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Enhanced adsorption of 2,4-dichlorophenol from aqueous solution using modified low cost Algerian geomaterial

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ABSTRACT

Natural geological material (GM) (CEC = 21 meq/100 g, $S_{BET} = 3.39$ m²/g), available in large amount in Timimoun (South Algeria), was modified with an ammonium quaternary dodecyl- and cetyl-trimethyl ammonium bromide (DTAB and CTAB, respectively). The X-ray diffraction (XRD) revealed that the natural geomaterial represents mainly muscovite mica; and organic molecules salts were not intercalated in the interlayers; the modification process was thus limited to the surface. Adsorption of 2,4-dichlorophenol (2,4-DCP) from aqueous solution via batch sorption experiments onto GM, GM-DTAB, and GM-CTAB was investigated. The results show increased 2,4-DCP adsorption on the GM composites compared to natural GM. The maximum uptake occurred at pH = 6, a contact time of 60 min, and an adsorbent dose of 4 g/L. The surface modification of muscovite by quaternary ammonium bromide and sequential adsorption of 2,4-DCP were also evaluated by XRD and FTIR. The kinetic adsorption data were in good agreement with a pseudo-second-order model. Freundlich adsorption model was best to describe adsorption equilibrium data for 2,4-DCP onto GM-DTAB and in the case of GM-CTAB, experimental data agree well with the Langmuir isotherm model. The monolayer adsorption capacity (q_m) was 110.75 mg/g for GM-DTAB, 239.8 mg/g for GM-CTAB, and 354.6 mg/g for activated carbon.

1. Introduction

Phenols, especially the chlorinated ones, represent pollutants of high priority concerns due to their toxicity and possible accumulation in the environment. They are present in the wastewater generated from paint, solvent, petroleum (petrochemical), coal conversion, pharmaceutical, wood preserving chemicals, plastic, rubber-proofing, pesticide, iron-steel, phenol-production, paper and pulp industries [1,2]. Phenols are toxic to human body and most aquatic organisms, and may cause denaturing of protein, tissue erosion, and paralysis of the central nervous system, and damage kidney, liver and pancreas [3]. 2,4-Dichlorophenol (2,4-DCP), one of the representative chlorophenols, is used in the production of herbicides (2,4-dichlorophenoxyacetate, etc.) and preservatives (pentachlorophenol, etc.), and considered to constitute the 11th of the 126 chemicals which have been designated as primary pollutants by the Environmental Protection Agency (EPA) of the United States [4–6]. Although attempts were made to regulate its use, large quantities of 2,4-DCP containing wastewater continue to be discharged into water bodies. The availability of clean water remains to be a challenge as the world population increases. According to a recommendation from the World Health Organization, the maximum permissible concentration of total phenolic content in tap water is 1 µg/L, and the minimum wastewater quality objectives impose 20 µg/L for 2,4-DCP [7,8]. Since chlorinated phenols are not completely removed by biodegradation in wastewater treatment plants, other methods such as chemical oxidation, coagulation, solvent extraction, liquid membrane permeation and adsorption are commonly employed for their removal [9,10]. Adsorption is considered as an effective way to remove several pollutants from wastewater, since this method is not destructive and easy to apply, especially if the applied adsorbents represent low-cost natural materials. Activated carbon is undoubtedly considered as effective adsorbent; however, widespread use of commercial activated carbon is sometimes restricted due to its higher costs. In recent years, scientific efforts have been directed toward application of economically expedient and easily available natural materials as efficient sorbents for phenol and chlorinated phenol removal from

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aqueous media. Numerous geomaterials (GMs), such as activated carbon [11,12], layered double hydroxides [13], metal oxides [14], silica [15], and natural biomasses [16] have been extensively investigated for environmental remediation. Larous et al. [17] reported about Sawdust, a very low cost adsorbent, to be a potent sorbent for the removal of phenol from industrial waste waters. The equilibrium adsorption level was determined as a function of the pH of the solution, temperature, contact time, adsorbent dose and the initial phenol concentration. The adsorption maximum for phenol using sawdust was 10.29 mg/L. Yapar and Yilmar [18] employed some clays and natural zeolite materials found in Turkey for the phenol removal. They found that calcined hydrotalcite was the best sorption material yielding 52% phenol adsorption from a solution of 1000 mg/L phenol using an adsorbent/phenol ratio of 1:100 while the others adsorbed only 8% of phenol. Roostari and Tezel [19] applied silica gel, activated alumina, activated carbon (Fitrasorb 400 and Hisir 1000) as adsorbents for the removal of phenol from aqueous solution. They found that Hisir 1000 was the best among the tested materials. Similarly, Das and Patnaik [20] utilized blast furnace flue dust (BFD) and slag to investigate phenol adsorption through batch experiment. In recent years, many efforts have been devoted to the investigation and development of other more effective 2,4-DCP GMs. Kusmierek et al. [21] have used carbonaceous materials $C–C_2Cl_6$ and $C–C_6Cl_6$, obtained by the combustion synthesis of mixtures containing hexachloroethane or hexachlorobenzene with sodium azide, for removal of 2,4-DCP and 2,4-dichlorophenoxyacetic acid from aqueous solutions. The carbonaceous materials showed faster adsorption kinetics than carbon blacks used as reference adsorbents and the adsorption isotherms were well described by both Freundlich and Langmuir models.

In recent years, several authors reported [22–24] that surfactant modified clays presented higher adsorption capacity than the original adsorbents. Although the modification of clay with surfactants increases their cost significantly, the resultant increase in adsorption capacity may still make surfactant modified clays cost effective. The adsorbed amounts of 2,4-DCP on bentonite exchanged by organic cations were found to be several times higher than those obtained using bentonite clay without surface modification [25,26]. Adsorption of phenol and 2-, 3-, and 4-chlorophenol from water by tetramethylammonium-smectite and tetramethyl-phosphonium-smectites [26], and adsorption of 2,4,5-trichlorophenol by organo-montmorillonites from aqueous solutions were also reported [27,28].

So far, literature surveying revealed that only few studies have been devoted to modifications of surface properties of muscovite/mica, using surfactants for the abatement of 2,4-DCP from aqueous solution. The Timimoun area in the south of Algeria represents rich deposits of muscovite/mica. Muscovite is found in igneous, metamorphic, and sedimentary rocks and can occur as isolated grains in schist and gneiss, or it can be abundant enough so that the rocks are called mica schist or micaceous gneiss. Muscovite is a major type of mica with the unit cell formula $2[Si_3AlO_{10}Al_2(OH)_2K]$, finding application as an insulating material in electrical appliances (high dielectric properties). Muscovite consists of a layered aluminosilicate mineral containing one octahedral aluminum ions layer sandwiched by two tetrahedral silicon layers. The micas are also called 2:1 or three-layer minerals [29,30]. In the silicon tetrahedral sheet, silicon is substituted by aluminum leading to a net negative surface charge compensated by interlayer K^+ cations [29]. The presence of strong electropositive K^+ cations is the reason for hydrophilicity of natural muscovite which represents an ineffective adsorbent for hydrophobic compounds. Organic modification of muscovite/mica changes the polarity of the surface of the mica sheets from polar into nonpolar and, therefore, reverses the reactivity of mica-sheets from hydrophilic into hydrophobic. Tailored muscovite shows thus high capability for hazardous waste removal.

This study has ambition to valorize GM without mining interest for environmental purposes. The present work was undertaken to investigate the feasibility of using chemically modified Algerian GM (organo-muscovite), to remove 2,4-DCP from aqueous solution by adsorption. Optimization of the adsorption conditions was performed by investigating the influence of adsorbent dose, contact time, pH, and initial concentration of 2,4-DCP. The obtained equilibrium data were evaluated using various adsorption isotherm models *i.e.* Langmuir, Freundlich, and Temkin. Kinetic studies were also applied to evaluate adsorption mechanism.

2. Materials and methods

2.1. Materials

The GM (muscovite) used in this study was obtained from a deposit located at Timimoun-South Algeria. The collected GM was soaked in excess distilled deionized water in a pre-treated plastic container. The mixture was stirred until the clay was completely dissolved and then filtered in order to get rid of suspended particles and plant materials. The collected filtrate was allowed to settle for 24 h. After the muscovite had settled at the bottom of the container, excess water was decanted from the top of the mixture. The muscovite obtained was sun dried for several days, and then oven dried for 2 h at 105 °C. After the drying process, muscovite was ground and sieved to obtain aggregates <0.2 mm. In order to respect the natural characteristics and to evaluate the retention behavior in wastewater, muscovite was not treated. The cationic surfactants selected for the preparation of organo-GM were dodecyltrimethylammonium bromide DTAB ($C_{15}H_{34}NBr$, with a critical micelle concentration (CMC) of 14 mM and FW: 308.34 g/mol), and cetyltrimethylammonium bromide CTAB ($C_{19}H_{42}NBr$, with CMC: 1 mM and FW: 364.45 g/mol), purchased from Acros-Organics with a purity of 99%. 2,4-DCP ($C_6H_3Cl_2OH$) was purchased from Sigma Aldrich Company as analytical grade reagent with 95% purity, and was used as received.

The commercially available activated carbon (AC) used in this study was obtained from Labbox company (CHAR-PWA-500), and was characterized by Mimanne et al. [31]. This AC was used as received, consisting essentially of amorphous carbonaceous material with specific surface area 1300–1400 m^2/g.

2.2. Preparation of organo-GM

The synthesis of organo-GM was performed as following: 1 g of aluminosilicate was initially dispersed in 100 mL of deionized water with a magnetic stirrer for about 24 h. The dissolved surfactant was slowly added to the clay suspension at room temperature that satisfied 300% CEC of GM, where the ratio of cationic surfactant solution to the GM was 24% for CTAB and 20% for DTAB (w/w). These materials, abbreviated as GM-DTAB and GM-CTAB, were stirred for 24 h at room temperature. All organoclay products were washed free of bromide anions as determined by the $AgNO_3$ method, dried at 60 °C, and ground in an agate mortar.

2.3. Adsorption experiments

The effect of amount of adsorbent, pH, stirring time and adsorption isotherms were investigated by a batch method. The results of control experiments showed that the non-adsorption loss (such as evaporation, degradation, and adsorption on the bottle walls) of 2,4-DCP during the adsorption progress was about 0.5%, so that the non-adsorption loss can be ignored under the chosen experimental conditions.

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