Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: Equilibrium, kinetic and thermodynamic study

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ABSTRACT

A natural bentonite modified with a cationic surfactant, cetyl trimethylammonium bromide (CTAB), was used as an adsorbent for removal of phenol from aqueous solutions. The natural and modified bentonites (organobentonite) were characterized with some instrumental techniques (FTIR, XRD and SEM). Adsorption studies were performed in a batch system, and the effects of various experimental parameters such as solution pH, contact time, initial phenol concentration, organobentonite concentration, and temperature, etc. were evaluated upon the phenol adsorption onto organobentonite. Maximum phenol removal was observed at pH 9.0. Equilibrium was attained after contact of 1 h only. The adsorption isotherms were described by Langmuir and Freundlich isotherm models, and both model fitted well. The monolayer adsorption capacity of organobentonite was found to be 333 mg g^{-1}. Desorption of phenol from the loaded adsorbent was achieved by using 20% acetone solution. The kinetic studies indicated that the adsorption process was best described by the pseudo-second-order kinetics ($R^2 > 0.99$). Thermodynamic parameters including the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were also calculated. These parameters indicated that adsorption of phenol onto organobentonite was feasible, spontaneous and exothermic in the temperature range of 0–40 °C.

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1. Introduction

As a result of rapid development of chemical and petrochemical industries, the surface and ground waters are polluted by various organic and inorganic chemicals such as phenolic compounds, dyes and heavy metals. Phenol and its derivatives are considered as noxious pollutants, because they are toxic and harmful to living organisms even at low concentrations [1]. Phenols are being discharged into the waters from various industrial processes such as oil refineries, petrochemical plants, ceramic plants, coal conversion processes and phenolic resin industries [2]. The utilization of phenol-contaminated waters causes protein degeneration, tissue erosion, paralysis of the central nervous system and also damages the kidney, liver and pancreas in human bodies [3]. According to the recommendation of World Health Organization (WHO), the permissible concentration of phenolic contents in potable waters is 1 μg L^{-1} [4] and the regulations by the Environmental Protection Agency (EPA), call for lowering phenol content in wastewaters less than 1 mg L^{-1} [5]. Therefore, removal of phenols from waters and

wastewaters is an important issue in order to protect public health and environment.

The traditional methods such as adsorption, chemical oxidation, precipitation, distillation, solvent extraction, ion exchange, membrane processes, and reverse osmosis, etc. have been widely used for removal of phenols from aqueous solutions [6]. Among them, removal of phenols by adsorption is the most powerful separation and purification method because this technique has significant advantages including high efficiency, easy handling, high selectivity, lower operating cost, easy regeneration of adsorbent, and minimized the production of chemical or biological sludge [7]. Adsorption process is strongly affected by the chemistry and surface morphology of the adsorbent. Therefore, new adsorbents, which are economical, easily available, having strong affinity and high loading capacity have been required. A number of adsorbents such as activated carbon, [8], red mud [9] and rubber seed coat [10], etc. have been used for phenol removal. Adsorption of phenol onto activated carbons is a well-known process because activated carbon has a large surface area and high adsorption capacity. However, its high cost and the difficulties in recovering of activated carbon particles from treated water, limit its use as an adsorbent. In recent years, clay minerals have been widely used as adsorbents for the removal of toxic metals and organic pollutants from aqueous solutions due

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to their low cost, large specific surface area, chemical and mechanical stability, layered structure and high cation exchange capacity [2,11–19].

Bentonite is a member of 2:1 clay minerals (meaning that it has two tetrahedral sheets sandwiching a central octahedral sheet) which consists essentially of clay minerals of montmorillonite group. Bentonite is characterized by an Al octahedral sheet between two Si tetrahedral sheets. It has a negative surface charge created by the isomorphous substitution of Al^{3+} for Si^{4+} in tetrahedral layer and Mg^{2+} for Al^{3+} in octahedral layer. The bentonite surface is hydrophilic in nature because inorganic cations, such as Na^+ and Ca^{2+}, are strongly hydrated in presence of water. As a result, the adsorption efficiency of natural bentonite for organic molecules is very low [20,21]. The adsorption properties of bentonite can be improved by the modification of clay mineral surface with a cationic surfactant. The cationic surfactants, known as quaternary amine salts, are in the form of $(CH_3)_3NR^+$, where R is an alkyl hydrocarbon chain. Replacement of inorganic exchangeable cations with cationic surfactants, converts the hydrophilic silicate surface of clay minerals to a hydrophobic surface and the obtained complex is referred as organoclay. It is generally accepted that adsorption of hydrophilic long-chain quaternary ammonium cations onto clays occurs according to the ion-exchange mechanism [22]. As a result organoclay complex is an excellent adsorbent for the removal of phenolic compounds, other organic contaminants and also heavy metals from aqueous solutions.

The objective of this study was to investigate the adsorption potential of bentonite for removal of phenol from aqueous solutions. The natural bentonite was obtained from Tirebolu-Giresun region of Turkey, and modified with a cationic surfactant, cetyl trimethylammonium bromide (CTAB), in order to increase the adsorption capacity. The structures of natural and organobentonite were characterized by using a variety of instrumental techniques including Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). Also the surface area, cation exchange capacity and pH of the bentonite samples were estimated. The effects of experimental parameters such as initial pH of the solution, contact time, initial phenol concentration, organobentonite concentration, etc. were studied. The adsorption mechanisms of phenol onto organobentonite were evaluated in terms of thermodynamics and kinetics. The adsorption isotherms were described by using Langmuir and Freundlich isotherm models.

2. Materials and methods

2.1. Preparation of organobentonite

The bentonite, which is a type of clay mineral, was used as an adsorbent for removal of phenol from aqueous solutions in the present study. Ca–bentonite samples were sieved to 0.15 mm of particle size before use. A known amount of Ca–bentonite was added to 1 M of Na_2CO_3 solution and stirred for 3 h at 800 rpm. In order to dissolve the $CaCO_3$, the concentrated HCl solution was added into the suspension drop-by-drop. The solid particles were separated from the mixture by filtration using Whatmann No. 42 filter paper and washed five times with deionized water until it was chloride free. This was checked by the addition of $AgNO_3$ after washing with deionized water to make sure that no precipitate is formed, which is the evidence of chloride existence. And then the obtained solid was dried at 110 °C for one day and designated as Na–bentonite. The Na–bentonite was modified with a cationic surfactant, cetyl trimethylammonium bromide (CTAB), $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$. The cationic surfactant can be adsorbed onto negatively charged clay surfaces and is not influenced by the pH of the solution because it is a quaternary ammonium salt

[23]. The CTAB consists of a 16-carbon chain tail group attached to a trimethyl quaternary amine head group with a permanent +1 charge. For modification process: 200 mL of 4% of CTAB solution was contacted with 20 g Na–bentonite by stirring on a mechanical shaker for 24 h. Then the bentonite was separated from the solution by filtration and washed twice with deionized water and then dried at 70 °C. This bentonite is designated as organobentonite $(CH_3(CH_2)_{15}N^+(CH_3)_3–Al_2O_34SiO_2H_2O)$ [24].

2.2. Characterization

The physical and chemical characteristics of the adsorbents are important in order to estimate the adsorbate binding mechanism of the adsorbent surface. Hence the structures of natural and organobentonite were characterized by using several techniques including FTIR Spectroscopy, XRD and SEM. Also the surface area, cation exchange capacity (CEC) and pH of the bentonite samples were estimated by using several analytical methods.

The IR spectra of the natural bentonite, organobentonite and phenol loaded organobentonite were obtained to determine the surface functional groups by using PerkinElmer 1600 FTIR spectrophotometer in the range of 4000–400 cm^{-1}.

The mineralogical compositions of the natural and organobentonite samples were determined from the XRD patterns of the samples taken on a Rigaku D–Max III automated diffractometer using Ni filtered Cu Kα radiation.

SEM analyses were applied on the natural bentonite, organobentonite and also phenol loaded organobentonite by JSM 6400 Scanning Microscope apparatus in order to disclose the surface texture and morphology of the adsorbent.

The surface areas of the natural and organobentonite were calculated according to Sears' method [25] as follows: 0.5 g of clay sample was mixed with 50 mL of 0.1 M HCl solution and 10.0 g of NaCl salt. The mixture had a pH value of 3.0, and titrated with standard 0.1 M NaOH solution in a thermostatic bath at 298 ± 0.5 K from pH 4.0 to 9.0. The surface area was calculated from the following equation:

$$S(m^2/g) = 32V - 25 \tag{1}$$

where S is the surface area, and V is the volume (mL) of NaOH solution required to raise the pH from 4.0 to 9.0.

The CEC of the natural bentonite was calculated by using bisethylenediamine copper (II) ($[Cu(en)_2]^{2+}$) complex method [26,27] 50 mL of 1 M copper(II) chloride ($CuCl_2$) solution was mixed with 102 mL of 1 M ethylenediamine ($C_2H_8N_2$) solution. The slight excess of the amine ensures complete formation of the complex. The solution was diluted with deionized water to 1 L to give a 0.05 M solution of the complex. 0.5 g of a dry clay sample was mixed with 5 mL of the complex solution in a 100 mL flask, diluted with deionized water to 25 mL and the mixture was shaken for 30 min in a thermostatic water bath and then centrifuged. The concentration of the complex remaining in the supernatant was determined by iodometric method. For this, 5 mL of the supernatant was mixed with 5 mL of 0.1 M HCl solution to destroy the $[Cu(en)_2]^{2+}$ complex and about 1 g of KI salt was added to this solution. The mixture was titrated with 0.02 M $Na_2S_2O_3$ solution with starch as indicator. The CEC was calculated from the following formula:

$$CEC(meg/100\,g) = \frac{MSV(x - y)}{1000m} \tag{2}$$

where M is the molar mass of Cu-complex, S is the concentration of thio solution, V is the volume (mL) of complex taken for iodometric titration, m is the mass of adsorbent (g) taken, x is the volume (mL) of $Na_2S_2O_3$ solution required for blank titration (without adding the adsorbent) and y is the volume (mL) of $Na_2S_2O_3$ solution required for the titration (with the clay adsorbent).