Chemosphere 153 (2016) 115–129

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

The influence of acid treatments over vermiculite based material as adsorbent for cationic textile dyestuffs

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HIGHLIGHTS

- Treatment of vermiculite (nitric and citric acids) increases its sorption capacity.
- A successful application in column tests for cationic textile dyestuffs removal.
- New perspectives arise for this sorbent in wastewater treatment.

ARTICLE INFO

Article history:
Received 17 July 2015
Received in revised form
22 February 2016
Accepted 3 March 2016
Available online 22 March 2016

Handling Editor: Min Jang

Keywords:
Vermiculite
Acid treatment
Citric acid
Nitric acid
Adsorption
Column

ABSTRACT

The influence of different acid treatments over vermiculite was evaluated. Equilibrium, kinetic and column studies have been conducted. The results showed that vermiculite first treated with nitric acid and then with citric acid has higher adsorption capacity, presenting maximum adsorption capacities in column experiments: for Astrazon Red (AR), 100.8 ± 0.8 mg g^{-1} and 54 ± 1 mg g^{-1} for modified and raw material, respectively; for Methylene Blue (MB) 150 ± 4 mg g^{-1} and 55 ± 2 mg g^{-1} for modified and raw material, respectively. Materials characterization by X-ray diffraction, UV–vis-diffuse reflectance spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy, X-ray fluorescence, N_2 adsorption and CEC determination, has been performed. The results suggest the existence of exchange of interlayer cations, leaching of metals from vermiculite's sheets and formation of an amorphous phase in the material. Adsorption follows pseudo 2nd order model kinetics for both dyestuffs and equilibrium occurs accordingly to Langmuir's model for AR and Freundlich's model for MB. In column systems Yan's model is the best fit. The enhanced properties of acid treated vermiculite offer new perspectives for the use of this adsorbent in wastewater treatment.

1. Introduction

According to "Water for People Water for Life" United Nations World Water Development Report UNESCO the demand for fresh water has greatly increased with domestic, industrial and agricultural sector consuming 8, 22 and 70% of the available fresh water respectively, what is directly linked with the generation of large amount of wastewaters (Lehr et al., 1980; Helmer and Hespanhol, 1997). The quality of water is a very important issue, which is vital to the maintenance of a hydrological environment and to human health. In accordance to the water Framework-Directive 2000/60/CE and subsequent changes, by Decision 2455/2001/CE and Directives 2006/11/CE, 2008/32/CE, 2008/105/CE, 2009/31/CE and 2013/39/UE, emissions of priority substances should be decreased and finally eliminated. The discharge of coloured effluents, namely in textile industry, is an important issue. The removal of dyestuffs from textile effluents contributes to achieve the ultimate goal of the directive, "good ecological and chemical status" for all community waters.

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http://dx.doi.org/10.1016/j.chemosphere.2016.03.004
0045-6535/

Nomenclature

C_e	equilibrium concentration in liquid phase (mg L^{-1})
F	flow rate (mL min^{-1})
k_1	pseudo 1st order kinetic rate constant (min^{-1})
k_2	pseudo 2nd order kinetic rate constant (g mg^{-1} min^{-1})
K_F	Freundlich's constant ((mg g^{-1})(L mg^{-1})$^{1/n}$)
K_L	Langmuir's constant related to energy of adsorption (L mg^{-1})
K_{Th}	Thomas's constant (mL (mg min)$^{-1}$)
a_Y	Yan's constant (dimensionless)
k_{YN}	Yoon-Nelson's constant (min^{-1})
M	amount of adsorbent in Thomas's model (g)
m	adsorbent mass (mg)
n	Freundlich's constant (dimensionless)
q	adsorption capacity (mg g^{-1})
Q_0	maximum solid-phase solute concentration (mg g^{-1})
q_e	adsorption capacity at equilibrium (mg g^{-1})
q_m	Langmuir's model maximum adsorption capacity (mg g^{-1})
q_t	adsorption capacity at time t (mg g^{-1})
q_y	maximum adsorption capacity in Yan model (mg g^{-1})
r^2	determination coefficient
s^2	variance coefficient
t	time (min)
τ	time required for 50% adsorbate breakthrough (min)

Coloured wastewater is created as a result of the production of the dye and as well as a direct consequence of its use in the textile and related industries. It is estimated that approximately 10%–20% of dyes in the textile dying process will be lost in residual dyeing baths through incomplete exhaustion and washing operations. Therefore, hundreds tons of dyestuffs daily find their way into the environment, primarily dissolved or suspended in water (Allen et al., 2004). Effluents which are coloured might be interfering with light penetrating in receiving water bodies and disturb the natural biological processes, moreover some dyestuffs might exhibit toxic effects towards microorganisms or toxic/carcinogenic effects to mammals. Most of the textile dyestuffs are poorly biodegradable, have a complex molecular structure and are difficult to remove from wastewaters by conventional treatments (Reife and Freeman, 1996; Forgacs et al., 2004; Bhatnagar and Jain, 2005).

Physico-chemical processes are often applied to treat coloured wastewater, namely coagulation/flocculation. However, most of these processes present high operation costs (Mall et al., 2005). Increasing stringent legislation on the purity of water resources has created a growing interest in the cleansing of water, wastewater and polluted effluents by adsorption processes (Leitão and Serrão, 2005). Adsorption is a process in which dissolved molecules are attached to the surface of an adsorbent by physical or chemical forces (Noroozi and Sorial, 2013). It is a method that generates high-quality treated effluent. Lots of adsorbents might be recycled due to reversible nature of most of the adsorption processes (Pan et al., 2009). It is very efficient in the treatment of industrial effluents (Vinod and Anirudhan, 2003). Layered minerals (clay minerals) seem to be interesting precursors for adsorbents preparation.

Clays are naturally occurring minerals, composed primarily of fine-grained 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. The layers may be negatively charged, positively charged or uncharged, depending on their composition (Bergaya and Lagaly, 2006). If the layers are charged, this charge is balanced by interlayer cations. In any case the interlayer may also contain water. Interlayer cations can be exchanged, which explains that the whole group of clay minerals is characterized by very good ion-exchange properties (Chmielarz et al., 2003). Depending on the type of layered mineral, cations and also anions can be removed from wastewater. Vermiculite is a clay mineral classified as 2:1 phyllosilicate (Bailey and Chairman, 1980; Rieder et al., 1998). It is very abundant and much cheaper in comparison with other clays. Due to its remarkable features, vermiculite is widely used in agricultural, industrial and environmental applications (Duman and Tunç, 2008; Duman et al., 2015) Studies have shown that treatment of vermiculites with mineral acids resulted in an increase of specific surface area and porosity (Chmielarz et al., 2010; Santos et al., 2015), which enhances their adsorption capacity. Clay minerals modified in this way were recognized to have various applications: selective adsorbents for specific contaminants from wastewater (Polubesova et al., 2006), support to luminescent complexes (Silva et al., 2014), selective catalyst for NO reduction (Chmielarz et al., 2010) therefore application of such materials for adsorption of textile dyestuffs is expected to be also effective. Systematic study about the influence of activation with different acids is still rare and only few studies focus on treatment with nitric acid. The combination of nitric and citric acid for adsorbents preparation was not reported before in scientific literature.

2. Materials and methods

2.1. Materials

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, have been used. Their structural and molecular formulas are presented in Fig.A.6 in the Appendix. The pH values of the solutions were adjusted with hydrochloric acid and sodium hydroxide. All reagents (nitric acid 65%, sulphuric acid 96%, hydrochloric acid 36%, citric acid) were of analytical grade.

Vermiculite from South Africa in its natural form (raw vermiculite, W) and its expanded version (Ve) were kindly supplied by ROMINCO POLSKA Sp. z o.o. The adsorbent has been ground and sieved. The fraction below 355 μm was collected and used for further experiments.

Prior to the preliminary adsorption screening experiments the material was treated following the procedure given below: 250 mL of 0.4 M sulphuric (VI) acid or 0.8 M hydrohloric acid or 0.8 M nitric (V) acid were placed into round-bottom flasks equipped with reflux condenser. In each flask a weighted portion of 25 g of expanded vermiculite was added and boiled at 98 °C for two hours at constant stirring. In the next step material was repeatedly washed with water and centrifuged (5 cycles, 10 min each at 4000 rpm). The rinsing water, containing traces of heavy metals, was collected and a concentrated solution of NaOH was added drop wise to precipitate hydroxides of the metals present in the solution. After that the solution was filtrated and its pH neutralised. The sediment was disposed of as a hazardous substance. Samples were left to dry (at 50 °C) and powdered again in a grinder.

Extensive optimization of activation parameters was