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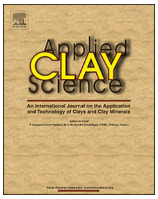

Research Paper

Sustainable adsorbents formed from by-product of acid activation of vermiculite and leached-vermiculite-LDH hybrids for removal of industrial dyes and metal cations

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ABSTRACT

Hydrotalcite-like layered double hydroxide (LDH) materials were synthesized from liquid waste by-product produced during acid activation of vermiculite (raw (W) and expanded (Ve)), and by combining the waste with the activated mineral, novel hybrid vermiculite-hydrotalcite-like materials were obtained in one-pot synthesis. Batch system adsorption experiments were performed on fresh and calcined (at 450 °C) materials using two anionic dyes (Congo Red - CR, and Reactive Red 184 - R), a cationic dye (Astrazon Red - AR), and Cu^{2+}. Calcination significantly increased the materials' adsorption capacities for all the pollutants. The highest adsorption capacities of the LDH derived from W were 289 ± 2, 137 ± 2, 38.2 ± 0.6 and 64 ± 2 $mg\,g^{-1}$, while for the ones derived from Ve were 214 ± 2, 119.5 ± 0.3, 35.9 ± 0.7 and 66 ± 3 $mg\,g^{-1}$ for CR, R, AR and Cu^{2+}, respectively. The hybrids obtained from W attained removal levels of 238 ± 3, 111 ± 2, 44 ± 1 and 70 ± 1 $mg\,g^{-1}$ and their counterparts derived from Ve reached 84 ± 1, 34.1 ± 0.5, 43 ± 2 and 75 ± 1 $mg\,g^{-1}$ for CR, R, AR and Cu^{2+}, respectively. Strong synergic effect on adsorption was observed in the hybrid materials, especially in these derived from Ve. These adsorbents had higher (up to 400%) adsorption capacities than theoretical ones prepared by mixing ex-situ appropriate amounts of activated vermiculite and LDH. All the materials were characterized by XRD, SEM-EDS, and ATR techniques. The proposed procedure is a sustainable approach to clay minerals valorization and my open new possibilities in fields such as wastewater treatment or catalysis.

1. Introduction

Decreasing the environmental impact of wastewaters to acceptable levels has become the first and major modern world's concern and the demand on technologies for pollutants removal has been rising (Sevekow, 2003; Pereira and Alves, 2011).

Dyes are common pollutants generated in various industries (Rozada et al., 2003; Angın et al., 2013) and are often accompanied by heavy metals in wastewaters (Pereira and Alves, 2011). Both pollutants pose a hazard to living organism and are resistant to conventional treatment methods (Forgacs et al., 2004; Bhatnagar and Jain, 2005). Adsorption is considered one of the best industrial wastewaters treatment methods due to its efficiency (even for low contaminant concentrations), broad applicability, ease of operation, and insensibility to toxicants (Leitão and Serrão, 2005; Ali et al., 2012). The desired adsorbent should be derived from easily available, inexpensive, non-hazardous and feasible to recycle materials (Ali et al., 2012; Ummartyotin and Pechyen, 2016). Different adsorbents such as activated carbon (Ayranci and Duman, 2009, 2010; Duman and Ayranci, 2010), sepiolite (Duman et al., 2015a), vermiculite (Duman et al., 2015b) and magnetic carbon nanotubes (Duman et al., 2016) have been used successfully for the treatment of wastewaters including dyes and metal ions. On the other hand, researches have been continued for inexpensive alternative adsorbents having reasonable adsorption efficiencies (Duman et al., 2015b).

Layered materials such as clay minerals and layered double

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hydroxides (LDH) are promising in the field of adsorption (Pinnavaia, 2004; Roy et al., 2006). The first are minerals with a structure built of layers that may carry a negative charge balanced by a cation localized between the layers. The second, have similar layered structure, however the sheets have a positive charge balanced by an interlayer anion (Braterman et al., 2004). These charge balancing ions can be replaced giving the materials good cation and anion exchange properties, respectively.

These materials can be subjected to modifications in order to change their properties (Bergaya and Lagaly, 2006; Komadel and Madejova, 2006; Lagaly et al., 2006; Stawiński et al., 2016; Stawiński et al., 2017a; Stawiński et al., 2017b; Stawiński et al., 2017c). One of the most common modifications of clay minerals, among thermal and surfactant treatments, is their acid activation resulting in increased maximum adsorption capacity (Komadel and Madejova, 2006; Duman and Tunç, 2008; Chmielarz et al., 2012; Stawiński et al., 2016; Stawiński et al., 2017c). However, that process might be considered as unsustainable because it usually produces highly acidic waste containing metals leached during the procedure. It was previously reported by Węgrzyn et al. (2018) that the procedure's environmental impact of may be diminished by applying fine wet milling of the clay mineral as a pretreatment step decreasing the acid concentration necessary to obtain desired adsorption capacity.

This study aimed to make the acid activation more sustainable by finding application of the waste produced during the procedure. The waste was successfully used to produce a layered hydrotalcite-like material characterized by good adsorption properties for anions (anionic dyes) and cations (metal) removal. Moreover, by using the waste and the acid treated clay a hybrid vermiculite-hydrotalcite material, capable of adsorbing metal ions and both anionic and cationic dyes, was prepared. Such adsorbents were subjected to thermal modification that increased their adsorption capacity for all aforementioned pollutants. To the authors' best knowledge such procedure and its application have not been reported in the literature so far. This work contributes to the search of solutions to decrease the environment impact of clay minerals acid activation and gives solution to remediation of waste waters leaden with cationic and anionic pollutants by means of versatile adsorbents obtained in simple one-pot synthesis.

2. Materials and methods

2.1. Materials

2.1.1. Adsorbates

The cationic dye Astrazon Red FBL 200% (AR), (CAS 12221–69-1), and two anionic dyes, Reactive Red 184 (R) (CAS 85496–37-3) and Congo Red (CR) (CAS 573–58-0), supplied by Dystar were used for the adsorption experiments. Analytical grade salt $CuCl_2{\cdot}2H_2O$, employed for preparation of Cu^{2+} solutions, $(NH_4)_2CO_3$ and Na_2CO_3 were obtained from Sigma-Aldrich. Raw (W) and expanded (Ve) vermiculites were kindly supplied by ROMINCO POLSKA Sp. z o.o. The dyes' structures are presented in the Supporting Materials in Fig.S1.

2.1.2. Adsorbents

2.1.2.1. Nomenclature. The first sample name's part stands for the material used in the synthesis (W and Ve, for raw and expanded vermiculite, respectively). The second part indicates the fraction obtained during the acid treatment of the starting materials, later used in the synthesis (L - only liquid; LS - liquid and solid, hybrid samples; S – only solid residual fraction-acid leached vermiculite). The next part indicates nitric acid concentration (M) used during the synthesis, and the last part, if present, denotes calcination at 450 °C.

2.1.2.2. Samples preparation

2.1.2.2.1. Adsorbents prepared from solid faction (S). Volume of 100 mL of 1.8 M HNO_3 was heated to 98 °C in a round bottom reactor equipped with a condenser. Then a 10 g portion of raw vermiculite (W) was added to it and stirred (400 r.p.m) for 2 h at constant temperature. The sample was centrifuged (10 min at 4500 r.p.m.) and the supernatant was collected. The sediment was washed in 5 cycles of mixing with distilled water and centrifugation (10 min at 4500 r.p.m. in each cycle), and dried at 40 °C overnight in order to obtain sample W-S-1.8. Similar procedure was applied using W and 3.2 M HNO_3 to produce sample W-S-3.2, and using Ve to obtain samples Ve-S-1.8 and Ve-S-3.2.

2.1.2.2.2. Adsorbents prepared from liquid fraction (L). The supernatant obtained after acid leaching of vermiculite (section above) was alkalinized with ammonium carbonate (pH about 6) and added dropwise to another reactor containing 0.1 M Na_2CO_3,. The pH was raised to 10.0 ± 0.2, the content was heated to 60 °C and left under constant stirring (400 r.p.m.) for 24 h. Then the material was centrifuged (10 min at 4500 r.p.m.), washed 5 times as described above, left to dry overnight at 40 °C and ground in a mortar in order to produce sample W-L-1.8. Similar procedure was applied using 3.2 M HNO_3 to obtain sample W-L-3.2 and to the expanded vermiculite for samples Ve-L-1.8 and Ve-L-3.2. The reference hydrotalcite (HT-REF), with the formula $[Mg_{0.667}\ Al_{0.235}\ Fe_{0.098}\ (OH)_2]\ (CO_3)_{0.167} \cdot 0.5\ H_2O$, was prepared by co-precipitation method to simulate cationic composition of the starting vermiculite (W), which was previously reported in Stawiński et al. (2016), assuming that maximum molar fraction of trivalent cations within LDH structure is used.

2.1.2.2.3. Hybrid adsorbents (LS). The hybrid adsorbents were formed according to the procedure described in the previous section however both liquid and solid fractions of the acid activated vermiculites, without separation, were used in the synthesis of samples W-LS-1.8, W-LS-3.2, Ve-LS-1.2 and Ve-LS-3.2.

2.2. Methods

2.2.1. Characterization of materials

X-ray fluorescence (XRF) analysis was performed using Skayray Instrument EDX 3600H - Alloy Analyser. The materials' structure was studied with X-ray powder diffractometer (Bruker, D2 Phaser) equipped with CuKα radiation source (λ = 0.154184 nm; measurement range 2–70° 2θ; step size 0.02° 2θ; slit width 0.6 mm; step scan size 0.02°; counting time 1 s). A field emission scanning electron microscope (FESEM) Hitachi S-4700 equipped with a Vantage Noran EDS system was used to record the SEM micrographs and to analyze elements distribution in the materials. The samples' surface were prepared by carbon coating. The Infrared spectra (ATR-FTIR) were recorded using Attenuated Total Reflectance technique with diamond crystal, in the range of 525–4000 cm^{-1} with 2 cm^{-1} resolution and 50 scans (Nicolet 6700 FT-IR, DTGS detector, Thermo Scientific). Second derivative method was used in the case of ATR-FTIR analyses for better peaks detection.

2.2.2. Adsorption experiments

Weighted portions of 20 mg of each material were placed in Erlenmeyer's flasks and mixed with 40 mL of solutions with concentrations equal 200 mg L^{-1} for the dyes (AR, R, CR) and 30 mg L^{-1} for Cu^{2+}. The flasks were closed and stirred (400 r.p.m.) for 2 h at room temperature (24 °C) without pH adjustment. Each experiment was made in triplicate. Then the samples were centrifuged (5 min at 4500 r.p.m.) and the adsorbates concentration in the supernatant determined. The dyestuffs concentrations were measured using UV–Vis spectrophotometer (Thermo Scientific, Evolution 300). Concentration of Cu^{2+} was determined by atomic absorption spectroscopy (Analytik Jena High-Resolution Continuum Source Atomic Absorption Spectrometer, ContrAA 700).

The adsorption capacity was calculated according to Eq.1:

$$q_{=}\frac{(C_0 - C_{eq})V}{m} \tag{1}$$