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Research paper

Kinetic, equilibrium and thermodynamic studies for sorption of 2,4-dichlorophenol onto surfactant modified fuller's earth

Jasmin Shah*, M. Rasul Jan, M. Zeeshan, M. Imran

Institute of Chemical Sciences, University of Peshawar, Khyber Pakhtunkhwa, Pakistan

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ABSTRACT

The applicability of surfactant modified fuller's earth (SMFE) for removing 2,4-dichlorophenol (2,4-DCP) from water has been investigated through batch sorption process. Fuller's earth was treated with sodium dodecyl sulphate (SDS) for conversion of fuller's earth into surfactant modified fuller's earth. The influence of pH, agitation time, sorbent dose, temperature and initial concentration of 2,4-DCP were investigated. A strong dependence of the sorption capacity on pH was observed, the capacity increased as the pH value decreased. The sodium dodecyl sulphate increased the hydrophobicity of the sorbent and provided particular affinity for 2,4-DCP molecules. The SMFE showed high efficiency towards 2,4-DCP and > 97% removal was achieved from an initial concentration of 20 mg/L at 100 °C using pH 3. The kinetics of the sorption process was described by a pseudo-second-order kinetic model. The mechanism of sorption kinetics was investigated using intraparticle diffusion model. The sorption isotherm was consistent with the Langmuir sorption isotherm and maximum monolayer capacity of the SMFE was found to be 126.58 mg/g at room temperature. The mean adsorption energy (E) value 18.25 kJ/mol indicated chemical sorption and endothermic sorption process.

1. Introduction

The rapid development of chemical industries has caused public concern due to the contamination of water by organic compounds which are generated during the manufacturing and processing stages of organic chemicals. Phenolic compounds are common contaminants in wastewater widely used in various processes such as petrochemicals, oil refineries, pharmaceutical, plastics, leather, pesticides, paint and other chemical manufacturing processes (Cao et al., 2014; Anirudhan and Ramachandran, 2014). Phenolic compounds are considered as priority pollutants in wastewater as they are highly toxic to organisms even at low concentrations. Degradation of phenolic compounds leads to the appearance of phenols and its derivatives in the aqueous environment (Oh et al., 2003).

Different methods are available for the treatment of organic pollutants such as chemical oxidation (Karthikeyan et al., 2012), bio-remediation (Kshirsagar, 2013), photocatalytic degradation (Gaya and Abdullah, 2008), adsorption (Shah et al., 2014), solvent extraction (Aydin et al., 2007) and membrane processes (Ojajuni et al., 2015). Among these treatment methods, adsorption has proven to be an efficient method in which activated carbon, macroporous resin or clay used for removal of phenolic compounds (Crini, 2006). For adsorption process, the cost and availability of adsorbent is important. There have been attempts to use locally available and low cost adsorbents for removal of organic pollutants from wastewater (El-Naas et al., 2010).

Fuller's earth is a type of sedimentary clay that contains high proportion of smectite group clay minerals. The most commonly occurring smectite clay mineral is montmorillonite. Smectite clay mineral consists of three-layers sheet structures composed of two tetrahedral sheets with one bound to each side of an octahedral sheet. Smectite are one of the largest and most important classes of the phyllosilicate clay mineral group. The most abundant smectite are ca-montmorillonite and Na-montmorillonite (Murray, 2007). The structural difference between the sodium and calcium montmorillonite is at the water layer. Calcium montmorillonite possesses two layers in the interlayer position while sodium montmorillonite have only one water layer. Sodium montmorillonite has high swelling capacity and viscosity as compared to calcium montmorillonite. The clay minerals usually possess a charge which exists in two forms: structural charge and surface charge. The structural charge is permanent and exists due to ion substitutions while the surface charge depends on the pH value. The structural charge originates in the tetrahedral and octahedral sheets of the smectite (a 2:1 clay mineral) and on the basal surface of tetrahedral sheets. In addition, the sheets edges also contribute to the surface charge.

In the laboratory fuller's earth is used for the detection of certain

* Corresponding author.
E-mail address: jasminshah@upesh.edu.pk (J. Shah).

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coloring matters in whisky, butter, and artificial vinegar (Kulkarni and Jatkar, 2013). In pharmacy it makes an excellent substitute for talcum powder on account of its absorptive power. Fuller's earth can also be used as an adsorbent for the removal of mercury from aqueous solution (Smith and Galam, 1995). Various organoclays have been synthesized with different surfactants (Wang et al., 2004; Sonawane et al., 2008; Chen et al., 2014). Due to unique sorption capabilities of organoclays, it has been of considerable interest in applying as sorbent for removal of organic compounds in wastewater.

The aim of the present study was to investigate the sorption capacity of surfactant modified fuller's earth for the removal of 2,4-DCP from aqueous solution. An anionic surfactant (sodium dodecyl sulphate) was used to prepare surfactant modified fuller's earth and the sorption properties of surfactant modified fuller's earth for 2,4-DCP in model wastewater were investigated. Sorption efficiency, sorption kinetics, sorption isotherms and sorption thermodynamics were studied using batch experiments. The results of the study are expected to be useful for removal of 2,4-DCP from aqueous samples.

2. Materials and methods

2.1. Materials

All the chemicals used were of analytical reagent grade. 2,4-dihlorophenol was supplied by Sigma-Aldrich. Sodium dodecyl sulphate (SDS), sodium hydroxide and hydrochloric acid were purchased from Merck (Darmstadt, Germany). Standard stock solution of 2,4-dihlorophenol was prepared in methanol and stored in dark. Working standards were prepared freshly from stock solution with distilled water. Fuller's earth was purchased from the British Drug Houses Limited BDH Laboratory Chemical group, Pool England (the constituent of British fuller's earth is montmorillonite a clay mineral of smectite with a main constituent of calcium montmorillonite). Major element analysis of fuller's earth was performed with S4-Pioneer (Bruker-AXS) WD-X-ray fluorescence and the composition found was as: Al_2O_3 15.3%, SiO_2 46.1%, Fe_2O_3 4.2%, CaO 5.0%, MgO 10.6%, K_2O 2.5%, Na_2O 3.8% along with some other elements in small percentage.

2.2. Instruments

UV–Vis Spectrophotometer (Optima SP-3000 plus, Tokyo, Japan), with matched 1 cm quartz cells was used for all spectrophotometric measurements. Thermostatically controlled water bath (Yu Jia, China), orbital Shaker (Model OS-340C, digisystem laboratory instrument Inc. Made in Taiwan R.C.O) and analog pH meter (Model-7020 Kent Industrial Measurement Limited Electronic Instrument Ltd., Chertsey Survey England) was used during the studies.

2.3. Sorbent preparation

Known amount of fuller's earth was placed in a conical flask and known concentration of 100 mL SDS aqueous solution was added, stirred for 60 min at 200 rpm and allowed to stand for 24 h. Fuller's earth was then separated through cellulose acetate filter, washed with distilled water and dried at 80 °C in an oven. The dry surfactant modified fuller's earth was ground, passed through standard mesh (150 μm), stored and used for further sorption process.

The SMFE was prepared using different ratio of fuller's earth and SDS to optimize the mass ratio of SDS and fuller's earth for sorption of 2,4-dichlorophenol from aqueous sample. The optimum ratio of fuller's earth with SDS was found 1:2 and the SMFE as sorbent was prepared with 1:2 ratio for further sorption study.

2.4. Characterization of sorbent

The surface morphology of the surfactant modified fuller's earth before and after sorption of 2,4-DCP was determined by Scanning Electron Microscope Model JEOL - JSM 5910, Japan, under high-vacuum microprobe. The successful modification of fuller's earth with SDS was confirmed from the infrared spectrum taken from FTIR Prestige–21 (Shimadzu, Japan) in the wavelength range between 4000 and 400 cm^{-1}. BET surface area of the modified and non-modified fuller's earth was determined with N_2 adsorption/desorption at 77.4 K using Surface Area Analyzer NOVA2200e Quantachrome, USA. Point of zero charge was determined by the method already mentioned in the literature (Shah et al., 2014).

X-ray diffraction (XRD) patterns were taken using a JDX-3532 JEOL (Japan) diffractometer with monochromatic Cu-Kα radiation (λ = 1.5418 Å) at 40 kV and 30 mA in the 2θ range of 0–80° with 1.03°/min.

2.5. Sorption of experiments

Batch sorption experiments were conducted in a series of conical flasks (100 mL). An accurately weighted amount of SMFE (100 mg) was added to each flask, followed by the addition of 2,4-DCP (10 mg/L) solution, pH was adjusted to pH 3.0 with Briton Robinson buffer (Britton, 1943) and final volume was maintained up to 25 mL. The contents in flasks were agitated at 150 rpm for 60 min. After agitation, the solutions were filtered through cellulose acetate filters and analyzed for residual 2,4-DCP concentration using a UV–visible spectrophotometer at a wavelength of 270 nm. The % sorption and sorption capacity (q_e) were calculated from the difference between initial (C_i) and equilibrium (C_e) concentration of 2,4-DCP using the following equations:

$$\text{Sorption } (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

$$\text{Sorption capacity } q_e = \left[\frac{C_i - C_f}{m}\right] V \quad (2)$$

where V is the volume of the solution (mL) and m is the mass of the sorbent (g). C_e and C_o are the equilibrium and initial concentrations (mg/L) of 2,4-DCP and q_e is the sorption capacity (mg/g).

For the effect of pH study, 100 mg of SMFE was added in a series of flasks containing 10 mg/L concentration of 2,4-DCP and the pH was adjusted with Briton Robinson buffer solution from 2.0 to 8.0. The flasks were agitated for 60 min at 150 rpm. After agitation, the solutions were filtered and analyzed for unadsorbed 2,4-DCP concentration. The same procedure was applied for the study of sorbent dose (50–500 mg), contact time (20–120 min), temperature (40–100 °C) and initial 2,4-DCP concentration (2–40 mg/L).

For the mechanism of sorption process of 2,4-DCP onto SMFE different kinetic models, thermodynamic and isotherm models were applied.

3. Results and discussion

3.1. Characterization of sorbent

Fig. 1(a) shows the SEM micrograph of SMFE before sorption. Material is relatively compact with layers distributed homogeneously on the surface, while after sorption of 2,4-DCP there are some morphological change (Fig. 1(b)) indicated. The surface became dense with solid no invisible pores.

The FTIR spectra were used for evaluation of fullers' earth modification with SDS (Fig. 2). Compared to the spectrum of fuller's earth, the spectrum of SMFE exhibited additional peaks at 2850 cm^{-1} and 2940 cm^{-1} that could be due to the symmetric and asymmetric stretching vibration mode of methyl and methylene groups. The broad band at about 3400 cm^{-1} due to H—O—H stretching in fuller's earth was observed to reduce, indicating that the content of water adsorbed