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

Wojciech Stawiński [a], Agnieszka Węgrzyn [b, *], Tomasz Dańko [b], Olga Freitas [a], Sónia Figueiredo [a], Lucjan Chmielarz [b]

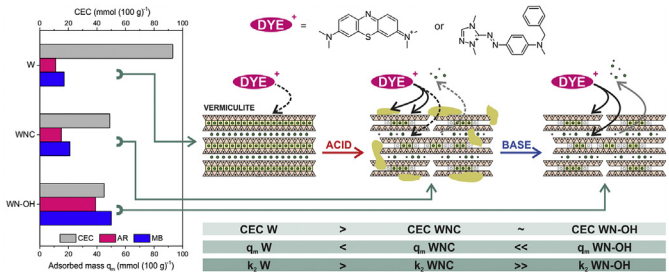
[a] REQUIMTE, LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida 431, 4200-072, Porto, Portugal

[b] Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060, Kraków, Poland

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



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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

* Corresponding author.
E-mail addresses: stawor@gmail.com (W. Stawiński), wegrzyn@chemia.uj.edu.pl (A. Węgrzyn), tom_91@o2.pl (T. Dańko), omf@isep.ipp.pt (O. Freitas), saf@isep.ipp.pt (S. Figueiredo), chmielar@chemia.uj.edu.pl (L. Chmielarz).

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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.

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 (Duman et al., 2015a).

Dyes are common in effluents discharged by various industries such as paper, plastics, food, cosmetics, and textile (Angın 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 (Leitão 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, 2010). 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., 1998). 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 Tunç, 2008; Duman et al., 2015b). 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 (Sposito, 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 (Stawiński 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.