

Acid-base treated vermiculite as high performance adsorbent: Insights into the mechanism of cationic dyes adsorption, regeneration, recyclability and stability studies

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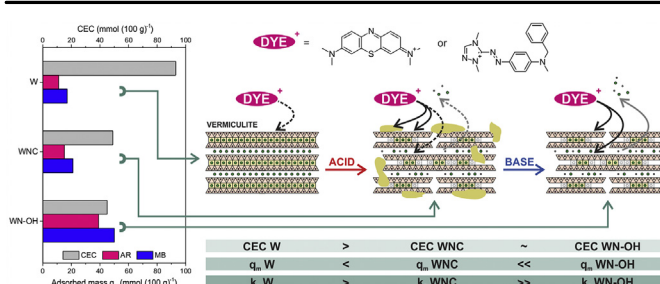
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HIGHLIGHTS

- Combined NaOH/acid treatment of vermiculite increased its adsorption capacity.
- Mixture of EtOH and NaCl solution was used for efficient adsorbent regeneration.
- Different behavior of dyes was observed in binary mixtures.
- Recyclable use of adsorbent for cationic textile dyestuffs removal was achieved.
- High adsorption level was maintained in a constant flow column system in 7 cycles.

GRAPHICAL ABSTRACT



Keywords:
Acid treatment
Base treatment
Vermiculite
Cationic dyes
Adsorption
Regeneration

ABSTRACT

Additional treatment with NaOH of acid activated vermiculite results in even higher increase in the adsorption capacity in comparison to samples modified only in acidic solution (first step of activation) with respect to raw material. Optimization of treatment conditions and adsorption capacity for two cationic dyes (methylene blue (MB) and astrazon red (AR)), also as binary mixture, was evaluated. The capacity, based on column studies, increased from 48 ± 2 to 203 ± 4 mg g⁻¹ in the case of methylene blue and from 51 ± 1 to 127 ± 2 mg g⁻¹ in the case of astrazon red on starting and acid-base treated material, respectively. It was shown that adsorption mechanism changes for both cationic dyes after NaOH treatment and it results in decrease of adsorption rate. In binary mixtures methylene blue is bound stronger by adsorbent and astrazon red may be removed in initial stage of adsorption. Extensive studies on desorption/regeneration process proved high efficiency in recyclable use of all materials. Although cation exchange capacity decreases due to acid treatment, after base treatment exchange properties are used more efficiently. On the other hand, increased specific surface area has less significant contribution into the adsorption potential of studied materials. Obtained adsorbents worked efficiently in 7 adsorption-regeneration cycles and loss of adsorption capacity was observed only in two first cycles.

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1. Introduction

Developing industry and increasing human population contribute greatly to deterioration of water quality. The European Union took step in keeping water in good condition by adopting Water Framework Directive 2000/60/CE (with subsequent changes by 2455/2001/CE, 2006/11/CE, 2008/32/CE, 2008/105/CE, 2009/31/CE, 2013/39/UE and 2014/101/UE), and Industrial Emissions Directive (2010/75/EU). Those documents determined priority substances to be eliminated from wastewaters and defined the obligations to be met by industrial activities, to avoid pollution, take preventive measures against it, and reduce, recycle and dispose of waste in the manner that generates less pollution. Chemical methods need the use of excess chemicals. In chemical methods, some toxic byproducts may occur (Juman et al., 2015).

Dyes are common in effluents discharged by various industries such as paper, plastics, food, cosmetics, and textile (Nguyen et al., 2013; Rozada et al., 2003). They usually have complex molecular structure, some of them may have toxic or carcinogenic effects on animals, they are hard to degrade biologically and change the light penetration in receiving waters disturbing natural biological processes. Moreover, they are one of the most problematic and difficult types of pollutant to be treated by conventional methods (Bhatnagar and Jain, 2005; Forgacs et al., 2004; Reife and Freeman, 1996).

Coagulation/flocculation methods are often applied to treat colored waters but their operation cost is high due to chemicals addition and sludge management (Mall et al., 2005). In the need of efficient and sustainable methods adsorption has been getting more interest in the application to wastewaters treatment (Lito and Serrão, 2005). It is considered as one of the best wastewater treatment methods due to its universal nature, ease of operation, ability to remove soluble and insoluble organic pollutants, high removal capacity and possibility to recycle and reuse many of adsorbents (Ali et al., 2012; Pan et al., 2009). One of the most commonly used adsorbents is activated carbon, having granular, powder, fiber and cloth form, due to its high specific surface area and high adsorption capacity for pollutants (Ayranci and Duman, 2009; Duman and Ayranci, 2006, 2011). However it is relatively expensive what makes it unattractive for discoloration purposes (Rozada et al., 2003). It is necessary to use an adsorbent that is freely available, inexpensive and non-hazardous in nature (Ali et al., 2012). Clays show good perspectives in this field.

Clays are minerals that have layer structure based on a tetrahedral (T) and an octahedral (O) phyllosilicate sheets, that may condense in either a 1:1 or 2:1 proportion to form T-O or T-O-T layer (Bergaya and Lagaly, 2006). If a charge is present on the sheets it is balanced by an ion located in between the sheets. These charge-balancing ions can be exchanged resulting in very good ion-exchange properties of the material (Chmielarz et al., 2003). Vermiculite is a clay mineral classified as 2:1 phyllosilicate (Bailey and Chairman, 1980; Rieder et al., 1993). Vermiculite is very abundant and much cheaper compared with other clays. Owing to its remarkable features, vermiculite is commonly used in agricultural, industrial and environmental applications (Duman and Tunc, 2008; Duman et al., 2015). It can be a subject to modifications in order to enhance its efficiency for the removal of pollutants from

wastewaters (Ali et al., 2012).

Mechanism of adsorption on a clay particle surface can take place via three mechanisms involving formation of complexes with charged surface functional groups: inner-sphere surface complexes (mostly ionic and covalent bonding), outer-sphere surface complexes and formation of diffuse-ion swarm, when the cation screens a delocalized surface charge. The last two mechanisms involve mostly electrostatic bonding. Ions adsorbed by outer-sphere complexes and diffuse-ion swarm are readily exchangeable and can be easily leached from the clay (Posito, 2008). Hence, the mechanism of adsorption determinates also possibility for regeneration and recycling of an adsorbent.

Acid activation of vermiculite is a common method of treatment of this clay however, to the best of authors' knowledge, little is known about complex modifications of already treated materials. The aim of this research was to investigate if any additional step to acid activation of vermiculite might result in further increase in the maximum adsorption capacity of the material. As shown in this work, when that modification is followed by treatment with a base it results in even more significant increase in the adsorption capacity compared to only acid treatment. The base treatment enhances the physicochemical characteristics of the material. The extensive adsorption experiments in batch and continuous flow (fixed bed column), as well as regeneration studies demonstrate the high performance of these materials, which offer interesting possibilities for industrial application as economical and sustainable adsorbent.

2. Experimental section

2.1. Materials

Vermiculite from South Africa (raw vermiculite, W) and its expanded derivative (Ve, obtained by rapid heating up to 1000 °C) were kindly supplied by ROMINCO POLSKA Sp. z o.o. Samples of acid activated vermiculite (WNC) were prepared by treating the raw material (W) for 2 h in 1.8 M nitric acid at 98 °C and then during 1 h in 10% citric acid solution at room temperature (24 °C) following the procedure described in previous study (Tawfiński et al., 2016). Experiments were conducted in Erlenmeyer flasks with caps or a reflux condenser in case where elevated temperature was used.

The basic dyestuffs methylene blue (MB), CI 52015, supplied by Riedel de Haen and astrazon red FBL 200% (AR), CI 85496-37-3, supplied by Dystar, were used for adsorption experiments (Fig. A.1 in the Supplementary Material).

In the first step 1 g of WNC and W were mixed with 10 mL of 1 M NaOH and stirred for 2 h and 24 h, after that, samples were washed, centrifuged (5 cycles of 10 min at 4000 rpm, Sartorius, Sigma 2-16) and left to dry. In the next step, in order to obtain base treated samples (WN-OH), weighted portions of 1 g of WNC were mixed with 10 mL of NaOH solutions of different concentrations (0.5 M, 1 M, 1.5 M and 2 M, respectively), stirred during 2 h at room temperature, washed and left to dry. In the last step, four samples of 1 g of WNC were placed in flasks with 10 mL of 0.5 M NaOH and stirred during 2 h and 4 h at different temperatures (room temperature (24 °C) and 98 °C), a reflux condenser was used where elevated temperature was applied.

2.2. Methods

The structure of the materials was studied with X-ray powder diffractometer (Bruker, D2 PHASER) equipped with CuK α radiation source (measurement range: 2-70 ° 2 θ , step size: 0.02° 2 θ , counting time: 1 s per step, slit width: 0.6 mm). Infrared spectra of the samples diluted with KBr (4 mg of sample ground with 96 mg of KBr) were recorded in the range of 650-4000 cm⁻¹ with resolution of 2 cm⁻¹ (200 scans), using diffused reflectance technique (Nicolet 6700 FT-IR, Thermo Scientific, MCT/A detector). The textural parameters of the samples were determined by adsorption of N₂ at -196 °C using a Quantachrome surface area and pore size analyzer, model 2200 E, on outgassed samples (25 °C, 2 h, pressure 0.001 bar). MB area was calculated based on adsorption studies of methylene blue taking 130 Å² as the surface occupied by one molecule of the dye. Cation exchange capacity was determined using the ammonium acetate method (Teudel, 2008). Chemical composition of samples was determined using atomic absorption spectroscopy (AAS) (Analytic Jena High-Resolution Continuum Source Atomic Absorption Spectrometer, ContrAA 700) method. The results are presented only for the most abundant elements (>0.25 wt%). Point of zero charge was determined using two different methods: according to procedures described by Mular (Mular and Roberts, 1969) and Riviera (Riviera-Utrilla et al., 2001) and given as an average of four pH values obtained in the experiment. The SEM/EDS analysis was performed using a High resolution (Schottky) Environmental Scanning Electron Microscope with X-Ray Microanalysis and Electron Backscattered Diffraction analysis: Quanta 400 FEG ESEM/EDAX Genesis X4M. Samples were coated with an Au/Pd thinfilm by sputtering, using the SPI Module Sputter Coater equipment.

Adsorbate concentration in batch adsorption experiments was measured using UV-VIS spectrophotometer (Thermo Scientific, Evolution 300) at the maximum absorbance wavelength (665 nm for MB and 531 nm for AR).

Models were fitted to the experimental data gathered in the kinetics, equilibrium and column experiments using non-linear regression analysis. Variances and correlation coefficients were determined and compared using Fisher's, and Akaike's Information Criterion (AIC) tests.

The pseudo 1st order Lagergren's model (Lagergren, 1898) and the pseudo 2nd order Ho's model (Ho and McKay, 1999) were fitted for the kinetic data, the Langmuir's (Langmuir, 1918) and the Freundlich's (Freundlich, 1906) models were fitted to the adsorption isotherm data. In the column experiments Yan's model (Yan et al., 2001) was fitted to the experimental data in order to determine the maximum adsorption capacity of the materials and Yoon-Nelson's model (Yoon and Nelson, 1984) to obtain breakthrough times. Models equations and description are given in section 6.2, in the Supplementary Material.

Batch adsorption experiments were performed in Erlenmeyer flasks with caps and a magnetic stirrer (Velp, Multistirrer 15) at room temperature (24 °C), without pH adjustment. Portions of 20 mg of each sample was placed in a flask and mixed with 50 mL of a 50 mg L⁻¹ solution of AR or MB, stirred for 2 h, centrifuged (5 min in 4500 rpm, Sartorius, Sigma 2-16) and concentration of adsorbate in the supernatant determined.

Kinetic experiments were carried out at room temperature (24 °C) using a magnetic stirrer (Velp, Multistirrer 15), without pH adjustment. A mass of 250 mg of the material was placed in a flask with 500 mL of dyestuff solution with an initial concentration of 100 mg L⁻¹. Samples were collected in selected time intervals using a micropipette and immediately centrifuged (1 min in 4500 rpm, Sartorius, Sigma 2-16) and concentration of the supernatant was determined.

Equilibrium studies were performed in 100 mL Erlenmeyer flasks with caps and 50 mL of dyes solutions of two concentrations (50 mg L⁻¹ and 100 mg L⁻¹) and varying amount of material (from 10 mg to 250 mg). Suspensions were agitated on a stirrer (Velp, Multistirrer 15) for 2 h, samples were collected, centrifuged (Sartorius, Sigma 2-16) and concentration of supernatant was determined.

Column experiments were performed using a glass column (Omnifit, 2.5 cm inside diameter, 15 cm height) and a peristaltic pump (Gilson, Miniplus 3). The studies were carried out with dyes concentration of 50 mg L⁻¹, at room temperature and flow rate of 2.0 mL min⁻¹. Weighted portions of 0.5 g of W and of 0.1 g of WNC and NaOH treated material (WN-OH), respectively, were mixed with 24 g of washed sand. In the next step, the column was washed with deionized water for 2 h and desorption proceeded using a solution of ethanol and sodium chloride, which was considered the best solvent according to the results in section 3.3, till the effluent showed no color. When the desorption process was finished, the column was washed with deionized water again and another cycle of adsorption performed (7 cycles on the raw material and 5 cycles on the modified materials). Three independent cycles of adsorption and desorption of MB and AR onto WN-OH were performed, during which changes of pH were monitored. In the last part of the studies co-adsorption of both dyestuffs was investigated on W, WNC and WN-OH. In each case the influent consisted of a mixture of both dyes in the proportion 50:50 to a final concentration of 50 mg of dyes per liter.

Desorption studies were performed by agitating 1 g of expanded (Ve) and acid activated vermiculite (WNC) in high concentration of AR for 2 h to prepare saturated material. Samples were washed with distilled water, centrifuged (5 cycles, 10 min at 4000 rpm) and left to dry. Desorption studies were carried out on saturated samples using different organic and inorganic eluents: cold water (H₂O COLD), hot water (H₂O HOT), hydrogen peroxide (Perox), 0.1 M hydrochloric acid (HCl), sodium chloride solutions (0.5 M; 1 M; 5 M respectively) (NaCl); acetone (Act), ethanol (EtOH), chloroform (Clfm), methanol (MeOH), carbon tetrachloride (CCl₄); mixture (50:50) of ethanol and 1 M aqueous sodium chloride solution (EtOH + NaCl) and mixture (50:50) of ethanol and 0.5 M nitric acid (EtOH + HNO₃). A mass of 100 mg of each saturated sample was put in a flask with a cap and mixed with 50 mL of eluent and stirred for 2 h or 24 h. After that time, the regenerated material was filtrated, washed and dried. In the next step, adsorption experiments on the recovered materials were performed by placing 50 mg of each sample in a flask and 100 mL of dyestuff of concentration of 100 mg L⁻¹ and stirred for 2 h, after which concentrations of solutions were determined.

3. Results and discussion

Detailed analysis of the results of specific surface area measurements and cation exchange capacity are presented in the Supplementary Material in section 3.3.1, chemical composition in section 3.3.2, point of zero charge determination in section 3.3.3, X-ray-diffraction analysis in section 3.3.4, and diffuse reflectance infrared Fourier transform analysis in section 3.3.5. Brief overview of obtained results is presented in Supplementary Material (Figures A.2 to A.6).

Particles morphology is visibly changing in each step of treatment. Crystals in starting material are characterized with relatively smooth edges, however between neighboring packets parallel stacking order is not always preserved. Upon acid treatment small clusters of amorphous products were formed and deposited on the surface, moreover numerous fragments of broken platelets may be observed. Leaching in sodium hydroxide solution results in removal

of irregular and rough particles. X-ray diffraction patterns indicate decrease of particle size as well as basal spacing. As expected, the highest decrease of cation exchange capacity was observed in the first stage of treatment (acid lixiviation), while it was almost unaltered after contact with solution of base. Results of chemical analysis confirm that components of octahedral layer were dissolved in acid in large extent. Similarly silica content was significantly decreased upon leaching in basic solution. Formation of amorphous silica, also confirmed by infrared spectra analysis, was accompanied with large increase of specific surface area and consecutive decrease after its dissolution. Point of zero charge on the other hand first decreased to rise again to higher values after the second stage of treatment (See Fig. 1).

3.1. NaOH treatment optimization

The raw material treated only with NaOH did not show any significant increase in the adsorption capacity, which stayed at an average level of $48 \pm 2 \text{ mg g}^{-1}$ (48 ± 2 , 45 ± 2 and $49 \pm 5 \text{ mg g}^{-1}$) for the raw (W), the raw treated for 2 h (W2h) and for 24 h (W24h), respectively. However, if the vermiculite is activated in acid (WNC) prior to the NaOH treatment, a big increase in the adsorption capacity, which reached an average level of $140 \pm 6 \text{ mg g}^{-1}$, was noticed and additionally a slight decrease in the capacity was observed after longer treatment time of 24 h compared to 2 h ($86 \pm 2 \text{ mg g}^{-1}$) for the WNC and 144 ± 1 and $135 \pm 1 \text{ mg g}^{-1}$ for WNC treated with NaOH for 2 h (WNC2h) and for 24 h (WNC24 h), respectively. Neither different concentrations of NaOH, nor time or temperature of the treatment resulted in statistically significant differences in the adsorption capacity of the material that was equal to an average level of $145 \pm 7 \text{ mg g}^{-1}$.

3.2. Kinetic and equilibrium studies

Pseudo 2nd order model was the best fit according to AIC for both dyes. However, in the case of Fisher's test pseudo 2nd order model fits better for MB but no statistically significant difference between the models exists for AR. Adsorption rate decreases after each treatment step for both dyes. Adsorption of MB occurs faster than adsorption of AR in the case of W and WNC. That trend changes however for NaOH treated material on which AR exhibits higher adsorption rate (Table 1). The time needed to reach equilibrium on NaOH treated material was approximately 110 min and 50 min for MB and AR, respectively (Fig. A.7A in the Supplementary Material).

Adsorption of each dye followed different mechanism (Fig. A.7B in the Supplementary Material and Table 1). In the case of MB Langmuir's model fits better for the starting (W) and the acid treated material (WNC) and adsorption of AR on those materials fits better to Freundlich's model according to AIC test. Fisher's test however, showed no difference between the models except for adsorption of MB on WNC, where Freundlich's model was a better fit. For the material after the NaOH treatment, this situation reverses and Langmuir's model fits better for adsorption of MB and Freundlich's for adsorption of AR. The results revealed that NaOH treatment increased greatly the adsorption capacity of vermiculite in relation to the starting material. Based on Langmuir's model the adsorption capacity raised from 44 ± 1 to $155 \pm 11 \text{ mg g}^{-1}$ in the case of AR and from 53 ± 10 to $161 \pm 5 \text{ mg g}^{-1}$ for MB, for raw and NaOH treated material, respectively (Table 1).

3.3. Pre-selection of eluent for regeneration

Solutions of inorganic substances (Fig. 2) did not show good desorbing properties (Ve HCl, Ve Perox, Ve H₂O COLD, Ve H₂O HOT,

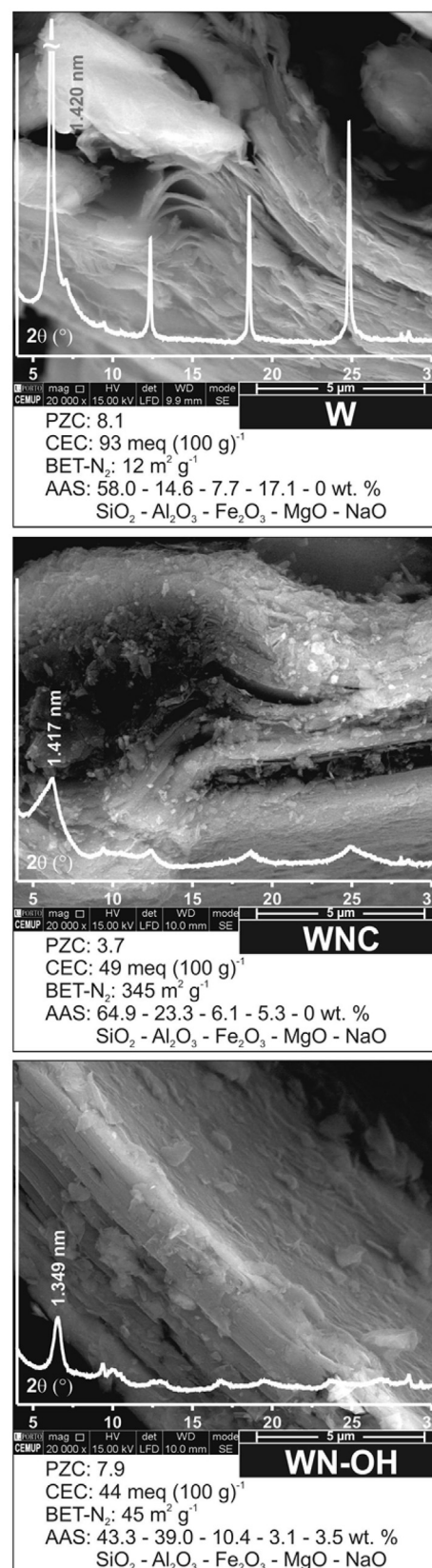


Fig. 1. Results of physicochemical characterization of acid-base treated vermiculite: particles morphology, XRD pattern, chemical composition, values of PZC, BET-N₂ and CEC.

Table 1

Parameters of kinetic and equilibrium equations obtained for adsorption of MB and AR on starting vermiculite (W), acid treated (WNC) and NaOH treated (WN-OH) vermiculite.

Sample	Experiment	Model	Parameter	AR	MB
WN-OH	kinetics	pseudo 1st	q_e (mg g ⁻¹)	130 ± 7	127 ± 4
			k_1 (min ⁻¹)	0.06 ± 0.01	0.19 ± 0.02
			s^2	80.43	25.21
			R^2_{adj}	0.945	0.978
			q_e (mg g ⁻¹)	147 ± 5	140 ± 4
		pseudo 2nd	k_2 (g (mg min) ⁻¹)	0.0005 ± 0.0001	0.0013 ± 0.0002
			s^2	16.96	12.97
			R^2_{adj}	0.988	0.989
			Fisher's Test	pseudo 2nd	no difference
			AIC	pseudo 2nd	pseudo 2nd
	equilibrium	Langmuir	q_m (mg g ⁻¹)	155 ± 11	161 ± 5
			K_L (L mg ⁻¹)	5 ± 48	0.8 ± 0.2
			s^2	297.12	7.36
			R^2_{adj}	0.513	0.998
			K_F ((mg g ⁻¹) (L mg ⁻¹) ^{1/n})	128 ± 2	116 ± 18
		Freundlich	n	1 ± 1	1 ± 8
			s^2	8.49	37.36
			R^2_{adj}	0.986	0.989
			Fisher's test	Freundlich	Langmuir
			AIC	Freundlich	Langmuir
WNC ^a	kinetics	pseudo 2nd	q_e (mg g ⁻¹)	6 ± 4	6 ± 4
			k_2 (g (mg min) ⁻¹)	0.004 ± 0.001	0.003 ± 0.001
	equilibrium	Langmuir	q_m (mg g ⁻¹)	6 ± 2	6 ± 3
		Freundlich	K_F ((mg g ⁻¹) (L mg ⁻¹) ^{1/n})	2 ± 2	4 ± 2
		Best fit	Fisher's test	no difference	Freundlich
			AIC	Langmuir	Freundlich
	kinetics	pseudo 2nd	q_e (mg g ⁻¹)	3 ± 2	4 ± 2
			k_2 (g (mg min) ⁻¹)	0.007 ± 0.002	0.005 ± 0.002
			q_m (mg g ⁻¹)	4 ± 1	5 ± 10
			K_F ((mg g ⁻¹) (L mg ⁻¹) ^{1/n})	3 ± 2	3 ± 6
W ^a	equilibrium	Best fit	Fisher's test	no difference	no difference
			AIC	Langmuir	Freundlich

Bold indicates positions of results of model comparison according to Fisher's test and Akaike's Information Criterion.

^a (Stawiński et al., 2016).

Ve NaCl). Organic solvents (Fig. 2) seem better for that purpose (Ve EtOH, Ve MeOH, Ve Act), however, the best results were obtained when a solution containing both, organic and inorganic compounds, was used (Ve EtOH+ NaCl, Ve EtOH+ HNO₃). The results also showed that time plays an important role in regeneration process. Significant increase in the regeneration efficiency was observed after 24 h in comparison to 2 h.

It was observed that methanol (Ve MeOH) desorbs better than ethanol (Ve EtOH) and the methanol-regenerated material showed adsorption capacity higher than the raw one (Fig. 2). Mixture of

ethanol and sodium chloride (WNC EtOH+ NaCl and Ve EtOH + NaCl) resulted in good desorption, also adsorption on the regenerated material is on the level of the starting one (Fig. 3). It should be noted that none of these solvents, ethanol or sodium chloride solution, is as effective as their combination.

3.4. Column studies

Results from column studies were adjusted to Yan's and Yoon-Nelson's models (Tables A.1 and A.2 in the Supplementary Material). Experimental data with fitted Yan's model are shown in Fig. A.8 and Table A.1. The experiments confirmed an increase in the

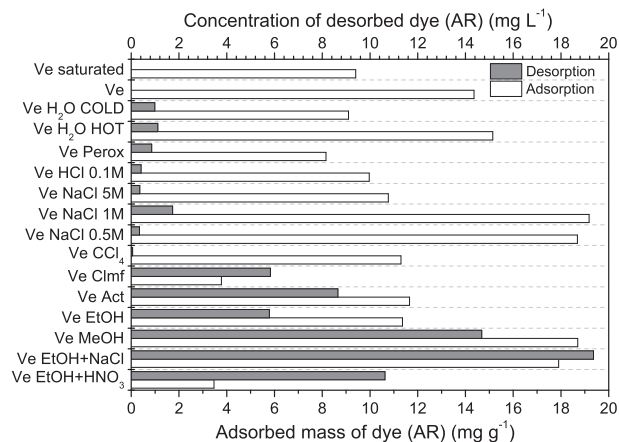


Fig. 2. Desorption efficiency after 2 h (bottom axis) from the expanded vermiculite (Ve) saturated with AR, and adsorption efficiency (top axis) on regenerated material (100 mL of 100 mg L⁻¹ AR solution, 2 h at 24 °C).

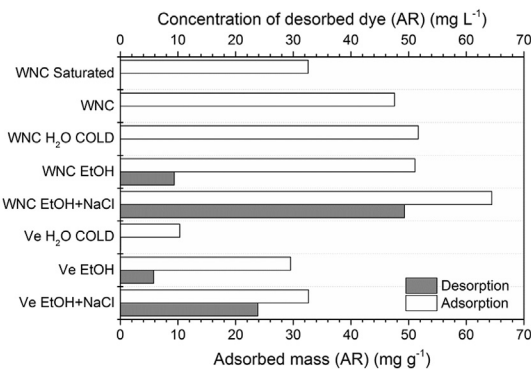


Fig. 3. Desorption efficiency after 24 h (bottom axis) from saturated materials (Ve and WNC) and adsorption efficiency (top axis) on regenerated material in selected conditions (100 mL of 100 mg L⁻¹ AR solution, 2 h at 24 °C).

adsorption capacity of vermiculite on each step of the treatment. Higher adsorption capacities were obtained for MB on modified materials (WNC and WN-OH) with an exception for the starting vermiculite on which AR reached higher adsorption level compared to MB (Fig. 4A). After two cycles the breakthrough time stabilized at an average level of 144 ± 15 and 212 ± 27 min on the raw material, 114 ± 25 and 88 ± 13 min on acid treated material, and 123 ± 25 and 99 ± 8 min on NaOH treated material, respectively for MB and AR (Fig. 4B).

Desorption studies showed that an average time of 100 min is enough to allow a satisfactory reuse of the column packing material (Fig. A.9 in the Supplementary Material). The experiments showed a general trend of changes in pH towards higher values in the case of AR and towards lower ones in the case of MB (Fig. A.10 and Fig. A.11 in the Supplementary Material). MB exhibited higher affinity to the material compared to AR which was being gradually desorbed from the column as adsorption of MB preceded (overshooting) when the column reached its maximum capacity. The values in that region were not considered during adjustments of the models. The materials showed higher adsorption capacity for MB compared to AR (Fig. 5). Table A.3 in the Supplementary Material contains full models' parameters.

4. Discussion

Vermiculite being a natural mineral, used without any additional purification, shows significant variances in measured properties, thus two methods were used to determine the point of zero charge (PZC). Shift between the measured PZC values was observed in different electrolyte concentrations, with a tendency towards lower pH with an increase of the ionic strength. That indicates electrolyte adsorption causing a release of protons associated with cation exchange sites (Conklin, 2014). Particle charge was then neutralized not only by adsorption of H^+ and OH^- but also electrolyte ions.

The pH measured when the following charges are neutralized: the charge depending on adsorbent structure (structural charge) and resulting from adsorption and immobilization of ions into surface complexes in adsorbent (net particle charge or net adsorbed surface charge), thus, a state when there is no more charge to be neutralized by ions in the diffuse layer, is simply called point of zero charge and corresponds to neutralization of net total particle charge (Sposito, 2008). PZC of raw vermiculite was found at about 8.1, which is in agreement with previous studies (Bollino et al., 2008; Fox and Malati, 1993). After treatment it shifted to 3.8, subsequent treatment with NaOH shifted the PZC back to

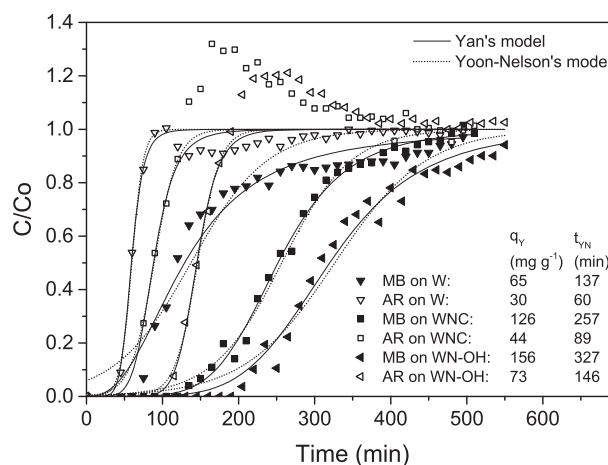


Fig. 5. Adsorption curves with models fitted to the experimental data of co-adsorption of MB and AR on starting (W), acid treated (WNC) and NaOH treated (WN-OH) material in column system; initial dyes concentrations: $50\ mg\ L^{-1}$, flow rate: $2.0\ mL\ min^{-1}$, temperature $24\ ^\circ C$.

approximately initial value of 7.9. The final product of acid treatment of clays is partly dissolved material of increased surface area, porosity and surface acidity, the final solid product also contains amorphous three-dimensional cross-linked silica (Komadel and Madejova, 2006). Chemical decomposition of clays causes an evolution of the surface functional groups from the pre-eminence of the siloxane ditrigonal cavity to an increase in abundance of inorganic hydroxides, that are capable of being ionized in contact with water (Molina, 2013; Sposito, 1984). When the crystalline surface of phyllosilicates is distorted, unsaturated broken bonds occur at the edge surface, these may be compensated by formation of reactive OH groups leading to Brønsted acid sites such as $SiOH$ and coordinately unsaturated Al and Mg easily formed at the edges behave as Lewis acids (Komadel and Madejova, 2006). When OH group is coordinated to Al (III) they can form inner-sphere complexes with a proton or hydroxide anion depending on pH values, when coordinated to Si, they tend to complex only hydroxide anions. Such prepared clays are also riddled with defects (vacant ion sites) that promote forming hollow spherule whose outer boundary contains many apertures through which small molecules or ions can enter (Sposito, 1984). Also the point of zero net charge (PZNC), thus PZC as well, for silica is relatively low (usually below 4) (Sposito, 2008). Those factors caused the shift of PZC in the treated material. The treatment with citric acid causes dissolution of metal hydroxides by

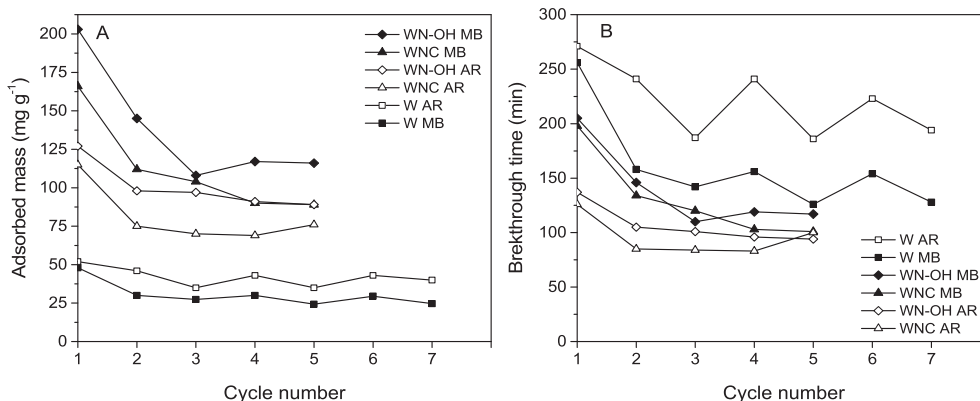


Fig. 4. Changes of the adsorption capacity during adsorption/desorption cycles obtained from Yan's model fit (A) and changes in breakthrough times obtained from Yoon-Nelson's model fit (B); initial dyes concentrations: $50\ mg\ L^{-1}$, flow rate: $2.0\ mL\ min^{-1}$, temperature $24\ ^\circ C$.

complexing the multivalent ions with citrate. Presence of such hydroxides prevents optimal dispersion of the clay causing coagulation and aggregation (Carrado et al., 2006). Citrate ions might also complex and remove the part of interlayer cations that had not been leached or exchanged during the mineral acid treatment and as well bulk metal oxides present on the layers surface. After the acid treatment deposits of amorphous silica, that act as a cementing agent impeding swelling and dispersion, are present in the material. During NaOH treatment that silica, as well as hydrous aluminosilicates (allophanes) formed during acid treatment, are dissolved (Carrado et al., 2006). This might clean the material and make the interlayer space more accessible for adsorption and removed degradation product responsible for lowering the PZC, as well as it was reported, the shift of PZC towards higher values is a normal phenomenon occurring in chemical weathering of clays provided that it involves removal of silica (Sposito, 2008).

The specific surface areas of the materials obtained by MB method are significantly higher than those from BET. This is due to the fact that specific surface area is an operational concept and obtained values may differ depending on an experimental method used, thus it precludes any interpretation of its numerical values in absolute geometric sense. Hence there is no one specific surface of a clay, but rather specific surfaces (Sposito, 1984). N_2 adsorption method creates limitations in samples containing layer-silicates (Airinghieri et al., 1992) due to the relatively large Van der Waals radius of the N_2 molecule that prevents it from interacting with surface functional group occluded in small void spaces and it is adsorbed only on the external surfaces of phyllosilicate quasicrystals (Sposito, 1984). The poor reactivity of non-polar molecule of N_2 to exposed surfaces might also contribute to lowering the values of specific surface area (Airinghieri et al., 1992). Methylene blue molecule, on the other hand, can penetrate the structure of the material, enter interlayer regions and the siloxane ditrigonal cavities. Another factor affecting the obtained specific surface area in MB experiment is the fact that the distribution of the dye cations on the surface of clays is influenced not only by electrostatic interactions, but also by dye-dye interactions (Lagaly et al., 2006). MB adsorption may follow the multilayer model (Weng and Pan, 2006) and on certain surfaces it can form dimmers or trimmers on the external surface of clay, which precedes the disaggregation and migration of the dyes in between the layers (Neumann et al., 2002). Decreasing particle size can increase the adsorption capacity since molecules don't penetrate the interlayer region but adsorb on the surface, smaller particles give larger surface areas. Also the inability to penetrate the micropores by large dyes molecules affects results obtained by dye adsorption (Izge et al., 2008; Gupta et al., 2003). Although it seems there was a reduction of specific surface area (N_2 adsorption method) after the base treatment, before that stage the total area available to adsorption was not accessible to the dyestuffs (inner surface of micropores). On the other hand, interlayers were not available to N_2 molecules after outgassing (Fig. A.2), while they can be penetrated by adsorbate molecules in the solution. Diffusion into interlayer galleries is possible due to base treatment and removal of silica clusters binding adjacent layers.

The DRIFT analysis showed that the acid treatment resulted in an increase in intensity and width of the peaks in mentioned range due increase in heterogeneity of OH species in the material (Węgrzyn et al., 2013). NaOH treatment decreased significantly that intensity, due to washing off hydroxyl group bearing species. After the NaOH modification hydrophilic cations of Na are present in the material strengthening the H-bonding of the polarized water. When the H-bonding is stronger, lower energy is required for an occurrence of OH-stretching vibration and thus the observed bands in NaOH treated vermiculite are shifted towards higher

wavenumbers (Tomíć et al., 2012). The bands in the spectrum of acid treated samples are broadened. This phenomenon may be due to decreasing crystallinity attributed to the weakening of H-bonds within the crystal and changes in Fe-O bonds associated with the tilting of octahedra rows within the structure (Farikh et al., 2014). Also it can be attributed to the partial transformation of the tetrahedral sublayers into a three dimensional framework of amorphous silica (Komadel et al., 1996; Madejová et al., 1998; Steudel et al., 2009). The shift of bands in the Si-O stretching region may correspond to progressive transformation of SiO-Mg-O-Si bonds in the silicate to the more rigid SiO-Si-O-Si bonds in amorphous silica when the octahedral cations were removed (Belver et al., 2002). Moreover, such shift in the band position of Si-O stretching region was reported as a result of reduction of Fe^{3+} and increasing amount of structural Fe^{2+} (Stucki, 2006).

The XRD analysis showed that upon the acid treatment some amorphous species of silica appear in the material (Maqueda et al., 2007) however, the vermiculite structure is preserved although the crystallinity significantly decreases. After the NaOH treatment the vermiculite structure changes, the material almost completely loses its crystallinity and some of the amorphous phase is leached from the material along with formation of another hydroxy phase.

Fisher's test showed no preference towards any model in the case of adsorption on the raw material and in the case of adsorption of AR on acid treated vermiculite. Adsorption of MB on acid treated material according to that test fits better to Freundlich's model, suggesting that it assumes multilayer adsorption on heterogeneous surface. AIC test however indicated Langmuir's model, which assumes monolayer adsorption on homogeneous surface, as a better fit in the case of adsorption of AR on the raw and acid treated material and Freundlich's in the case of adsorption of MB on those materials. The adsorption seems to change its mechanism after the material had been treated with NaOH. The trend of adsorption of AR driven by Langmuir's model's assumptions changes to Freundlich's and the opposite happens in the case of MB, both tests indicated the same models as the best fits in each case. Cation can be adsorbed on clays directly to the surface by forming an outer-sphere complexes as well as in a form of an outer-sphere complexes where water molecules are located between the cation and the clay surface (Sposito, 1984). Astrazon red is a bigger molecule so it should have lower ionic potential, which is a ratio of charge and molecule radius, compared to methylene blue, and that is why it has less affinity to the material. Additionally the interactions between the dyes and the clay are weakened due to decreasing of layer charge occurring during the dissolution of the vermiculite during the treatment. Such process also renders the layer charge distribution more heterogeneous (Penttrák et al., 2012). Those facts may explain the change of adsorption mechanism of AR on NaOH treated material. Some of the molecules can migrate from the inner-sphere complexes and outer-sphere complexes forming multilayer, also AR is a more flexible molecule and has more resonance structures than MB, which may allow different geometric coordination of the molecule on the surface making the layer more heterogeneous. The fact of MB tending to form multilayers might be explained by its ability to form dimmers and trimmers on external surfaces of adsorbents as a first step followed by disaggregation and migration of dye molecules in between the layers (Neumann et al., 2002). Moreover after the acid treatment the sample contains amorphous material that may provide additional adsorption sites and as they occupy also micropores what impedes access to some internal structures rendering the surface more heterogeneous (Ajaji and El Arfaoui, 2009). After the final step of treatment, during which the amorphous phase is leached, the material becomes more homogeneous allowing MB to form more ordered layers on the surface and Langmuir's model becomes again the best fit. It has been

reported (Pentřák et al., 2012) that MB tends to form monolayer on clays with reduced layer charge due to their decomposition. Decreasing particle size can increase the adsorption capacity, since the dyestuff molecules don't penetrate the interlayer region but adsorb on the external surface which may be significantly higher for small particles. It has to be mentioned that no matter how good the fit of a model is, it does not mean that an actual phenomenon the model expresses takes place. Most of the time, adsorption is controlled by various factors. Thus the adsorption isotherms equation, as well as rate laws should be rather considered as curve fitting models without actual mechanistic significance as they do not always reflect the actual phenomena taking place. However they are useful means with predictive capability of the adsorption to design adsorption units (Hameed and El-Khaiary, 2008; Sposito, 2008).

Desorption studies showed promising results in terms of regeneration the material. It is shown that contact time plays an important role in this process. Better desorption results of methanol compared to ethanol might be attributed to the fact that methanol being a smaller and more polar molecule than ethanol has easier access the interlayer space it displaces the adsorbed dyes molecules and interlayer water more efficiently. However, methanol due to its toxicity was no longer considered in this research. Adsorption capacity of the material regenerated that way is higher than of the raw sample. This phenomenon can be attributed to so called propping-open procedure. Ethanol and methanol molecules, previously adsorbed onto the material, are exchanged and facilitate intercalation of bigger organic molecules, which are not intercalated directly but in a stepwise process (Lagaly et al., 2006). Significant increase in the adsorption capacity of the material regenerated with a solution containing NaOH is due to changes in the structure of the material and its partial dissolution that causes significant loss of the sorbent mass. This is an undesired effect in this case of a material that is supposed to be used in continuous adsorption-desorption cycles. This process is discussed later in the article. Mixture of ethanol and sodium chloride and ethanol and sodium hydroxide give good desorption results, better than when the organic solvents are used isolated, due to enhanced adsorption of counter ions, in this case Na^+ , that occurs in the presence of organic solvents in the solution (Lagaly, 2006), thus removal of the adsorbed dyes is enhanced. This phenomenon can be explained by the fact that when ethanol is added to water it decreases the dielectric constant of the solution, thus the columbic attraction between exchangeable cations and negative silicate surface increases. The higher adsorption capacity of the regenerated material can be attributed to exchange of remaining interlayer divalent metal cations to sodium. This results in better delamination of the clay (Lagaly, 2006) and better accessibility of the surface to dyes. Also the saturated material still showed some adsorption abilities.

By means of the column experiments it was shown that the material can be re-used in several adsorption-regeneration cycles. The maximum adsorption capacity decreased during the first two cycles to maintain a stable level in the case of treated materials but remained unchanged in the case of the raw vermiculite. This phenomenon can be explained in terms of the changes occurring during the acid/base treatment. The material becomes more porous and its specific surface increases. Some of the adsorption sites might not be available to the solvent to penetrate (micropores, interlayer spaces) thus not all of the dyes molecules are able to be displaced and desorbed. It was also noticed that the total capacity in the case of co-adsorption was higher than in the case of systems with only one dye, it also proves that each dye might be adsorbed on different sites. Another factor contributing to lowering the capacity in adsorption-regeneration cycles is that the eluent reaches the mentioned structures and occupies them not allowing the dyes to adsorb there

in a following cycle. Also some of the dye or eluent molecules might adsorb on the materials with creation of chemical bonds permanently being attached to the surface. After the two cycles equilibrium is reached and adsorption takes place in more available sites. In the case of the raw material, that has crystalline structure and is more ordered, the diffusion of the solvent is easier rendering the desorption more efficient. The affinity of a dye seems to be a determinant factor in the removal of adsorbed molecules/ions. The molecule with the lowest affinity will always break through the column first, followed by other components of the feed having higher affinity. Concentration overshooting of one of the component occurs at the column outlet when an ion or molecule being less strongly adsorbed is pushed further in the column by more slowly moving, more strongly adsorbed species. That results in an increase in the solution concentration at the outlet of the column that can be higher than the initial one. Another factor causing overshooting may be the interference of ions or molecules displaced by ion exchange from the adsorbent surface, by that which have higher affinity to the adsorbent (Franca and Oliveira, 2010). The dye structure, molecular flexibility and differences in dimensions can influence the competition for the adsorption sites (Putra and Visa, 2015). MB molecule is more rigid (heterocyclic aromatic rings), thus it has slower diffusion rendering the adsorption slower, but it is able to give use to a larger amount of adsorption sites (e.g., inside micropores). AR however, being more flexible shows faster diffusion and adsorption process at the easily accessible sites.

5. Conclusions

Acid treatment of clays is a well-known procedure to increase their adsorption capacity. However, if such modification is followed by treatment with sodium hydroxide, which is reported in our work for the first time, it increases the adsorption properties even more. That treatment removes amorphous phase formed during the acid attack on the material, decreases its crystallinity and greatly increases its specific surface area (MB method). Adsorbent prepared by consecutive acid and base modification was successfully used in column recyclable system with a possibility of regeneration. The adsorption capacity of two cationic dyes in column studies, increased from 48 ± 2 to $203 \pm 4 \text{ mg g}^{-1}$ for methylene blue on starting material and from 51 ± 1 to $127 \pm 2 \text{ mg g}^{-1}$ for astrazon red on acid-base treated material. The loss of the adsorption capacity was observed only during the first two cycles, after that it maintained a stable level. Adsorption and regeneration was performed efficiently for 7 cycles. Acid-base treated vermiculite proved to be an economical, recyclable and high performance adsorbent.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2017.01.039>

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