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Treatment of an automobile effluent from heavy metals contamination by an eco-friendly montmorillonite

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A B S T R A C T

Unmodified montmorillonite clay was utilized as a low cost adsorbent for the removal of heavy metals from a contaminated automobile effluent. Fourier transform infrared spectroscopy, X-ray diffraction and scanning electron microscopy were used to characterize the adsorbent. Batch sorption experiments were performed at an optimum effluent pH of 6.5, adsorbent dose of 0.1 g, particle size of 100 μm and equilibrium contact time of 180 min. Thermodynamic analysis was also conducted. Equilibrium data were analyzed by the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models. A heterogeneous surface of the adsorbent was indicated by the Freundlich model. The Langmuir maximum adsorption capacity of the montmorillonite for metals was found in the following order: Zn (5.7 mg/g) > Cu (1.58 mg/g) > Mn (0.59 mg/g) > Cd (0.33 mg/g) > Pb (0.10 mg/g) ≡ Ni (0.10 mg/g). This was directly related to the concentration of the metal ions in solution. The pseudo-first order, pseudo-second order, intraparticle diffusion and liquid film diffusion models were applied for kinetic analysis. The mechanism of sorption was found to be dominated by the film diffusion mechanism. The results of this study revealed the potential of the montmorillonite for treatment of heavy metal contaminated effluents.

Introduction

The pollution of the environment with toxic substances has been on the increase in recent years as a result of the rapid growth of industries. Most industries such as automobile, mining, electroplating, iron–steel and battery industries utilize substances containing heavy metals [1]. Subsequently, these heavy metals are discharged into the environment from the effluents obtained from the industries. Although small amounts of some heavy metals are necessary for the normal development of

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biological cycles, most of them are toxic at high concentrations [2]. The release of heavy metals into the environment poses a serious health threat to aquatic lives, plants and humans due to their persistence, non-biodegradability and bio-accumulation in the food chain. Therefore, the removal of these metals from industrial effluents is necessary to maintain environmental quality [3]. Several techniques have been utilized for heavy metal removal, which include solvent extraction, filtration, ion-exchange, coagulation, sedimentation, oxidation and activated carbon adsorption [4]. However, these techniques have the disadvantages of high cost, low removal efficiency and the problem of secondary contamination. As a result, many researchers have utilized low cost, eco-friendly and highly efficient adsorbents for removal of heavy metals from effluents. These adsorbents include biomass materials, clays, charcoal, sludge ash, microorganisms and lateritic materials, just to mention a few [5].

Montmorillonite has been found to be suitable for heavy metals adsorption through cation exchange mechanism in the interlayer and the formation of inner sphere complexes through Si–O and Al–O groups at the clay particle edges [6–8]. However, most studies in literature have not been focused on the use of montmorillonite for adsorption of heavy metals from automobile effluent in particular. This study is therefore focused on the removal of heavy metals from a contaminated automobile effluent unto a montmorillonite. The automobile industry (Innoson) is located in Nnewi, Anambra State, Nigeria and was chosen due to the reasonably high metal concentration. Similarly, the montmorillonite was utilized because it is found in an abundant amount in Nigeria and can be utilized as a low cost and eco-friendly adsorbent.

The montmorillonite was used without any modification (chemical or physical) in order to keep the process cost low. The effect of various experimental conditions such as pH, adsorbent dose, contact time and particle size was investigated. Equilibrium, kinetic and thermodynamic analyses were also determined to understand the adsorption mechanism.

Experimental

Processing of the montmorillonite

The montmorillonite was collected from Oji river local government area of Enugu State, Nigeria. It was immersed in excess distilled water in a pretreated plastic container and stirred uniformly for proper mixing. Thereafter, the mixture was passed through a mesh sieve of size 500 μm to get rid of plant materials and other suspended particles. The obtained filtrate was kept for 24 h to settle after which excess water was decanted. The residue was sundried and then dried in an oven at 378 K for 4 h. The dried clay was then pulverized and passed through different mesh sieves of sizes 100–500 μm to obtain the unmodified montmorillonite clay (UMC).

Physicochemical analysis

The automobile effluent was collected from the discharge outlet of Innoson automobile industry located in Nnewi, Anambra State, Nigeria. The effluent was stored at 277 K in a refrigerator. Sample collection was based on the technique described [9]. The physicochemical analysis of the effluent was determined using standard methods [10]. Heavy metal concentration in the effluent was analyzed by the use of the Atomic absorption spectrophotometer (AAS) (Buck scientific model 210VGP). All the reagents used were of analytical grade, obtained from Sigma Aldrich (Steinheim, Germany) and used without further purification. Chemical composition of UMC was determined by the AAS after digestion of the sample with nitric acid. The cation exchange capacity (CEC) of the adsorbent was obtained by the ammonium acetate method [11], while the pH point of zero charge was determined by the method described [12]. The slurry pH was obtained as described previously [5]. X-ray diffractometer (Randicon MD 10 model) was utilized for the X-ray diffraction (XRD) analysis. The Fourier transform infrared (FTIR) of UMC was taken by the help of the Fourier transform infrared spectrophotometer (Shimadzu FTIR 8400s). BET surface area and pore properties of UMC were obtained by nitrogen adsorption–desorption isotherms by the use of the micromeritics ASAP 2010 model analyzer. Scanning electron microscopy (SEM) (Hitachi S4800 model) was used to determine the morphology of the adsorbent.

Effluent treatment

The automobile effluent was treated by the batch adsorption technique by contacting 0.1 g of the adsorbent with 50 ml of effluent solution in 100 ml plastic bottles under optimum conditions as described: The effect of pH was studied by adjusting the pH of the effluent from 2 to 8 by the drop wise addition of 0.1 M NaOH or 0.1 M HCl when required before the addition of the adsorbent, this was performed using an adsorbent particle size of 100 μm, contact time 180 min and temperature of 300 K. The influence of adsorbent dose was performed using different doses of 0.1–0.5 g, effluent pH 6.5, adsorbent particle size 100 μm and contact time of 180 min at temperatures of 300, 313 and 323 K. Temperature regulation was performed by the use of a thermostat water bath. By varying the particle size of the adsorbent from 100 to 500 μm the influence of adsorbent particle size on adsorption was investigated, this was performed at pH 6.5, adsorbent dose 0.1 g, contact time 180 min and temperature of 300 K. Finally, the effect of contact time on adsorption was performed at an effluent pH of 6.5, particle size 100 μm at temperatures of 300, 313 and 323 K by varying the contact time of experiment from 10 to 300 min.

At the end of the given contact time for each experiment, the solution was filtered and the concentration of heavy metals remaining in the filtrate was determined by the AAS. The adsorption capacity of UMC for heavy metals was determined by the mass balance equation given as:

$$\mathrm{qe} = v(C_\mathrm{I} - \mathrm{Ce})/m \quad (1)$$

where qe (mg/g) is the amount of heavy metal adsorbed per unit weight of UMC, C_I (mg/L) is the initial concentration of heavy metals in the effluent, Ce (mg/L) is the equilibrium concentration of heavy metals remaining in the effluent, v (L) is the volume of effluent solution used and m (g) is the mass of UMC utilized for adsorption.

Isotherm modeling

The equilibrium isotherm model analysis was studied by the application of the Langmuir, Freundlich, Temkin and