Research paper

Effect of acid activation of Saudi local clay mineral on removal properties of basic blue 41 from an aqueous solution

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ABSTRACT

Local clay mineral from Khulais area, was activated at different acid to clay mineral ratios (in mass) at 90 °C. The local clay mineral contained a major phase of smectite, in addition to kaolinite and quartz as impurities. Upon acid activation, structural changes in the treated clay minerals occurred for the smectite phase. The other phases were not affected as indicated by powder x-ray diffraction and Fourier transform infrared. Decrease in contents for Al_2O_3, MgO, Fe_2O_3, and Na_2O, followed by a relative increase in SiO_2 occurred. The acid activated clays exhibited lower cation exchange capacity, and higher specific surface areas. These changes in chemical compositions and other properties were related to the extent of the acid activation process. The acidity of local clay mineral was enhanced up to a certain level of activation, then it decreased gradually. A maximum specific surface area of 330 m^2/g was achieved at an acid to clay mineral ratio of 0.5. The increase of surface area was not the main key that controlled the removal capacity of the acid activated clays for basic blue-41 dye. The acid activation has improved the removal capacity of the raw clay mineral from 50 mg/g to 73 mg/g. This capacity was reduced with the extent of the acid activation, and was related to the destruction of the removal sites during the acid activation and not to the specific surface areas of the clay mineral. The recycling of spent acid activated clay was achieved by the sulfate radical oxidation, and about 85% of dye removal could be still retained after six recycle runs.

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1. Introduction

Clay minerals find wide range of applications, in various areas of technology, due to their natural abundance and their ability to be chemically or physically modified (Murray, 2006). Several methods have been proposed to modify the properties of natural clay minerals, among them, the efficient acid activation method (Hussin et al., 2011). This method is a single step process and it did not consume a lot of time. It consists of treating the clay minerals with inorganic (hydrochloric, sulphuric, phosphoric, and nitric) or organic (acetic, citric, oxalic and lactic) acid solutions at certain conditions (Hussin et al., 2011). During the acid treatment, many changes occurred in the aluminosilicate structure due to dissolution of structural ions and the rearrangement of the structure (Korichi et al., 2009). The acid treatment firstly rendered the surface of clay mineral acidic, then it leached metal ions from the clay mineral lattice leading to an increase of the external surface area of the clay mineral and introduces permanent mesoporosity (Jozefaciuk and Sarzynska, 2006). The extent of these changes depended on different parameters such as the geographical origin of the clay mineral, the type of the used acid, its concentrations, temperature and time of acid

activation (Noyan et al., 2007; Amari et al., 2010; Komadel and Madejová, 2013; Kooli and Liu, 2013). These acid activated clays have found many applications in industrial process such as the decolorization of the vegetable oil in edible oil industry (Temuujin et al., 2006; Nguetnkam et al., 2008; Didi et al., 2009) and as adsorbents for heavy metals and dyes (Eren and Afsin, 2008; Yener et al., 2012).

The production of acid activated clays caused environmental problems due to the use of inorganic acids in large quantity. These acid activated clays are usually washed until ions free before being used, thus creating a waste stream which its disposal would introduce additional expense. To resolve these problems, the use of organic acids was proposed (Khan et al., 2015), or the use of low concentration of sulphuric acid (mass%) was proposed. In this case, all of the acid added to the clay mineral remained associated with it, and it did not need any subsequent washing and filtration steps (Hill et al., 2002).

The removal of dyes from contaminated water has been considered as main concern to preserve the water resources and eliminate the dangers associated with these dyes for the human and aquatic lives. They have been reported to cause carcinogenesis, mutagenesis, chromosomal fractures, teratogenecity and respiratory toxicity (Bae and Freeman, 2007). The existence of different structures of dyes made their treatment and elimination from contaminated water by a single standard methodology difficult, and needed many steps (Robinson et al., 2001;

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Forgacs et al., 2004). These techniques were reported in many reviews. Adsorption is one of the processes, being widely used for dye removal from aqueous solutions (Gupta and Suhas, 2009). The efficiency of the adsorption method depended on the used adsorbents and their capacities and cost. Among the low cost materials, clay minerals were proposed as potential candidate because of their low cost, abundance in most continents of the world, high adsorption properties and potential for ion-exchange (Rahman et al., 2013). The adsorption properties depended in many factors, among them the specific surface area, and many studies have related the increase or the decrease of adsorption capacity to the surface areas of the adsorbent materials (Yang et al., 2008). The specific surface area of clay mineral could be enhanced by different methods, such as pillaring process (Kloprogge et al., 2005), acid activation (Jozefaciuk and Sarzynska, 2006).

The clay mineral became saturated during the adsorption of dyes, and it has to be regenerated and recycled. The cost of their disposal or regeneration determines the feasibility of applying the adsorbent systems in large-scale operations, and it is considered an important economical aspect to minimize the cost of adsorption process. The common reported regeneration methods are thermal, solvent, photocatalytic and chemical oxidation regeneration (Chen et al., 2008; Song et al., 2009; Vimonsesa et al., 2009; Zhang et al., 2010). In this study, the acid activation process was performed to increase these properties. There were few studies related to the use of Saudi local clay minerals as removal agent for metals and acidic dye as eosin (Al-Jlil and Alsewailem, 2009; Alshammari, 2014; Al-Faze and Kooli, 2014). In this study, local clay mineral was collected from Khulais region, and treated by aqueous sulphuric acid solution at different acid/clay mineral ratios (in mass) at 90 °C. The effect of acid activation on the physico-chemical properties of raw mineral was examined by different techniques. The application of the acid activated clays in the removal properties of basic blue-41 (BB-41) was examined from aqueous solutions. BB-41 is a basic dye, once is dissolved in water, it carries a net positive charge due to the presence of protonated amine or sulfur containing groups (Roulia and Vassiliadis, 2005). The Langmuir model was used to estimate the maximum removal capacity of the different clay minerals, the removed amounts were associated to the properties of the treated clay minerals. The regeneration of a selected spent acid activated clay at an acid/mineral ratio of 0.2, after BB-41 adsorption was examined. The sulfate radical-based advanced oxidation technology was used due to the high efficiency, low cost and fast reaction kinetics of this catalytic process.

2. Material and methods

The local montmorillonite was collected from Khulais area (assigned as MtKhl), in Jeddah province, with initial humidity of 13%. It was used as received. The BB-41 dye was purchased from Aldrich, with molecular mass of 482.57 g/mol, sulphuric acid (H_2SO_4), Co (NO_3)$_2 \times 6H_2O$ and oxone ($2KHSO_5 \times KHSO_4 \times K_2SO_4$) were purchased from Aldrich, and used without further purification.

2.1. Acid activation

The acid activation was performed by adding the raw MtKhl to an aqueous solution of sulphuric acid at 90 °C and left overnight under stirring at 90 °C. The acid/clay mineral (a/c) ratios (in mass) between 0.1 and 0.5 were used, based on dry mass of MtKhl and aqueous solution of H_2SO_4 (Kooli and Liu, 2013). The resulting acid activated clays were repeatedly washed with distilled water and dried at ambient temperature. The samples are assigned as follows: MtKhl-0.1 indicates that the clay mineral was acid-activated at an a/c ratio of 0.1, etc. …

2.2. Removal of basic blue 41

The removal of BB-41 was performed in batch process and in a shaker water bath with controlled temperature at 25 °C (Kooli et al., 2015).

Preliminary experiments demonstrated that the equilibrium was established in 6 h, however, more time was used to attain equilibrium for 18 h. 0.100 g sample of raw clay mineral and acid activated clays were mixed with 10 ml of BB-41 solution of different concentrations from 25 to 1000 ppm. The supernatant was collected by centrifugation, for 10 min at 4700 rpm using labofuge 200 centrifuge. The BB-41 concentration was determination from the maximum absorbance characteristic in the UV–vis range at 610 nm using a Cary (100 Conc) spectrophotometer. In all our solutions, the UV–visible spectrum exhibited a maximum absorbance at 610 nm indicating that the monomers of BB-41 are dominant, and a shoulder near 575 nm, was partially due to dimers and the 0–1 vibronic transition of monomers.

2.3. Regeneration of spent MtKhl-0.2

The MtKhl-0.2 was added to 10 mL of BB-41 solution (200 ppm) for overnight, the solid was collected by centrifugation, and identified as BB-MtKhl-0.2. The solid then dispersed into 10 mL of Co (NO_3)$_2 \times 6H_2O$ aqueous solution. The Co^{2+} cations served as the homogeneous catalyst. The oxidant, 12 mg of oxone ($2KHSO_5 \times KHSO_4 \times K_2SO_4$) was added into the mixture to degrade the adsorbed BB-41. The mixture was stirred for 30 min, separated by centrifugation, washed a few times with deionization water and then recycled for the next run. The same Co(NO_3)$_2$ solution was used throughout the whole recycle runs

2.4. Characterization techniques

Elemental analysis was performed to get information about the main elements in the MtKhl and its activated counterparts. X-ray fluorescence (XRF) S4 explorer from Bruker, was used for this purpose. The mineralogical phase identification of MtKhl and the structural changes during the acid activation was examined by using X-ray diffractometer advance D8, from Bruker, operating with Copper (CuKα) wavelength of 0.15406 nm. The cation exchange capacity (CEC) values were estimated using as described somewhere else (Meier and Guenter, 1999). The FTIR spectra of raw clay mineral and acid activated clays were obtained using Shimadzu Model FTIR-8400 s, to describe the changes in the clay mineral structures. FTIR spectra were recorded in the region of 4000–400 cm^{-1}. The thermogravimetric analysis (TGA) features were recorded on a TA instrument, model SDT600. The measurements were carried out in air flow 100 ml/min, and heated from 25 to 800 °C, with a heating rate of 10 °C/min. The specific surface areas (SSA) and total pore volume (TPV) of the samples were determined from nitrogen adsorption isotherms at 77 K, obtained from a Micromeritics ASAP2020, after outgassing the samples overnight at 120 °C. The SSA values were determined by applying the Brunauer–Emmet–Teller (BET) equation in the range of relative pressures from 0.05 to 0.3. The total pore volume (TPV) was estimated at the adsorption P/P$_o$ value of 0.97. The pore width distribution was calculated using the adsorption branch of the isotherm. The acidity contents of the raw and acid-activated clays were measured by the absorption of cyclohexylamine followed by a thermal gravimetric analysis (TGA) using a TGA machine from TA instruments model SDT600. The mass loss due to cyclohexylamine desorption from acid sites between 290 °C and 420 °C was computed to quantify the acidity in mmole of cyclohexylamine. Since each cyclohexylamine molecule reacted with one proton (H$^+$), it can be assumed that each mmole of cyclohexylamine corresponds to one mmole of proton (H$^+$).

3. Results and discussion

3.1. Characterization of acid activated clays

3.1.1. XRF data

The chemical composition (% of mass) of raw MtKhl and acid activated counterparts is given in Table 1. The MtKhl is mainly composed of silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3). Traces of calcium,