contact conditions. The initial concentrations (C_0) of the dye solutions were within the range of 1–1000 mgL^{-1} , compost dosages were 50 gL^{-1} (the ratio solid phase (m):solution (V) equal to 1:20) and 20 gL^{-1} (the ratio solid phase (m):solution (V)

equal to 1:50). The compost suspensions were shaken for 24 h and centrifuged at 4000 rpm for 20 min.

The blank dye solutions, without adsorbent, were checked for possible dye adsorption onto the flasks. After 24 h contact, no adsorption of the dyes onto the walls of flasks was observed.

The initial (C_0) and final (C_{eq}) concentrations of the dyes in solution were determined by means of visible spectrophotometry (Varian Cary 50 Scan UV-VIS spectrophotometer, 1 cm long cell). The absorbance of AR-18, AB-9, AG-16 and ABk-1 was measured at the wavelengths 506, 630, 426 and 619 nm, respectively. All the batch adsorption measurements were performed three times. The sorption experiments were carried out at 296 ± 1 K.

The amounts of the dyes adsorbed onto compost (S) and the percentages of the dyes removed from the solution (R, efficiency of adsorption) were calculated from the equations:

$$S = \frac{(C_0 - C_{eq}) \cdot V}{m} \quad (1)$$

$$R = \frac{(C_0 - C_{eq})}{C_0} \cdot 100 \quad (2)$$

where: S – amount of dye taken up by the compost (mg kg^{-1}), R – amount of dye removed from the solution (%), C_0 and C_{eq} – concentrations of dyes in initial and equilibrium solutions (mg L^{-1}), respectively, m – mass of compost (g), V – volume of solution (mL).

In all equilibrium solutions the after-sorption pH was measured.

Freundlich, Langmuir and Dubinin-Radushkevich adsorption isotherm models

The Freundlich, Langmuir and Dubinin-Radushkevich adsorption isotherm models were used to describe the sorption of the acid dyes onto compost mathematically.

The Freundlich isotherm is an empirical model. It is widely applied to describe heterogeneous systems, especially adsorption of organic compounds or highly interactive species onto activated carbon and molecular sieves. It is expressed as:

$$S = K_F C_{eq}^{1/n} \quad (3)$$

where K_F and $1/n$ are constants. $1/n$ is a measure of surface heterogeneity – closer $1/n$ to zero, more heterogeneous the surface. A value of $1/n$ above 1 implies chemisorption, below 1 – cooperative adsorption, $1/n = 1$ – the adsorption is linear [9].

The Langmuir isotherm describes homogeneous adsorption, where each molecule possesses constant enthalpy and sorption activation energy (all sites possess the same affinity for the adsorbate), there is no transmigration of the adsorbate within the surface and the adsorbate molecules form a monolayer on the adsorbent surface. It is given by the equation:

$$S = \frac{Q \cdot K_L C_{eq}}{1 + K_L C_{eq}} \quad (4)$$

where Q is the maximum sorption capacity of the adsorbent for a dye (mg kg^{-1}), K_L is the adsorption equilibrium (Langmuir) constant (L mg^{-1}).

The constant dimensionless separation factor R_L is expressed as:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (5)$$

where C_0 is the highest initial concentration of a dye ($\text{mg}\cdot\text{L}^{-1}$).

R_L indicates the adsorption nature: adsorption may be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Dubinin-Radushkevich isotherm is an empirical model, generally to describe the adsorption with a Gaussian distribution of energy on a heterogeneous surface. It is expressed as:

$$Q_e = Q_D \cdot \exp(-\beta \varepsilon^2) \quad (6)$$

where Q_D is the model constant, β is a constant depending on the free energy of sorption per mole of the sorbate, ε is the Polanyi potential:

$$\varepsilon = RT \ln(1 + 1/C_{eq}) \quad (7)$$

where: R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the absolute temperature (K), C_{eq} is the equilibrium concentration of the adsorbate ($\text{mol}\cdot\text{L}^{-1}$).

This isotherm is usually used to distinguish the physical and the chemical adsorptions of metal ions, where the free energy per molecule of adsorbate (E) may be computed from the relationship:

$$E = \frac{1}{(2\beta)^{1/2}} \quad (8)$$

The sorption parameters may be estimated from linear or non-linear forms of the isotherms [2, 30]. In this paper, the linear forms of the isotherms are used.

To determine the constants K_F and $1/n$ from the Freundlich equation (Eq. 3), the linear form of the equation, received by taking the logarithm of the Eq. 3 sides, is used:

$$\ln S = \ln K_F + 1/n \ln C_{eq} \quad (9)$$

The Langmuir constants, K_L and Q , are evaluated through linearization of Eq. 4:

$$\frac{C_{eq}}{S} = \frac{C_{eq}}{Q} + \frac{1}{K_L Q} \quad (10)$$

Hence, by plotting C_{eq}/S against C_{eq} , the value of K_L may be obtained from the intercept $1/K_L \cdot Q$, and the value of Q from the slope $1/Q$.

To determine the constants Q_D and β from the Dubinin-Raduskevich Eq. 6, the linear form of the equation has been used:

$$\ln Q_e = \ln Q_D - \beta \varepsilon^2 \quad (11).$$

RESULTS AND DISCUSSION

Characterization of adsorbent

The specific surface area and total porosity of the studied compost were $14.54 \text{ m}^2\text{g}^{-1}$ and 49%, respectively. The point of zero charge of the compost was 7.72. There were amorphous iron oxides present on the compost surface (pH_{PZC} was between 3.0 and 3.5 for pure humic substances and between 8.0 and 8.5 for iron oxides). At the solution pH lower than 7.72, the surface of the compost particles was positively charged and might bind pollutants charged negatively. At the solution pH greater than 7.72, the surface of the compost particles was negatively charged and might bind pollutants charged positively.

The FTIR spectra of the compost revealed the presence of four groups: COOH ($3300\text{--}2500 \text{ cm}^{-1}$), OH (3427 cm^{-1}), C = C (1675 cm^{-1}), C = O (1680 cm^{-1}).

The ash content of the compost was 22.47%. The compost comprised 4.89% of SiO_2 , 1.21% of Al_2O_3 , 3.36% of Fe_2O_3 , 5.24% of CaO, 2.98% of K_2O , 1.34% of MgO and 0.21% of Na_2O .

The heavy metal concentrations in the compost were: Cu – $172.49 \text{ mg}\cdot\text{kg}^{-1}$, Zn – $1112 \text{ mg}\cdot\text{kg}^{-1}$, Ni – $15.73 \text{ mg}\cdot\text{kg}^{-1}$, Pb – $22.17 \text{ mg}\cdot\text{kg}^{-1}$, Cr – $145.8 \text{ mg}\cdot\text{kg}^{-1}$ and Cd – $5.55 \text{ mg}\cdot\text{kg}^{-1}$. The concentrations of these metals in water solutions were low: Cu – $0.23 \text{ mg}\cdot\text{L}^{-1}$, Zn – $1.23 \text{ mg}\cdot\text{L}^{-1}$, Ni – $0.05 \text{ mg}\cdot\text{L}^{-1}$, Pb – $0.18 \text{ mg}\cdot\text{L}^{-1}$, Cd – $0.012 \text{ mg}\cdot\text{L}^{-1}$, and Cr – $0.04 \text{ mg}\cdot\text{L}^{-1}$. Low heavy metal content of the solutions was the effect of the alkaline reaction of the water suspension (pH about 7.98). Moreover, the extract CODs were high, about $482 \text{ mgO}_2\cdot\text{L}^{-1}$, due to dissolved humic acids.

Sorption of acid dyes onto compost as the organic-matter-rich substance

The sorption of four acid dyes, AR-18, AB-9, AG-16 and ABk-1, at different initial concentrations, onto compost at its two dosages, was investigated.

Fig. 2A illustrates the sorption of the acid dyes onto compost at the solid phase:solution ratio equal to 1:20 (50 g of compost per one liter of solution). When the initial dye concentration increases from 1 to $1000 \text{ mg}\cdot\text{L}^{-1}$, the sorption capacity of compost at the equilibrium conditions increases from 12 to $4580 \text{ mg}\cdot\text{kg}^{-1}$ for AR-18, from 12 to $5780 \text{ mg}\cdot\text{kg}^{-1}$ for AB-9, from 16 to $11440 \text{ mg}\cdot\text{kg}^{-1}$ for AG-16 and from 18 to $12740 \text{ mg}\cdot\text{kg}^{-1}$ for ABk-1 (Fig. 2A).

The compost bound the dyes at their low concentrations most efficiently. With increasing initial concentrations of the dyes, the efficiency R of the compost for removing AR-18, AB-9, AG-16 and ABk-1 decreased by the percent from within the intervals 65.11–22.39%, 60–28.55, 88.89–58.90% and 96.55–65.13%, respectively (Fig. 2B).

The pH of equilibrium solutions are presented in Fig. 3. The values of pH of the final solutions were between 7.93 and 8.11 – all dyes were sorbed at almost constant pH. Because $\text{pH}_{\text{PZC}} < \text{pH}_{\text{solution}}$, it means that the surface of the compost particles was negatively charged during the sorption.

The experimental isotherms of sorption were classified according to the Gilles' classification scheme [10] basing on their initial slopes and curvatures. The isotherms for ABk-1 and AB-9 were L-type, for AR-18 and AG-16 – S-type.

At the solid phase (m):solution (V) ratio equal to 1:50 (20 g of compost per one liter of solution), the sorption capacity of the compost (S) for the dyes increased with increasing dye concentration from 35 to $3940 \text{ mg}\cdot\text{kg}^{-1}$ for AR-18, 30 and $4600 \text{ mg}\cdot\text{kg}^{-1}$ for AB-9,

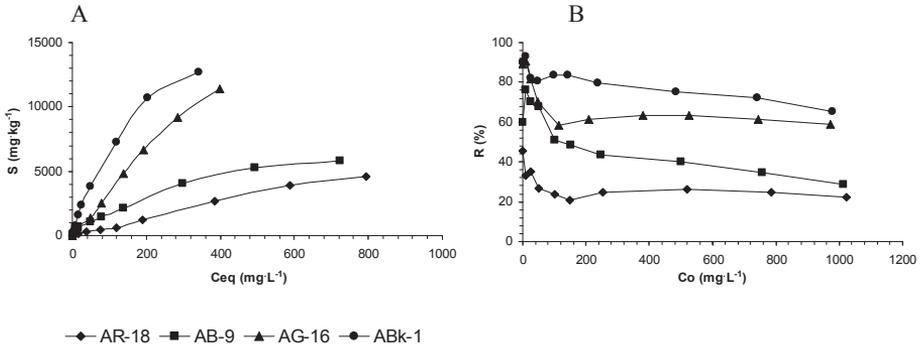


Fig. 2. Adsorption isotherms for acid dyes (A) and dependence of removal percentages of the dyes on the initial concentration (B); m:V = 1:20 (50 g of compost per liter)

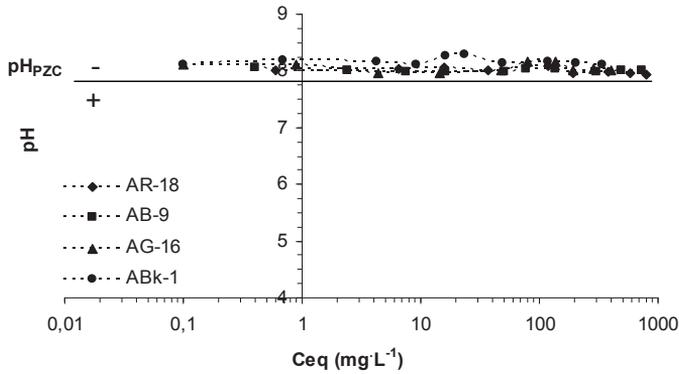


Fig. 3. Dependence of pH on the dye concentration in equilibrium solution (Ox axis scaled semi-logarithmically)

40 and 11200 mg·kg⁻¹ for AG-4, and 45 and 12580 mg·kg⁻¹ for ABk-1 (Fig. 4A). The removal percentage (R) changed between 63.64 and 7.62% for AR-18, 54.55 and 9.06% for AB-9, 72.73 and 22.48% for AG-16 and 90 and 25.83% for ABk-1 (Fig. 4B).

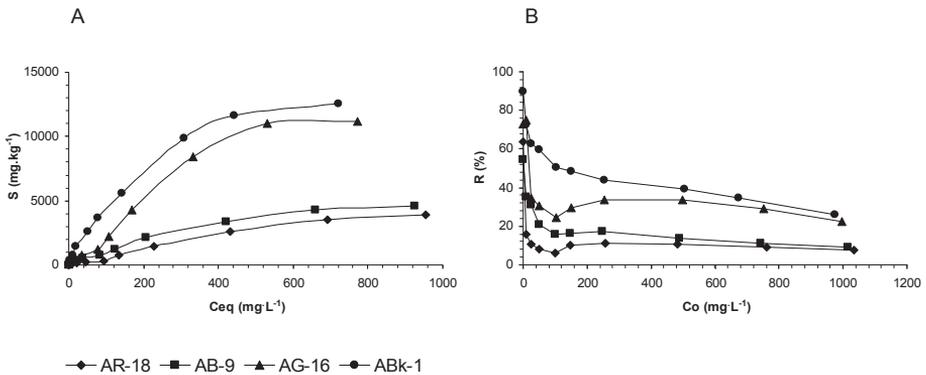


Fig. 4. Adsorption isotherms for acid dyes (A) and dependence of removal percentages of the dyes on the initial concentration (B); m:V = 1:50 (20 g of compost per liter)

The effect of the compost dosage on the compost sorption capacity for dyes depends as well on the dye as on the dye initial concentration. At low dye concentrations (up to $25 \text{ mg}\cdot\text{L}^{-1}$), the amount of bound dyes was higher when the ratio solid phase (m):solution (V) was 1:50 than when it was 1:20. At the dye concentrations greater than $25 \text{ mg}\cdot\text{L}^{-1}$, the amount of the compost-bound dyes was greater at greater compost suspension concentration (Fig. 5).

The percentages (R) of removal of dyes from the effluent depend on the dosage of the adsorbent. The increase of R with increasing adsorbent mass may be attributed to the increase of adsorbent uptake surface. It was also observed by Calvete *et al.* [5].

The sorption ran at almost constant pH, independently of the dye concentration. Neither was the effect of the compost concentration on pH in the equilibrium solution observed (Fig. 5).

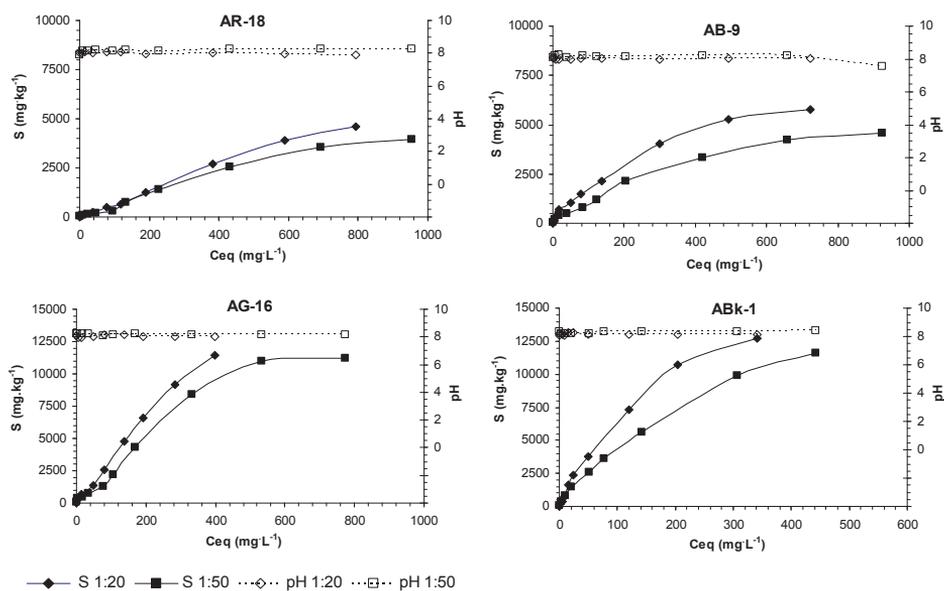


Fig. 5. Effect of the compost dosage on the sorption isotherms of the studied dyes

Moreover, the compost dosages had no effect on the type of the isotherms.

The pairwise comparison of the result series by using STATISTICA showed no statistically significant differences between the series of results for AR-18 and AG-16 at both compost concentrations. Instead, the series of the results for AB-9 and ABk-1 differed significantly.

The studied dyes differ in their molecular structures. The compost efficiency for adsorption of acid dyes depends on the dyes structure: AR-1 and ABk-1 form negative ions, AB-9 is inner and AG-16 forms positive ions (Fig. 1). A molecule of ABk-1 has one hydroxyl ($-\text{OH}$) and one amine ($-\text{NH}_2$) group substitutions, AR-18 has one hydroxyl group substitution ($-\text{OH}$). So, AR-18 has one and ABk-1 – two H-bond donors. These groups may take part in binding dyes onto compost by forming functional surface groups

and creating hydrogen bonds. The surface of the particles of organic matter in compost is negatively charged at $\text{pH} > 7.72$, therefore AG-16 may be bound onto the compost surface through electrostatic bonds. Thus, two possible mechanisms of adsorption of the studied acid dyes onto the compost may be considered: electrostatic interaction between negatively charged surface and dye cations at $\text{pH} > \text{pH}_{\text{pzc}}$ for AG-16 and/or hydrogen bonds between functional surface groups of humic matter of compost ($-\text{OH}$, $-\text{COOH}$) and functional groups ($-\text{OH}$, $-\text{NH}_2$) of AR-18, AB-9 and ABk-1. The dependence of sorption of synthetic dyes onto different materials on the dye structure was also reported by Sahadevan *et al.* [28], Wong and Yo [32].

Freundlich, Langmuir and Dubinin-Raduskevich adsorption isotherm models

The parameters of the isotherm of the dye sorption, estimated from Eqs. 9, 10 and 11, and the corresponding values of R^2 are listed in Table 1. The sorption was very well represented by the Freundlich and Dubinin-Raduskevich models, the correlation coefficient (> 0.97) was higher than for the Langmuir model.

The values $1/n < 1$ in the Freundlich isotherm indicate favourable adsorption. The Freundlich model fitted the equilibrium data well, and this proves that the dye molecules formed a multilayer coverage of the sorbent surface. A similar observation is reported for the dye adsorption onto activated carbons prepared from sawdust and rice husk [18].

The free energy E per molecule of adsorbate, estimated from Eq. (8), informs whether an adsorption mechanism is the ion-exchange ($8 < E < 16 \text{ kJ}\cdot\text{mol}^{-1}$) or the physical adsorption ($E < 8 \text{ kJ}\cdot\text{mol}^{-1}$) [22]. The values of E for the adsorption of all the studied acid dyes onto compost were within the range from 7.2548 to 8.0761 $\text{kJ}\cdot\text{mol}^{-1}$, corresponding to physical adsorption.

The Langmuir model fits also the AB-9 and ABk-1 data well (R^2 , Table 1). It means formation of the dye molecule monolayer on the surface of the compost. Ho and Chiang [12] also report that the sorption of AB-9 onto mixed sorbent may be described by the Langmuir equation.

The sorption of AR-18 and AG-18 cannot be described by the Langmuir model in the whole range of their concentrations. K_L , estimated from the AB-9 and ABk-1 sorption equations, was used to compute the constant R_L from Eq. 5. The values of R_L lie between 0 and 1, meaning the AB-9 and ABk-1 favourable sorption.

CONCLUSION

The sorption capacity of compost for four acid dyes, Acid Red 18, Acid Blue 9, Acid Green 16 and Acid Black 1, was examined. It depended on the initial concentrations of dyes in solutions, the concentration of compost suspension and on the structure of dyes. The maximum sorption capacities of the compost for these dyes may be arranged into the following sequence:

$$\text{ABk-1} > \text{AG-16} > \text{AB-9} > \text{AR-18}.$$

The amount of bound dyes and the removal percentage depended on the adsorbent mass in the solution. The growth of the removal percentage with growing adsorbent mass may be attributed to the growth of the uptake surface area caused by growing adsorbent

Table 1. The isotherm constants for the adsorption of the studied dyes onto compost

Dye	S:L	Freundlich isotherm			Langmuir isotherm					Dubinin-Radushkevich isotherm				
		1/n	K_F (L.kg ⁻¹)	R ²	S (mg.kg ⁻¹)	Q (mg.kg ⁻¹)	K_L (L.mg ⁻¹)	R ²	R _L	β (mol ² .kJ ⁻²)	q (mg.kg ⁻¹)	R ²	E (kJ.mol ⁻¹)	
AR-18	1:20	0.8611	13.71	0.9933	4580	13513	0.00062	0.2715	n.e.	0.0079	10113	0.9700	7.9556	
	1:50	0.6752	28.39	0.9834	3940	11235	0.00059	0.1375	n.e.	0.0085	8441	0.9480	7.6696	
AB-9	1:20	0.7576	50.36	0.9799	5780	7692	0.00369	0.8206	0.2112	0.0081	7118	0.9785	7.8567	
	1:50	0.6826	47.93	0.9937	4600	6211	0.00287	0.8419	0.2551	0.0095	6132	0.9781	7.2548	
AG-16	1:20	0.7525	112.9	0.9835	11440	17857	0.00330	0.4242	n.e.	0.0079	21964	0.9711	7.9255	
	1:50	0.7089	95.49	0.9699	11200	21739	0.00148	0.3531	n.e.	0.0075	24630	0.9320	8.0761	
Abk-1	1:20	0.7983	154.3	0.9864	12740	18182	0.00648	0.8759	0.1363	0.0080	20440	0.9851	7.9008	
	1:50	0.6599	198.0	0.9972	12580	15385	0.00574	0.9261	0.1517	0.0074	18948	0.9982	7.9988	

n.e. – not estimated

amount. The dyes were bound onto the surface of the compost through electrostatic interaction between the surface, negatively charged at $\text{pH} > \text{pH}_{\text{PZC}}$ and the dye cations (AG-16) and/or the hydrogen bonds between the surface functional groups of the compost humic matter ($-\text{OH}$, $-\text{COOH}$) and the dye functional groups ($-\text{OH}$, $-\text{NH}_2$) in AR-18, AB-9 and ABk-1. In the experiment conditions, the Freundlich and Dubinin-Raduskevich adsorption isotherm models fitted the equilibrium data very well, better than the Langmuir one. The favourable adsorption was indicated by the values of $1/n$ in Freundlich and E in Dubinin- Raduskevich isotherms.

It may be concluded that the compost may be used as a low cost sorbent for the removal of dyes from the wastewater released by textile industries. However, elevated values of chemical oxygen demand (COD) in the final solutions may enhance the humic compounds solubility.

Acknowledgments

This research was supported by the Ministry of Science and High Education, grant No. N523 350933.

REFERENCES

- [1] Aksu Z.: *Application of biosorption for the removal of organic pollutants: a review*, Process Biochem., **40**(3–4), 997–1026 (2005).
- [2] Allen S.J., G. McKay, J.F. Porter: *Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems*, J. Colloid Interface Sci., **280**, 322–333 (2004).
- [3] Babel S., T.A. Kurniawan: *Low-cost adsorbents for heavy metals uptake from contaminated water: a review*, J. Hazard. Mater., **97**(1–3), 219–243 (2003).
- [4] Bhattacharyya K.G., A. Sharma: *Kinetics and thermodynamics of Methylene Blue on neem (Azadirachta indica) leaf powder*, Dyes Pigm., **65**, 51–59 (2005).
- [5] Calvete T., E.C. Lima, N.F. Cardoso, S.L.P. Dias, F.A. Pavan: *Application of adsorbents prepared from the Brazilian-pine fruit shell for removal of Procion Red MX 3B from aqueous solution – kinetic, equilibrium, and thermodynamic studies*, Chem. Eng. J., **155**, 627–636 (2009).
- [6] Cardoso N.F., E.C. Lima, I.S. Pinto, C.V. Amaavisca, B. Royer, R.B. Pinto, W.S. Alencar, S.F.P. Pereira: *Application of cupuassu shell as biosorbent for removal of textile dyes from aqueous solution*, J. Environ. Manage., **92**, 1237–1247 (2011).
- [7] Clarke E.A., R. Anliker: *The handbook of Environmental Chemistry*, In: O. Hutzinger (ed), vol. 3A, Springer-Verlag, Berlin 1980.
- [8] Lima de R.O.A., A.P. Bazo, D.M.F. Salvadori, C.M. Rech, D.P. Oliveira, G.A. Umbuzeiro: *Mutagenic and carcinogenic potential of a textile azo dye processing plant effluent that impacts a drinking water source*, Mutat. Res., **626**, 53–60 (2007).
- [9] Foo K.Y., B.H. Hameed: *Insights into the modeling of adsorption isotherm systems*, Chem. Eng. J., **156**, 2–10 (2010).
- [10] Giles C.H., D. Smith, A. Huitson: *A general treatment and classification of the solute adsorption isotherm. I. Theoretical*, J. Colloid Interface Sci., **47**, 755–765 (1974).
- [11] Gong R., Y. Sun, J. Chen, H. Liu, C. Yang: *Effect of chemical modification on dye adsorption capacity of peanut hull*, Dyes Pigm., **67**(3), 175–181 (2005).
- [12] Ho Y.S., C.C. Chiang: *Sorption studies of acid dyes by mixed sorbents*, Adsorption, **7**, 139–147 (2001).
- [13] Ho Y.S., G. McKay: *Sorption of dye from aqueous solution by peat*, Chem. Eng. J., **70**, 115–124 (1998).
- [14] Ho Y.S., T.H. Chiang, Y.M. Hsueh: *Removal of basic dye from aqueous solution using tree fern as biosorbent*, Process Biochem., **40**, 119–124 (2005).
- [15] Ho Y.S., G. McKay: *The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat*, Can. J. Chem. Eng., **76**, 822–827 (1998).
- [16] Janos P., P. Michalek, L. Turek: *Sorption of ionic dyes onto untreated low-rank coal – oxihumolite: A kinetic study*, Dyes Pigm., **74**, 363–370 (2007).
- [17] Kyziol-Komosinska J., Cz. Rosik-Dulewska, M. Pajak: *The potential of metal-complex dyes removal*

- from wastewater using the sorption method onto organic matter-rich substances, Environmental Engineering III, CRC Press, Boca Raton, New York 2010.
- [18] Malik P.K.: *Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36*, Dyes Pigm., **56**, 239–249 (2003).
- [19] Mohan S.V., J. Karthikeyan: *Removal of lignin and tannin colour from aqueous solution by adsorption onto activated charcoal*, Environ. Pollut., **97**, 183–187 (1997).
- [20] Mohan S.V., N.C. Rao, J. Karthikeyan: *Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study*, J. Hazard. Mater., **90**(2), 189–204 (2002).
- [21] Ofomaja A.E.: *Sorptive removal of methylene blue from aqueous solution using palm kernel fibre: Effect of fibre dose*, Biochem. Eng. J., **40**, 8–18 (2008).
- [22] Ozcan A., E.M. Oncu, A.S. Ozcan: *Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite*, Colloids Surf., A, **277**, 90–97 (2006).
- [23] Pavan F.A., E.C. Lima, S.L.P. Dias, A.C. Mazzocato: *Methylene blue biosorption from aqueous solutions by yellow passion fruit waste*, J. Hazard. Mater., **150**, 703–712 (2008).
- [24] Ramakrishna K.R., T. Viraraghavan: *Dye removal using low cost adsorbents*, Water Sci. Technol., **36**(2–3), 189–196 (1997).
- [25] Reddad Z., C. Gerente, Y. Andres, P.L. Cloirec: *Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies*, Environ. Sci. Technol., **36**, 2067–2073 (2002).
- [26] Rozporządzenie MB z dnia 28 lipca 2006 r. w sprawie sposobu realizacji obowiązków dostawców ścieków przemysłowych oraz warunków wprowadzania ścieków do urządzeń kanalizacyjnych, Dz.U. 2006, nr 136, poz. 964.
- [27] Rozporządzenie Ministra Środowiska z dnia 24 lipca 2006 r. w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi, Dz. U. 2006, nr 137, poz. 984.
- [28] Sahadevan R., D.K. Mahendradas, V. Shanmugasundaram, K. Shanmugam, M. Velan: *Sorption kinetics and equilibrium analysis for the removal of Reactive Red 2 and Reactive Blue 81 dyes from synthetic effluents using dried soybean meal*, Int. J. Chem. Reactor Eng., **7**, A33 (2009).
- [29] Shen D., J. Fan, W. Zhou, B. Gao, Q. Yue, Q. Kang: *Adsorption kinetics and isotherm of anionic dyes onto organo-bentonite from single and multisolute systems*, J. Hazard. Mater., **172**, 99–107 (2009).
- [30] Vasanth K.K., S. Sivanesan: *Prediction of optimum sorption isotherm: Comparison of linear and non-linear method*, J. Hazard. Mater., **126**, 198–201 (2005).
- [31] Wei Y.L., Y.C. Lee, Y.W. Yang, J.F. Lee: *Molecular study of concentrated copper pollutant with a compost*, Chemosphere, **57**, 1201–1205 (2004).
- [32] Wong Y., J. Yu: *Laccase-catalyzed decolorization of synthetic dyes*, Water Res., **33**, 3512–3520 (1999).

ZASTOSOWANIE KOMPOSTU JAKO BIOSORBENTA W USUWANIU BARWNIKÓW KWASOWYCH ZE ŚCIEKÓW PRZEMYSŁU WŁÓKIENNICZEGO

W pracy przedstawiono wyniki badań sorpcji wybranych barwników kwasowych: Acid Red 18 (AR-18), Acid Blue 9 (AB-9), Acid Green 16 (AG-16) i Acid Black 1 (ABk-1) na kompoście wytwarzanym w Miejskim Zakładzie Gospodarki Komunalnej. Określono wpływ zarówno stężenia barwników w roztworze, jak i masy kompostu na pojemność sorpcyjną badanego kompostu. Badania przeprowadzono w statycznych warunkach kontaktu faza stała roztwór (metoda batch) dla stężeń barwników 1–1000 mg L⁻¹. Badany kompost wykazywał wysoką pojemność sorpcyjną w stosunku do barwników kwasowych. Pojemność sorpcyjna badanego kompostu w stosunku do barwników zmieniała się w szeregu: ABk-1 > AG-16 > AB-9 > AR-18. Zdolność ich usuwania zależała od stężenia zawiesiny kompostu w roztworze i od stężenia barwników. Najwyższą skuteczność usuwania barwników stwierdzono dla stężenia zawiesiny 50 g L⁻¹ i stężenia barwników w roztworze 1–50 mg L⁻¹. Stwierdzono, że barwniki kwasowe były wiązane na powierzchni cząstek kompostu w wyniku oddziaływań elektrostatycznych między ujemnie naładowaną powierzchnią kompostu a kationami barwnika (AG-16) i/lub poprzez wiązania wodorowe wytworzone między grupami funkcyjnymi kwasów humusowych obecnych w kompoście (–OH, –COOH) i grupami funkcyjnymi barwników (–OH, –NH₂). Wyniki badań doświadczalnych najlepiej opisywały równania izoterm Freundlicha i Dubinina-Raduskevicha a oszacowane parametry w równaniach wskazywały na adsorpcję. Na podstawie przeprowadzonych badań stwierdzono, że badany kompost może być brany pod uwagę jako skuteczny i ekonomiczny sorbent barwników kwasowych, jednak nie należy zapominać o wzroście wartości ChZT w oczyszczanych ściekach w wyniku rozpuszczania kwasów huminowych obecnych w kompoście.