

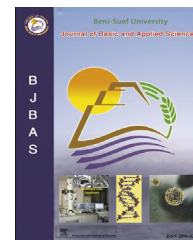
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Full Length Article

Acid-modified montmorillonite for sorption of heavy metals from automobile effluent

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ARTICLE INFO

Article history:

Received 11 March 2015

Received in revised form 27

December 2015

Accepted 2 January 2016

Available online

Keywords:

Acid-activation

Automobile effluent

Heavy metals

Sorption

Isotherm

Kinetic

ABSTRACT

An acid treated montmorillonite was utilized as a low-cost adsorbent for the removal of heavy metals from an automobile effluent. The adsorbent was characterized by the Fourier transform infrared spectrophotometer and scanning electron microscope. The effects of pH, adsorbent dose, particle size and contact time on the sorption process were determined by batch methodology. Acid modification increased the Brunauer Emmett and Teller (BET) surface area and total pore volume of the montmorillonite from 55.76 to 96.48 m²/g and from 0.0688 to 0.101 cm³/g, respectively. The removal of heavy metals from the effluent followed the order: Zn > Cu > Mn > Cd > Pb > Ni, which is directly related to the concentration of metal ions in the effluents. The Freundlich isotherm was found to fit the experimental data properly than the Langmuir, Temkin and Dubinin–Radushkevich isotherm models. Kinetic analysis was performed by the application of the pseudo-first order, pseudo-second order, intraparticle diffusion and liquid film diffusion model. The process was found to be physisorption, controlled by the film diffusion mechanism. The acid treatment enhanced the adsorption capacity of the montmorillonite and was suitable for the removal of heavy metals from the automobile effluent.

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1. Introduction

The rapid growth of industries has resulted to an increase in discharge of wastewaters containing heavy metals, which is a serious environmental problem. These heavy metals are usually toxic at certain concentrations to living organisms,

persistent in nature, non-biodegradable and tend to accumulate in the food chain (Ahluwalia and Goyal, 2007). It is therefore necessary to remove these metals from industrial effluents before their discharge into receiving water bodies. Well established methods for treating heavy metals contaminated effluents include ion exchange, filtration, chemical precipitation, electrochemical treatment, oxidation/reduction, solvent

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<http://dx.doi.org/10.1016/j.bjbas.2016.01.003>

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extraction, evaporation and adsorption (Akpomie and Dawodu, 2015). However, few of these processes are accepted due to high cost, low efficiency, inapplicability to a wide range of pollutants and results in secondary contamination (Liang et al., 2010). Adsorption has been found to be the most effective technique in terms of initial cost, ease of operation, flexibility and simplicity of design, and activated carbon is known to be the most effective adsorbent (Wang and Li, 2007). The disadvantage of the high cost involved in using activated carbon led to the search for cheaper alternative adsorbents by researchers. Recently, many low cost adsorbents have been utilized for heavy metals removal, which includes biomass materials, fertilizer waste, tea waste, microorganisms, charcoal, yeast, sludge ash, date pits, laterite, red mud and clay (Dawodu and Akpomie, 2014). Montmorillonite has also been used for the removal of heavy metals from effluents (Abollino et al., 2003; Guo et al., 2011). Our previous work has showed a local Nigerian montmorillonite and its alkaline modified derivatives suitable for treatment of an automobile effluent contaminated with heavy metals (Akpomie and Dawodu, 2015). Acid modifications have been reported to increase the adsorption capacity of montmorillonite for heavy metals (Bhattacharaya and Gupta, 2006). However, most studies have been focused on the removal of heavy metals from laboratory prepared solution. This study reports for the first time the use of an acid modified montmorillonite of Nigerian origin for the treatment of automobile effluent contaminated with heavy metals. The montmorillonite is present in abundant amount in Nigeria, easily accessible and can thus be used as a low cost sorbent (Akpomie and Dawodu, 2014). The influence of pH, adsorbent dose, particle size and contact time on the sorption process was investigated. Equilibrium isotherm and kinetic models were also analyzed.

2. Materials and methods

2.1. Preparation of adsorbents

The montmorillonite was collected from Ugwuoba in Oji River, a local government area of Enugu state in Nigeria, and then processed as described (Akpomie and Dawodu, 2014) to obtain the Unmodified Montmorillonite (UM). The acid treatment of the montmorillonite was performed by contacting 50 g of UM with 250 mL of H₂SO₄ acid at different concentrations ranging from 0.5 to 2.5 M in a glass beaker. The mixture was stirred for 30 min and left for 24 h at a room temperature of 28 °C, after which the aqueous phase was decanted. The clay residue was washed with excess distilled de-ionized water and then sundried, after which it was heated at different temperatures ranging from 50 to 300 °C using the muffle furnace at different heating times of 30 to 360 min. The samples were then pulverized and passed through mesh sieves of sizes 100 to 500 µm to obtain the Acid Modified Montmorillonite (AMM).

2.2. Physicochemical characterization

The automobile effluent was collected in a pretreated plastic bottle from the discharge outlet of Innoson automobile indus-

try located in Nnewi, Anambra state, Nigeria, and stored at 4 °C in a refrigerator. The sample was collected based on the method described (Pearson et al., 1987). The physicochemical analysis of the effluent was determined using standard methods (AOAC, 2005) by the use of analytical grade chemicals obtained from Sigma Aldrich. The heavy metal concentration of the effluent was determined by the use of the Atomic Absorption Spectrophotometer (AAS) (Buck scientific model 210VGP).

The chemical composition of the adsorbents was determined by the AAS after digestion of the samples with nitric acid and hydrofluoric acid. The ammonium acetate method (Rhoades, 1982) was used to determine the cation exchange capacity (CEC). The slurry pH was obtained as described (Akpomie and Dawodu, 2014), while the pH point of zero charge (pHpzc) was determined by the method explained (Onyango et al., 2004). X-ray diffraction (XRD) analysis was determined using a model MD 10 Randicon diffractometer operating at 25 kV and 20 mA. The scanning regions of the diffraction were 16–72 °C on the 2θ/X019F; angle. The Fourier-transform infrared spectrophotometer (FTIR; Shimadzu 8400s) was used to investigate the surface functional groups on the adsorbents, while scanning electron microscope (SEM; Hitach S4800) was utilized to access the morphology. The pore properties and Brunauer, Emmett and Teller (BET) surface area of the adsorbents were determined via nitrogen adsorption-desorption isotherms using a micrometrics ASAP 2010 model analyzer.

2.3. Batch adsorption studies

The adsorption experiment was performed using batch sorption technique. This was performed by adding 0.1 g of the adsorbent to 50 mL of the effluent solution in a 100 mL pretreated plastic bottle. The effect of effluent pH was studied by varying the pH of the effluent from 2.0 to 8.0 by the dropwise addition of 0.1 M HCl or 0.1 M NaOH when required, using adsorbent particle sizes of 100 µm, contact time of 180 min at a room temperature of 300 K. The influence of adsorbent dose and particle size were also studied under similar optimum experimental conditions at an effluent pH of 6.5, but by varying the adsorbent dose from 0.1 to 0.5 g and particle size from 100 to 500 µm, respectively. Also, the influence of contact time was performed under similar conditions at various contact times of 10–300 min in order to investigate the effect of a particular parameter, which was varied, while others were kept constant at the optimum conditions. At the end of the given contact time for a particular sorption, the mixed solution was filtered and the residual metal ion concentration in the filtrate was determined by the AAS. The amount of metal ions adsorbed onto the adsorbents was calculated from the mass balance equation:

$$q_e = v[C_0 - C_e]/m \quad (1)$$

where q_e (mg/g) is the adsorption uptake capacity of the adsorbent for metal ions at equilibrium, C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of metal ions in solution, respectively, m (g) is the mass of the adsorbent and v (L) is the volume of effluent used for sorption.

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