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ORIGINAL PAPER

Removal of dyes by adsorption on magnetically modified activated sludge

Z. Maderova[1] · **E. Baldikova**[1,2] · **K. Pospiskova**[3] · **I. Safarik**[1,3,4] · **M. Safarikova**[1,4]

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Abstract The ability of magnetically modified activated sludge affected by thermal treatment to remove water-soluble organic dyes was examined. Twelve different dyes were tested. Based on the results of the initial sorption study, four dyes (namely aniline blue, Nile blue, Bismarck brown Y and safranin O) were chosen for further experiments due to their promising binding onto magnetic activated sludge. Significant factors influencing adsorption efficiency such as dependence of contact time, initial pH or temperature were studied in detail. The adsorption process was very fast; more than 88 % of dye content (55 mg/L) was adsorbed within 15 min under experimental conditions used. The equilibrium adsorption data were analyzed by Freundlich, Langmuir and Sips adsorption isotherm models, and the fitting of each isotherm model to experimental data was assessed on the basis of error functions. The maximum adsorption capacities of magnetic activated sludge were 768.2, 246.9, 515.1 and 326.8 mg/g for aniline blue, Bismarck brown Y, Nile blue and safranin O, respectively. The kinetic studies indicated that adsorption of all selected dyes could be well described by the pseudo-second-order kinetic model, and the thermodynamic data suggested the spontaneous and endothermic process.

Keywords Biosorption · Dyes · Magnetic adsorbent · Magnetic modification · Microwave-assisted synthesis

✉ E. Baldikova
baldie@email.cz

1 Global Change Research Institute, CAS, Na Sadkach 7, 370 05 Ceske Budejovice, Czech Republic

2 Department of Applied Chemistry, Faculty of Agriculture, University of South Bohemia, Branisovska 1457, 370 05 Ceske Budejovice, Czech Republic

3 Regional Centre of Advanced Technologies and Materials, Palacky University, Slechtitelu 27, 783 71 Olomouc, Czech Republic

4 Department of Nanobiotechnology, Biology Centre, ISB, CAS, Na Sadkach 7, 370 05 Ceske Budejovice, Czech Republic

Abbreviations

ARE	The average relative error
AS	Activated sludge
MIOP	Magnetic iron oxides particles
SEE	The standard error of estimate
A_0	The initial absorbance of dye used in the experiment
A_f	The final absorbance of dye used in the experiment
a_L	The Langmuir constant related to the energy of adsorption (L/mg)
C_0	The initial concentration of used dye (mg/L)
C_e	The concentration of free (unbound) dye in the supernatant (mg/L)
C_t	The concentration at time t (mg/L)
$\Delta G°$	The standard free energy change of sorption (kJ/mol)
$\Delta H°$	The standard enthalpy change (kJ/mol)
k_1	The rate constant of pseudo-first-order kinetic model (1/min)
k_2	The rate constant of pseudo-second-order kinetic model (g/mg min)
K_F	The Freundlich isotherm constant related to adsorption capacity [(mg/g) $(L/mg)^{1/n}$]
K_L	The thermodynamic equilibrium constant
n	The Freundlich isotherm constant connected with adsorption intensity
n'	The number of the experimental measurements
p'	The number of parameters

q_e The amount of dye bound to the unit mass of the adsorbent (mg/g)
q_m The maximum adsorption capacity (mg/g)
q_t The amount of dye bound to the unit mass of the adsorbent at time t (mg/g)
R The universal gas constant (8.314 J/mol K)
$\Delta S°$ The standard entropy chase (J/mol K)
t Time (min)
T Temperature (K)
V Volume of solution (L)
w Dry mass of magnetic AS (g)
y_i The experimental value of the dependent variable
$y_{i,theor}$ The estimated value of the dependent variable

Introduction

Organic dyes are important water pollutants; currently, more than 100,000 dyes are available commercially. It is estimated that over 7×10^5 tons of dyestuffs is produced annually (Celekli and Bozkurt 2013; Ramaraju et al. 2014). Two percent of produced dyes are discharged directly in aqueous effluent, and 10–15 % are subsequently lost during the textile coloration process (Liu et al. 2016). These data indicate a scale of threat to water systems. The presence of very small amounts of dyes in water (<1 ppm for some dyes) is highly visible and undesirable (Banat et al. 1996). Many of these dyes are also toxic and even carcinogenic, and this poses a serious hazard to aquatic living organisms (Kyzas et al. 2013). Wide range of dyes which are diversified in their structure and physicochemical properties exists, such as acidic, basic, reactive, disperse, azo, diazo, anthroquinone-based and metal complex dyes (Buthelezi et al. 2012).

Numerous techniques focusing on dye removal have been published (Banat et al. 1996; Salleh et al. 2011; Srinivasan and Viraraghavan 2010). Among them, adsorption provides prime results and can be used to remove different types of dyes. In the specific type of adsorption, named biosorption, dead bacteria (Nacèra and Aicha 2006), yeast (Yu et al. 2013), fungi (Aydogan and Arslan 2015) and microalgae (Hernandez-Zamora et al. 2015) have been employed as biosorbents for the removal of target dyes.

Activated sludge (AS) is formed by particles produced in wastewater treatment process containing many living organisms (such as bacteria, fungi, yeasts, algae and protozoa). The cell walls of the microorganisms contain various functional groups that can interact with different organic and inorganic matter. This material is easily available and has a great potential for applications. Recently, a lot of studies have been reported on the removal of heavy metal ions and organic compounds from water systems by differently treated activated sludge (Chu and Chen 2002; Gobi et al. 2011; Gulnaz et al. 2004; Hammaini et al. 2007; Hyland et al. 2012; Ju et al. 2008).

Magnetic modification of originally diamagnetic materials using various ferro- and ferrimagnetic nano- and microparticles [see an excellent review describing various procedures for their preparation (Laurent et al. 2008)] provides new unique characteristics of such materials. Magnetic modification facilitates the separation process in the presence of external magnetic field. This is widely applied to separations in complex and difficult-to-handle media (blood, waste waters etc.). Very simple and easy to scale-up method for magnetization of cells was developed by our group. Inspired by previous studies of magnetic modification of pure yeast and algae cell cultures (Pospiskova et al. 2013; Prochazkova et al. 2013), we employed this method for activated sludge as an example of mixed cultures. Subsequently, magnetic AS was tested as a low-cost adsorbent for removal of organic compounds, specifically organic dyes. The dyes adsorption on magnetic biomass was quantified by means of three adsorption models, namely Langmuir, Freundlich and Sips ones. The kinetic model and thermodynamic parameters were also determined.

Materials and methods

Materials

The AS samples were taken from the Sewage Treatment Plant, Zliv, Czech Republic, which handles 668 m^3/day of wastewater and uses primary (mechanical) and secondary (biological–denitrification and nitrification) treatments, in May 2015. A fraction of particles obtained by passing through a sieve of mesh size 100 µm was utilized. Twelve water-soluble dyes (see Table 1) were tested during the study. Iron (II) sulfate heptahydrate and HCl were supplied by LachNer (Neratovice, Czech Republic), while NaOH was obtained from Penta (Prague, Czech Republic). All chemicals were of guaranteed reagent (G.R.) grade.

Preparation of magnetic iron oxide particles (MIOP)

As described earlier (Safarik and Safarikova 2014; Zheng et al. 2010), magnetic iron oxides nano- and microparticles were prepared from ferrous sulfate at high pH using microwave irradiation. For small-scale experiments, 1 g $FeSO_4 \cdot 7\ H_2O$ was dissolved in 100 mL of water in an

Table 1 Specification of tested dyes

Dye	Synonym	CI number	Declared purity (%)	Type of dye	Manufacturer/supplier	Sorption [%]
Acridine orange	Basic orange 14	46,005	75	Acridine	Loba Feinchemie, Austria	51.8
Amido black 10B	Acid black 1	20,470	50	Disazo	Merck, Germany	2.0
Aniline blue	Acid blue 22	42,755	55	Triarylmethane	Lachema, Czech Republic	81.8
Azocarmine G	Acid red 101	50,085	60	Quinone-imine	Lachema, Czech Republic	17.7
Bismarck brown Y	Basic brown 1	21,000	56	Disazo	Sigma, USA	81.7
Congo red	Direct red 28	22,120	50	Disazo	Sigma, USA	12.3
Crystal violet	Basic violet 3	42,555	75	Triarylmethane	Lachema, Czech Republic	56.8
Indigo carmine	Acid blue 74	73,015	85	Indigo	Lachema, Czech Republic	8.1
Methylene blue	Basic blue 9	52,015	75	Quinone-imine	Sigma, USA	53.4
Nigrosine, water soluble	Acid black 2	50,420	not declared	Nigrosin	Lachema, Czech Republic	15.0
Nile blue A (sulfate)	Basic blue 12	51,180	75	Oxazin	Chemische Fabrik GmbH, Germany	82.0
Safranin O	Basic red 2	50,240	96	Safranin	Sigma, USA	45.5

The higher the sorption [%], the better the adsorption properties

800 mL beaker and solution of sodium or potassium hydroxide (1 mol/L) was dropped slowly under mixing until the pH reached the value ca 12; during this process, a precipitate of iron hydroxides was formed. Then the suspension was diluted up to 200 mL with water and inserted into a standard kitchen microwave oven (700 W, 2450 MHz). The suspension was treated for 10 min at the maximum power. Then, the beaker was removed from the oven and the formed magnetic iron oxides microparticles were repeatedly washed with water. The synthesized MIOP were suspended in water until further use.

Preparation of magnetic adsorbent

In order to prepare a safe adsorbent based on AS, the sludge was heated in the autoclave for 15 min at 120 °C (75 mL settled volume of activated sludge in 1L Erlenmeyer flask). The magnetization of sterilized AS with microwave-synthesized MIOP was performed by simple mixing of both suspended materials similarly as described previously (Pospiskova et al. 2013) using the ratio 1 mL of settled volume of activated sludge (corresponding to 16.9 mg, dry weight) to 0.1 mL of settled volume of MIOP (corresponding to 7.6 mg, dry weight) in 10 mL of water. The settled volumes of both materials were measured in calibrated containers after 18 h of sedimentation. The mixture of MIOP and AS was mixed by rotator at 25 rpm for 30 min at room temperature. The resultant magnetic activated sludge was washed and suspended in water until further use.

The magnetic untreated (living) activated sludge was prepared by the same method in order to compare the adsorption capacity of heat-treated and untreated magnetic adsorbents.

Batch adsorption experiments

The sorption of dyes onto magnetic AS was studied in batch systems. Twelve different dyes (Table 1) were chosen to test magnetic AS as an adsorbent. In total, 100 µL settled volume of AS (1.69 mg dry weight) was mixed with 9 mL of water and 1 mL of selected dye (1 mg/mL). After 1 h of incubation on orbital rotator (25 rpm) and subsequent magnetic separation by magnetic separator, the samples (supernatants and control dye samples without adsorbent) were analyzed by UV–Vis spectrophotometer. The percentage of sorption was determined by the formula

$$(\%) = 100\frac{A_0 - A_f}{A_0} \quad (1)$$

For isotherms studies, the experiments were carried out using 100 µL settled volume of AS and 10 mL of dye solutions with the initial concentrations of 10–500 mg/L. The tubes were agitated on orbital rotator (25 rpm) under constant temperature (295.15 K) for 90 min. The magnetic AS was separated from the suspension by magnetic separator, and samples were analyzed by UV–Vis spectrophotometer.

The studies of temperature effect on the sorption of dyes onto magnetic heat-treated AS were performed as isotherms studies at different temperature (282.15, 295.15 and 313.15 K).

The concentration of free dye in the supernatant (C_e) was determined from the calibration curve. The amount of dye bound to the unit mass of the adsorbent at equilibrium (q_e) was calculated using the following formula:

$$q_{\mathrm{e}} = \frac{(C_0 - C_{\mathrm{e}})V}{w} \quad (2)$$

The amount of dye bound to the unit mass of the adsorbent at time t (q_t) was calculated using the following formula

$$q_{\mathrm{t}} = \frac{(C_0 - C_{\mathrm{t}})V}{w} \quad (3)$$

All experiments were repeated three times. Average values obtained during the experiments are presented.

Adsorption kinetics

The adsorption kinetics study was determined by evaluation of dye quantity adsorbed onto magnetic AS at different time intervals (0–140 min). The initial concentration of dye solution was 55 mg/L. Amount of adsorbent, volume of dye solution and sample analysis were kept in the same way as isotherm studies.

The data were analyzed using the Lagergren equation, pseudo-first-order model (Chairat et al. 2008) and pseudo-second-order model (Ho 2006).

The linear form of Lagergren pseudo-first-order model is represented by following equation

$$\ln(q_{\mathrm{e}} - q_{\mathrm{t}}) = \ln q_{\mathrm{e}} - k_1 t \quad (4)$$

where k_1 and q_e were calculated from the slope and intercept of the plots of $\ln(q_e - q_t)$ versus t.

The linear form of pseudo-second-order kinetic model is presented by following equation

$$\frac{t}{q_{\mathrm{t}}} = \frac{1}{k_2 q_{\mathrm{e}}^2} + \frac{1}{q_{\mathrm{e}}} t \quad (5)$$

where the values of k_2 and q_e were calculated from the slope and intercept of the plots of t/q_t versus t.

Degree of fit of the model is evaluated on the basis of the correlation coefficient R^2 value.

Adsorption isotherms

The equilibrium data were fitted using two (Freundlich and Langmuir isotherms) and three (Sips isotherm) parameter equations. The adsorption isotherms were processed using nonlinear regression analysis (solver add-in function of the Microsoft Excel). Langmuir isotherm model (Langmuir 1918) assumes monolayer adsorption on the surface of adsorbent and no interaction between adsorbed molecules. The mathematic expression of Langmuir isotherm model is

$$q_{\mathrm{e}} = \frac{q_{\mathrm{m}} a_{\mathrm{L}} C_{\mathrm{e}}}{1 + a_{\mathrm{L}} C_{\mathrm{e}}} \quad (6)$$

Freundlich isotherm model (Freundlich 1906) is used to describe the non-ideal and reversible adsorption. It is applied to the adsorption on heterogeneous surface. The mathematic expression of Freundlich isotherm model is defined as

$$q_{\mathrm{e}} = K_{\mathrm{f}} C_{\mathrm{e}}^{1/n} \quad (7)$$

Sips isotherm model (Sips 1948) is a combination of the Langmuir and Freundlich isotherm models and is expected to describe better adsorption on heterogeneous surfaces. The Sips equation is presented by:

$$q_{\mathrm{e}} = \frac{q_{\mathrm{m}} (a_{\mathrm{L}} C_{\mathrm{e}})^{1/n}}{1 + (a_{\mathrm{L}} C_{\mathrm{e}})^{1/n}} \quad (8)$$

The assessment of applicability of isotherm models for experimental data processing is discussed by error functions. In this study, the standard error of estimate and average relative error were used to confirm the best fitting. If data from the model are similar to the experimental data, error is a small number.

The standard error of estimate (SEE) was calculated in each case as follows:

$$\mathrm{SEE} = \sqrt{\frac{\sum_{i=1}^{n'} \left(y_{\mathrm{i}} - y_{\mathrm{i,theor}}\right)^2}{(n' - p')}} \quad (9)$$

Average relative error (ARE) is expressed by:

$$\mathrm{ARE}\,(\%) = \frac{100}{n'} \sum_{i=1}^{n'} \left| \frac{(y_{\mathrm{i}} - y_{\mathrm{i,theor}})}{y_{\mathrm{i}}} \right| \quad (10)$$

Thermodynamic parameters

The data measured from the study of temperature effect were analyzed, and thermodynamic parameters were calculated by the following equations (Gobi et al. 2011)

$$\Delta G^{\circ} = -RT \ln K_{\mathrm{L}} \quad (11)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (12)$$

Equation (13) is obtained by combining Eqs. (11) and (12).

$$\mathrm{In} K_{\mathrm{L}} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (13)$$

where K_L was computed according to Liu (2009) and ΔH° and ΔS° values were calculated from the slope and intercept of the plot of ln K_L versus $1/T$ using Eq. (13).

Materials characterization

The morphological study was performed using scanning electron microscopy (SEM) measurements. The samples were analyzed by SEM 120 Hitachi SU6600 (Hitachi, Tokyo, Japan) with accelerating voltage 5 kV, equipped with energy-dispersive spectroscopy (EDS)—Thermo Noran System 7 (Thermo Scientific, Waltham, MA, USA) with Si (Li) detector (accelerating voltage of 15 kV and acquisition time 300 s). X-ray powder diffraction (XRD) pattern of synthesized magnetite was recorded on PANalytical X́Pert PRO (Almelo, the Netherlands) instrument in Bragg–Brentano geometry with Fe-filtered Co$K\alpha$ radiation (40 kV, 30 mA). The acquired pattern was evaluated using the X́Pert HighScore Plus software (PANalytical, Almelo, the Netherlands), PDF-4+ and ICSD databases. Fourier transform infrared (FTIR) absorption spectra were measured using Thermo Scientific Nicolet iS5 FTIR spectrometer (Thermo Nicolet Corp., Madison, WI, USA) with iD Foundation accessory (ZnSe crystal, range 4000–650 cm^{-1}, 32 scans, resolution 4 cm^{-1}). The IR absorption spectra are presented in transmittance after advanced attenuated total reflectance (ATR) and automatic baseline corrections.

Results and discussion

Magnetic modification of activated sludge

The combination of microwave-synthesized magnetic iron oxide nano- and microparticles and AS led to the formation of "smart" magnetically responsive material. One of the great advantages of this material is its easy manipulation using a permanent magnet or commercially available magnetic separator. The magnetic AS prepared as described was completely magnetically separated in a short time (<20 s).

Microwave-assisted synthesis resulted in the formation of iron oxides nanoparticles with diameters ranging between ca 25 and 100 nm (Fig. 1a). During synthesis, the nanoparticles formed micrometer-sized stable aggregates (maximum aggregate size ca 20 μm) (Baldikova et al. 2016). XRD pattern of the synthesized magnetic particles shows features typical of magnetite nano- to microparticles (Fig. 1b); further analysis using Mössbauer spectroscopy confirmed the presence of non-stoichiometric magnetite (Ochmann 2015).

The appropriate ratio between AS and MIOP was selected on the basis of separation velocity of the formed magnetic composite in the external magnetic field (created by the NdFeB magnet, diameter 20 mm, height 10 mm, remanence 1 T) in preliminary experiments (data not shown). Magnetic modification led to the interaction of iron oxide nanoparticle aggregates with the microorganisms and released material present in activated sludge; flocs with diameters between tens and several hundred micrometers were formed (Fig. 1c). SEM has confirmed efficient interaction of microbial cells and magnetic nanoparticles; surface of microbial cells is covered by the magnetic nanoparticles (Fig. 1d). Energy-dispersive X-ray spectroscopy verified the presence of iron in the magnetically responsive activated sludge (Fig. 2a).

The formation of magnetic adsorbent by direct mixing of MIOP and AS is an extremely rapid, inexpensive and simple method, which can be easily scaled up. On the contrary, Hu and Hu (2014) used dried sewage sludge for magnetic modification by coprecipitation method; however, this method is time and energy consuming. Lakshmanan and Rajarao (2014) described the application of magnetic nanoparticles as suitable flocculants for reduction in sludge water content and enhancement of sludge settling in the presence of external magnetic field, thereby reducing the sludge handling time and simplifying future processing.

Activated sludge contains, in addition to microbial cells, also extracellular polymeric substances (EPSs), which are microorganism-produced macromolecules, mainly consisting of polysaccharides, proteins and nucleic acids (Zhang et al. 2006); they represent a large pool of functional groups, which are involved in adsorption of various dyes and other compounds of interest.

FTIR spectral analysis (Fig. 2b) shows typical peaks indicating the presence of important groups. Peaks between 3100 and 2900 cm^{-1} (main at 3077 and 2924) represent the asymmetric and symmetric stretchings of $-CH_2$ from proteins, polysaccharides and lipids. Peaks with their maxima at 1622 and 1547 cm^{-1} are typical of primary and secondary amino group in proteins (peptide bond). The peaks at 1114 and 1033 cm^{-1} are characteristic of all sugar derivatives (O–C–O stretching vibrations in polysaccharide groups) (Andreassen 2008).

The bacteria present in the activated sludge have isoelectric points between pH 2 and 4, and thus, their surface will be negatively charged at higher pH (Sanin 2002). Some pretreatment processes can modify the adsorption capacity of the microbial biomass, such as autoclaving as high-temperature treatment causes cell rupture with a consecutive increase in surface area (Solis et al. 2012).

Screening of dyes

The adsorption properties of magnetically modified heat-treated AS were studied using water-soluble organic dyes (Table 1). The dyes used for preliminary adsorption experiments were selected to cover wide range of dye types. Dyes were dissolved in distilled water without

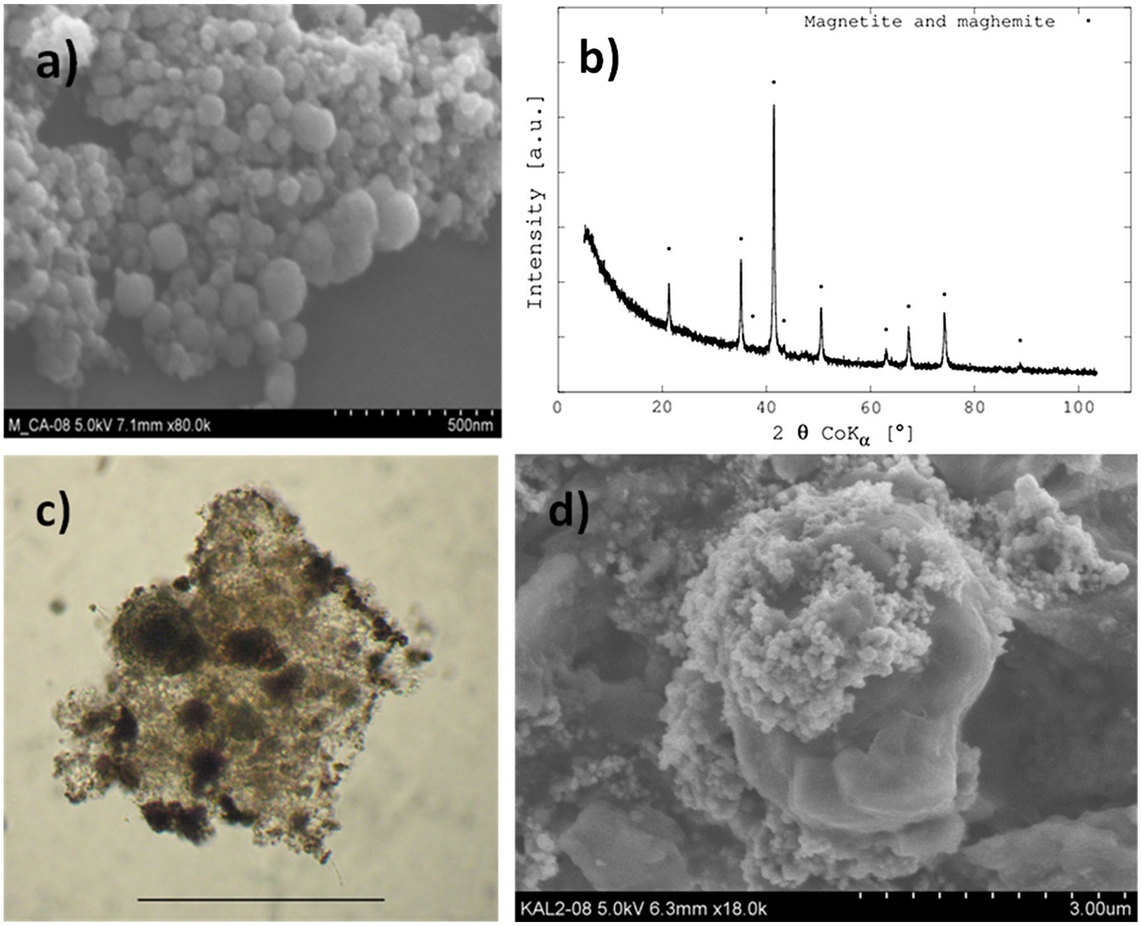

Fig. 1 **a** SEM of magnetic nanoparticles prepared by microwave-assisted synthesis (80,000× magnification). Reproduced, with permission, from (Baldikova et al. 2016); **b** XRD pattern of magnetic nano- and microparticles prepared by microwave-assisted synthesis (*black dots* mark the position of magnetite and maghemite diffractions); **c** optical microscopy of the typical magnetic activated sludge floc (the *bar* corresponds to 100 µm); **d** SEM of magnetically modified activated sludge (18,000× magnification)

buffering the solution. Several dyes exhibiting high biosorption, belonging to the different dye classes, namely aniline blue, Nile blue, Bismarck brown Y and safranin O (see Fig. 3a) were selected for detailed adsorption study. The dyes exhibiting good adsorption properties can be in most cases characterized as basic dyes, which suggest strong involvement of ion exchange interactions between dyes and cell surfaces.

Effect of pH

The effect of pH on adsorption of tested dyes onto magnetic heat-treated activated sludge was investigated. As can be seen from Fig. 3b, each dye exhibits different behavior at various pH. The adsorption efficiency of safranin O remained nearly constant up to pH 7, but at pH 8 there is a significant decrease. The lowest percentage removal of Nile blue was found at pH 3, and at higher pH values, the adsorption efficiencies significantly increased and kept almost the same values up to pH 8. The behavior of Bismarck brown Y seemed to be very similar to Nile blue; nevertheless, at pH higher than 6, there is apparent a slight fall. Aniline blue exhibited definitely another behavior; the most suitable pH values took place at pH 4 and 5, while at pH 3 and at pH values higher than 5 the adsorption efficiencies decreased substantially.

Adsorption kinetics

The contact time is one of the important factors to achieve equilibrium required for description of the adsorption process. The adsorption equilibrium studies for removal of selected dyes (aniline blue, Bismarck brown Y, safranin O, Nile blue, 55 mg/L) on magnetic AS and kinetic studies were performed in batch system at room temperature (295.15 K) under mixing. The effect of contact time on the adsorption of tested dyes is shown in Fig. 3c; it is evident that the dyes adsorption was a fast process, and 93 % of the

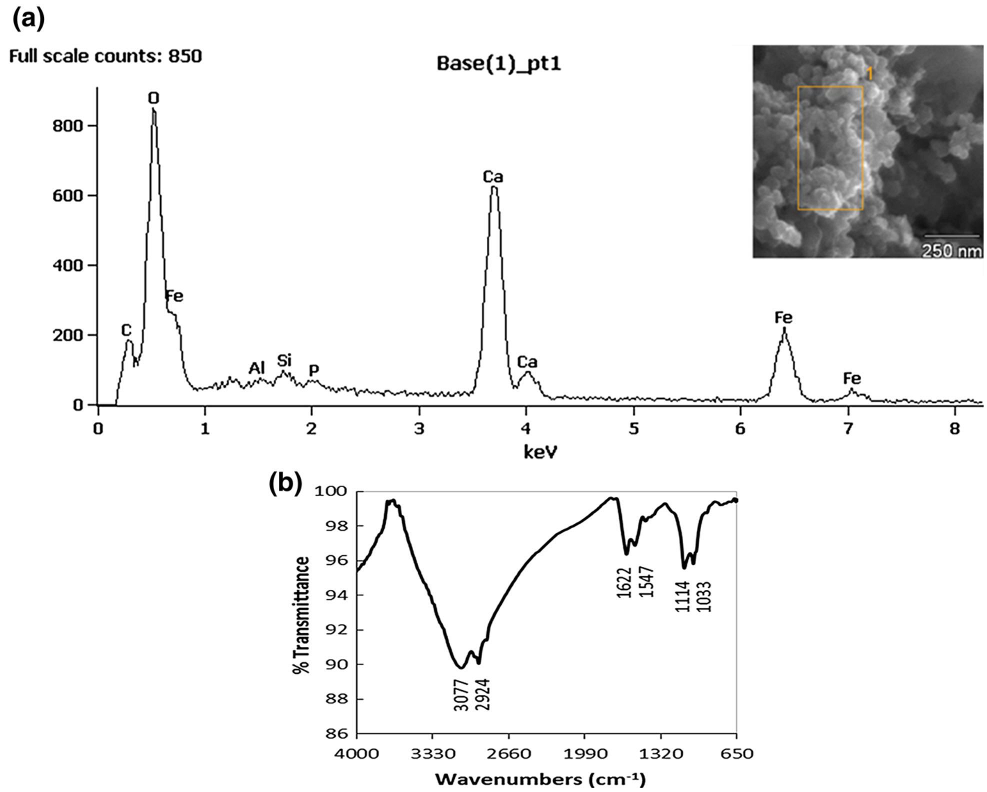

Fig. 2 **a** EDS of magnetically modified activated sludge; **b** FTIR spectrum of magnetically modified activated sludge

sorption took place in the first 15 min except Bismarck brown Y sorption where only 88 % of dye was adsorbed in the first 15 min. Nevertheless, the process needs approximately 60 min to reach the equilibrium.

The results obtained during examination of contact time dependence were subsequently analyzed to investigate kinetics of adsorption process. Pseudo-first- and pseudo-second-order kinetic equations were used. The pseudo-first-order kinetic model is the earliest known one describing the adsorption rate based on the adsorption capacity (Ho 2006). It is apparent from the predicted values of q_e and correlation coefficient R^2 shown in Table 2 that the kinetic data of the dyes sorption on magnetic heat-treated AS were not well fitted to the pseudo-first-order model. On the other side, the values of correlation coefficient R^2 for pseudo-second-order model (see Table 2) were close to 1.0 for all cases and the theoretical values of q_e calculated from this model approached the experimental data. This indicates that the sorption mechanism of selected dyes on magnetically modified heat-treated AS follows the pseudo-second-order model.

Adsorption isotherms study

The adsorption isotherm is a significant parameter to understand the behavior of the adsorption process. In this study, the distribution of dyes between liquid phase and solid phase (magnetic AS) was described using two and three parameters isotherm models, namely Langmuir, Freundlich and Sips ones. The first two models are widely used for investigating the adsorption of dyes on various materials. Figure 4 demonstrates the plots of the experimental data and predicted isotherm models for sorption of selected dyes onto magnetic heat-treated activated sludge. Determined isotherm parameters computed for all examined dyes are listed in Table 3. The average relative error (ARE) and standard error of estimate (SEE) based on the actual deviation between the experimental points and predicted values are also shown.

Langmuir isotherm model is the two parameters model. This empirical model assumed monolayer adsorption, and all sites possess equal affinity for the sorbate (Vijayaraghavan et al. 2006). High value of a_L indicates high affinity. In the case of aniline blue (Table 3), SEE and ARE for Langmuir isotherm model exhibited lower values than for Freundlich and Sips isotherm models. Consequently, Langmuir isotherm model was considered to be a better fit compared to the other two.

Freundlich isotherm model (two parameters model) assumes that the surface of adsorbent is heterogeneous, and surface sites have a spectrum of different binding energies. The constant K_F relates to the effectiveness of magnetic AS to adsorb dyes. Higher values of K_F indicate larger capacities of adsorption. The constant n is a function of the strength of

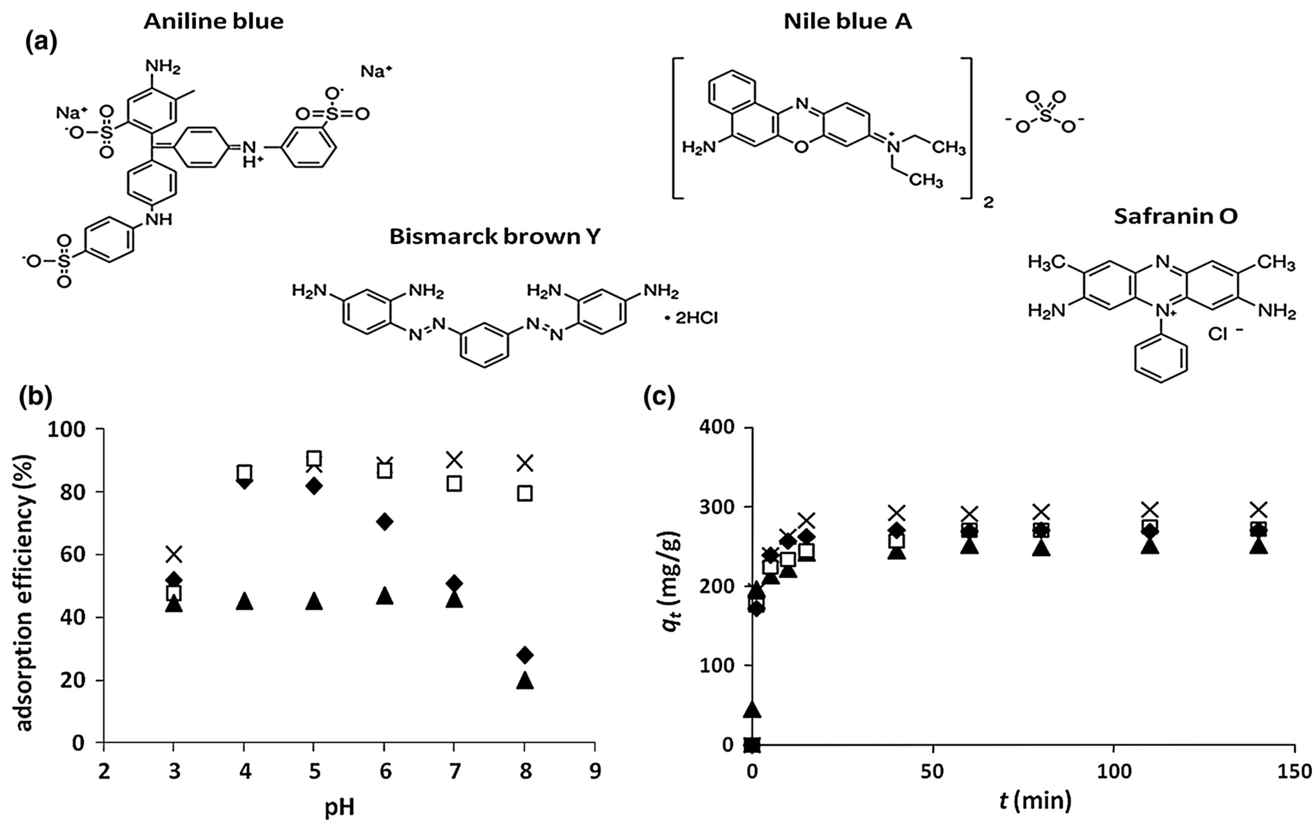

Fig. 3 **a** Chemical structures of dyes used for the experiments; **b** the effect of pH on dye adsorption on heat-treated magnetic AS (agitation time 90 min, 10 mL of 100 mg/L dye solution, 1.69 mg of magnetic AS, 295.15 K); **c** time dependence of dye adsorption on heat-treated magnetic AS at 295.15 K. [aniline blue (*filled diamond*), Bismarck brown Y (*open square*), safranin O (*filled triangle*) and Nile blue (*cross mark*)]

Table 2 Values of rate constants, capacities and regression coefficients from pseudo-first- and pseudo-second-order kinetic models

Dye	q_e (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg min)	R^2
Aniline blue	274	24.3	0.0200	0.6293	270	0.0069	1.0000
Bismarck brown Y	275	54.0	0.0332	0.7920	278	0.0025	0.9998
Safranin O	254	29.6	0.0236	0.7683	256	0.0004	0.9999
Nile blue	299	45.5	0.0286	0.8689	303	0.0030	0.9999

adsorbent and indicates the favorability of adsorption. It is generally stated that the values n in the range of 2–10 represent good, 1–2 moderately difficult and <1 poor adsorption characteristics (Hadi et al. 2010). Error values (Table 3) and Fig. 4 representing adsorption fitting curves for dyes onto magnetic AS suggest that the Freundlich isotherm is more accurate to describe the Nile blue—magnetic AS interaction in comparison with other three dyes.

Sips isotherm model (three parameters model) combines the features of Freundlich and Langmuir models. As shown (Table 3), the Sips isotherm generated a satisfactory fit to the experimental data as indicated by the error functions. However, the Langmuir isotherm showed a better fit to the adsorption data for aniline blue and the Freundlich isotherm in the sorption of Nile blue. Nevertheless, for aniline blue Sips model closely approached the Langmuir model with their exponents (α_L) being close to unity.

Table 4 represents some other adsorbents, and their adsorption capacity employed for adsorption of selected dyes from water; it can be observed that heat-treated magnetically responsive AS is an efficient adsorbent for dyes removal.

The effect of activated sludge heat treatment on dyes adsorption

The three isotherm models (Langmuir, Freundlich and Sips) were applied to describe the adsorption process of aniline blue on living and heat-treated magnetic AS.

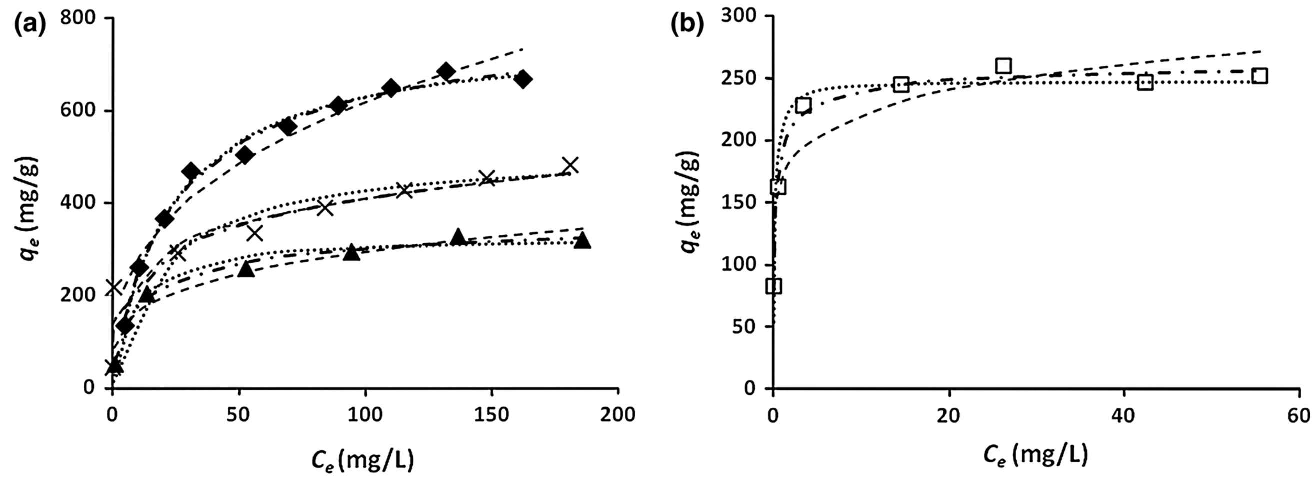

Fig. 4 Comparison of isotherms models of aniline blue (*filled diamond*), Nile blue (*cross mark*), safranin O (*filled triangle*) (**a**) and Bismarck brown Y (*open square*) (**b**) onto heat-treated magnetic AS; *dotted line* Langmuir model; *straight line* Freundlich model; *dashed line* Sips model

Table 3 Parameters of Langmuir, Freundlich and Sips adsorption isotherm models

Type of adsorbent	Dye	Langmuir		Sips		Freundlich	
Heat-treated magnetic AS	Safranin O	q_m (mg/g)	326.8	q_m (mg/g)	385.9	K_F [(mg/g)(L/mg)$^{1/n}$]	92.2
		a_L (L/mg)	0.12	a_L (L/mg)	0.08	n	3.97
		SEE	20.23	n	1.60	SEE	25.39
		ARE (%)	11.00	SEE	13.20	ARE (%)	15.64
				ARE (%)	4.15		
Heat-treated magnetic AS	Nile blue	q_m (mg/g)	515.1	q_m (mg/g)	492.2	K_F [(mg/g)(L/mg)$^{1/n}$]	155.8
		a_L (L/mg)	0.05	a_L (L/mg)	0.004	n	4.77
		SEE	75.35	n	9.55	SEE	36.22
		ARE (%)	21.86	SEE	38.72	ARE (%)	19.03
				ARE (%)	19.03		
Heat-treated magnetic AS	Bismarck brown Y	q_m (mg/g)	246.9	q_m (mg/g)	265.9	K_F [(mg/g)(L/mg)$^{1/n}$]	167.3
		a_L (L/mg)	5.72	a_L (L/mg)	4.69	n	8.31
		SEE	19.03	n	1.74	SEE	25.45
		ARE (%)	7.83	SEE	7.87	ARE (%)	11.93
				ARE (%)	2.69		
Heat-treated magnetic AS	Aniline blue	q_m (mg/g)	768.2	q_m (mg/g)	806.9	K_F [(mg/g)(L/mg)$^{1/n}$]	123.9
		a_L(L/mg)	0.05	a_L (L/mg)	0.04	n	2.87
		SEE	20.11	n	1.10	SEE	43.92
		ARE (%)	2.87	SEE	20.59	ARE (%)	10.36
				ARE (%)	3.33		
Live magnetic AS	Aniline blue	q_m (mg/g)	493.0	q_m (mg/g)	570.4	K_F [(mg/g)(L/mg)$^{1/n}$]	65.6
		a_L (L/mg)	0.03	a_L (L/mg)	0.02	n	2.76
		SEE	14.37	n	1.26	SEE	19.307
		ARE (%)	3.30	SEE	12.93	ARE (%)	5.90
				ARE (%)	3.09		

Computed isotherm parameters and errors (ARE and SEE) are shown in Table 3. In both cases, the Sips model closely approached the Langmuir model. Sips isotherm fitted better the experimental data for the living magnetic AS and Langmuir isotherm for heat-treated magnetic AS as indicated by the error functions. The maximum amount of pure dye adsorbed at equilibrium by heat-treated magnetic AS was 806.9 mg/g adsorbent, while it was only 570.4 mg/

Table 4 Comparison of maximum adsorption capacities (q_m) of different adsorbents for selected dyes according to Langmuir isotherm model

Dye	Adsorbent	q_m (mg/g)	References
Safranin O	Biopolymer poly(γ-glutamic acid)	502.8	(Inbaraj et al. 2006)
	Heat-treated magnetic activated sludge	326.8	This study
	Magnetically modified yeast cells	138.2	(Safarik et al. 2007)
	Sugarcane bagasse	58.8	(Farahani et al. 2015)
Nile blue	Heat-treated magnetic activated sludge	515.1	This study
	Magnetic spent tea leaves	87.1	(Safarik et al. 2012)
	Magnetically modified spent grain	64.1	(Safarik et al. 2011)
	Cocoa shell activated carbon	55.8	(Mylsamy 2013)
Bismarck brown Y	Biopolymer poly(γ-glutamic acid)	667.1	(Inbaraj et al. 2008)
	Heat-treated magnetic activated sludge	246.9	This study
	Magnetically modified spent grain	72.4	(Safarik et al. 2011)
	Flower like iron oxide nanostructure	64.1	(Khosravi and Azizian 2014)
Aniline blue	Heat-treated magnetic activated sludge	768.2	This study
	Magnetic *Saccharomyces cerevisiae*	228.0	(Safarikova et al. 2005)
	Iodo polyurethane foam	188.9	(Moawed et al. 2015)
	Magnetically modified spent grain	44.7	(Safarik et al. 2011)

g adsorbent by live magnetic AS according to Sips isotherm model. The higher sorption ability of dead microorganisms in comparison with live microorganisms was observed in the literature (Du et al. 2012; Srinivasan and Viraraghavan 2010); it was proposed that the increased biosorption of dyes by the heat-treated biomass could be caused by increased permeability of the cell walls after heating, such that the dye could enter into the cells and be adsorbed to the intracellular adsorption sites.

Thermodynamic parameters

Thermodynamic parameters (associated with the dye adsorption process) were determined from adsorption data at different temperatures (282.15; 295.15 and 313.15 K, respectively). The sorption increased with increasing temperature indicating that sorption process was endothermic in nature. Similar observations were reported, suggesting that this situation may be caused by increasing the mobility of the dye molecules and an increase in the porosity and in the total pore volume of the adsorbent with the increase in temperature (Salleh et al. 2011; Senthilkumaar et al. 2006).

The thermodynamic data are summarized in Table 5. The plot ln K_L versus 1/T straight lines ($R^2 > 0.98$) for all the four systems and R^2 values indicate that the values of enthalpy and entropy calculated for adsorbent are convenient. The negative values of Gibbs free energy change indicated the spontaneous reactions. The endothermic nature of selected dyes sorption on magnetic heat-treated AS was confirmed by the positive values of $\Delta H°$. The positive values of $\Delta S°$ suggested an increase in randomness at the solid/liquid interface.

Potential fate of the used adsorbent

One of the important characteristics of a biosorbent is its processing after finishing the sorption process. Biosorbents can be regenerated by selected organic solvents (e.g., methanol, ethanol), surfactants (e.g., Tween), as well as acidic and alkaline solutions; alternatively they are disposed in an environmentally acceptable manner. Thorough economical calculation is necessary to suggest the potential optimal setup of the pollutant adsorption process using low-cost biosorbents formed from biological waste materials.

Conclusions

The activated sludge was easily modified by microwave-synthesized magnetic iron oxides nano- and microparticles and used as an adsorbent for removal of dyes from aqueous solution. The prepared adsorbent can be selectively removed from many difficult-to-handle samples using an appropriate magnetic separator. It was demonstrated that magnetic activated sludge (especially heat treated) could be effective sorbent for dyes removal. This material contains a large number of functional groups, which are involved in efficient adsorption of various dyes. It was observed that Sips isotherm model described well the adsorption of safranin O and Bismarck brown Y, while Langmuir isotherm model was better for aniline blue adsorption and Freundlich isotherm model for Nile blue adsorption on magnetic heat-treated activated sludge, respectively.

Table 5 Thermodynamic parameters of the adsorption of selected dyes on magnetic heat-treated AS

Dye	R^2	ΔH° (kJ/mol)	ΔS° (J/mol/K)	ΔG° (kJ/mol)		
				282.15 K	295.15 K	313.15 K
Aniline blue	0.985	25.219	192.63	−29.030	−31.822	−35.013
Bismarck brown Y	0.996	42.773	263.29	−31.429	−35.097	−39.601
Safranin O	0.987	12.871	127.89	−23.260	−24.788	−27.220
Nile blue	0.989	28.441	197.44	−27.169	−30.016	−33.300

The kinetic study revealed that the process followed pseudo-second-order kinetics. The thermodynamic parameters obtained in all cases confirmed spontaneous and endothermic process.

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