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Organo-modified sericite in the remediation of phenol-contaminated waters

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ABSTRACT

Hexadecyltrimetyl ammonium bromide and alkyldimethylbenzyl ammonium chloride-modified sericite samples were obtained by wet cation exchange process. The solid materials were then characterized by the FT-IR and XRD data whereas the surface morphology was obtained by the scanning electron microscopic images. Further, the suitability of these solids was assessed for the decontamination of phenol-contaminated waters under the batch reactor operations. Batch reactor data showed that an increase in sorbate concentration (from 1.0 to 20.0 mg/L) favoured the uptake of phenol from aqueous solution whereas an increase in pH (from 2.0 to 10.0) caused for significant decrease in percent uptake of phenol. The equilibrium state concentration dependence data were well modelled with the Freundlich adsorption isotherm.

Keywords: Organo-sericite; Phenol; Removal; pH; Freundlich isotherm; Interlayer-spacing

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1. Introduction

Phenol and its derivatives are common pollutants of petrochemical and coal conversion industries. These are considered as priority pollutants of soil and ground waters or leachates. Phenols are entering into the water bodies from various industrial processes viz., oil refineries, petrochemical plants, coal conversion processes and phenolic resin industries [1]. The toxic effects of phenols are reported as protein degeneration, tissue erosion, paralysis of the central nervous system and damage of kidney, liver and pancreas [2,3]. Because of its high toxicity, the US Environmental Protection Agency (EPA) regulations have lowered the phenol content in the water bodies to less than 1.0 mg/L [4].

Clay and minerals are known as potential sorbents for the attenuation of several cationic or even anionic (viz., As(III), As(V), Cr(VI) etc.) contaminants from soil or aquatic environment. However, its applicability towards "organics" of non-polar or polar compounds is reported to be very limited [5]. However, the organic modification of clay minerals showed significant increase in attenuation of several organics. The permanent negative charge along with the exchangeable cations with in the crystal structures of clay materials makes them suitable for surface modification by long-chain or short-chain organic cation surfactants [6–9]. The suitable organo-modification makes it more

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organophilic materials which possess varied applications in the treatment of wastewaters contaminated with several organics.

Sericite is a layered silicate mineral, abundantly available in Korea, generally recognized as white fine powder of muscovite form. The interlayer spacing of (002) plane is reported to be 10 Å [9]. Sericite possesses relatively less sorption capacity towards several heavy metal toxic ions, perhaps, due to its compact structure and relatively low cation exchange capacity (CEC). Moreover, the hydrophilic nature makes it difficult to employ in the treatment of wastewaters contaminated with organic pollutants. However, a suitable organo-modification of sericite could make it more hydrophobic and enhanced organophilic nature. Koh and Dixon obtained organo-sericite, modifying the sericite with quaternary ammonium cations, viz., benzyldimethyltetradecylammonium, hyamine 1622® and benzyltrimethylammonium, and it is employed in the attenuation of several non-ionic organic contaminants, viz., phenol, benzene and toluene from aqueous solutions [10]. The present investigation is dealing with the suitable organic modification of sericite using different organic cations, and further, the materials are employed in assessing their suitability in the removal of phenol from aqueous solutions.

2. Materials and methods

2.1. Reagents and materials

Sericite was obtained from Sam Kyong Company, Korea, and the chemical composition provided by the company is given elsewhere [9]. The cationic surfactants hexadecyltrimetyl ammonium bromide (HDTMA) and alkyldimethylbenzyl ammonium chloride (AMBA) were obtained from Junsei Chemicals, Korea. Phenol was procured from Sigma–Aldrich, USA. Potassium hydroxide and nitric acid were obtained from Merck, India. Whatman filter paper (100 mm, GF/C, England) was used for the filtration. All solutions were prepared in the distilled water as obtained by Milli Q-Plus Instrument (Millipore SA 67120, Molshiem, France).

2.2. Preparation of organo-sericite

Sericite sample was crushed and sieved to obtain 200 ~ 300 BSS (British Standard Seive i.e. 0.075–0.053 mm) mesh size. The CEC of sericite was obtained by the US EPA method 9080 (http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/9080.pdf), which was found to be 8.85 meq/100 g of sericite. Organo-modified sericite was prepared by taking 20.0 g of sericite powder into 1.0 L of 0.5 CEC HDTMA solutions. The mixture was refluxed for 48 h at 60°C. The slurries were filtered. It was washed with distilled–deionized water for about 10 times. Soxhlet extraction was conducted to remove any excess of free surfactants. The organo-modified sericite was then dried at 90°C for 6 h in a drying oven. The resultant organo-sericite was labelled as H0.5 and was then stored in an airtight polyethylene bottle. Similarly, the sericite was loaded with the 1.0, 1.5, 2.0 CEC of HDTMA and labelled as H1, H1.5 and H2 HDTMA-modified sericite samples, respectively. The AMBA-modified sericite was also obtained using an identical procedure and was labelled as A0.5, A1, A1.5 and A2 samples. The organo-modified sericite along with the virgin sericite was characterized by FT-IR (Bruker, Tensor 27, USA using KBR disc method) and XRD (Rigaku, Geigerflex RAD3-C, Japan) analytical tools. The surface morphology of these solids was obtained by taking scanning electron microscopic (SEM) images using a SEM machine (Model FE-SEM SU-70, Hitachi, Japan).

2.3. Batch experiment

Batch experiments were performed by taking 40 mL of 2.0 mg/L phenol solution. The pH of the solution was adjusted by the addition of drops of HNO_3 (0.1 N)/or NaOH (0.1 N) solutions. 0.2 g of organo-sericite was then added, and the solution mixture was equilibrated at 25 ± 1°C for 24 h in an automatic shaker. The suspension was taken out and filtered with 0.2-μm syringe filter, and the bulk phenol concentration was measured using spectroflourimeter using the excitation and emission wavelength of 255 and 261.3 nm, respectively (fluorescence spectrometer Perkin–Elmer, LS55, UK). The blank measurements were always conducted for necessary fluorescence intensity correction in measurement. Moreover, the concentration of phenol was estimated by using the calibration curve obtained by taking the fluorescence intensities against the known phenol concentrations.

2.4. Effect of pH

Effect of pH was studied in the pH range of 2.0–10.0. The initial phenol concentration was taken 2.0 mg/L. The sorption experiments were performed as described previously. The results were presented as the amount of phenol removed as a function of pH.

2.5. Effect of initial phenol concentration

The concentration dependence data were collected taking sorbate solutions having varied concentrations from 1.0 to 20.0 mg/L at a constant pH 7.0 and temperature 25 ± 1 °C. The sorption experiment was carried out as described earlier. Results obtained were then reported with percent removal of phenol as a function of sorbate concentrations. Moreover, the equilibrium concentration dependence sorption data were further employed to deduce the equilibrium modelling studies using the known Freundlich adsorption isotherm [11].

3. Results and discussion

3.1. Characterization of sericite and organo-modified sericite

FT-IR spectra of the sericite and organo-modified sericite are illustrated in Fig. 1. The IR stretching frequencies obtained at 3,623 and 3,443 cm^{-1} were attributed, respectively, to the structural hydroxyl groups within the clay sheets and the water molecule present within the interlayer space [12–14]. A vibrational band occurred at 3,443 cm^{-1}, which was almost disappeared with the H1 and A1 samples, was indicated the replacement of the organic molecule with hydroxyl group or grafting with the hydroxyl groups [15]. Moreover, a band at 3,625 cm^{-1} was also shifted slightly to its higher frequency. The appearance of new bands in the spectra of the modified clay, centred at 2,920 cm^{-1} and 2,856 cm^{-1} were considered to the C–H stretching, and C–H scissoring vibrations, respectively [12]. Band at 1,652 cm^{-1} occurred with sericite was assigned to the characteristics of Al and Mg bound water molecules which were diminished significantly with modified sericite. A band at 1,041 cm^{-1} was assigned as asymmetric stretching vibrations of Si–O–Si of sericite. Also, bands from 737 to 842 cm^{-1} were characterized to the presence of quartz, and the bands in between 478 and 536 were assigned as OSiO bending vibrations of sericite [16]. These results confirmed the presence of organic cation within the interspace region of the sericite.

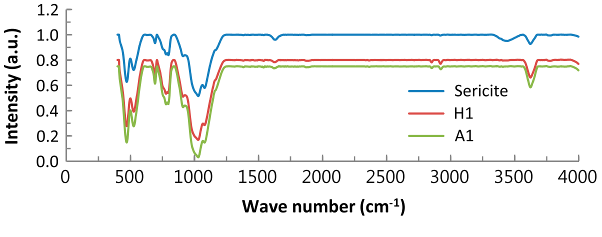

Fig. 1. FT-IR spectra of sericite, HDTMA-sericite (H1) and AMBA-sericite (A1).

Further, X-ray diffraction data for sericite and organo-sericite, that is, H1 and A1 were shown in Fig. 2. The diffraction peaks obtained at the 2θ values of 8.81, 17.88, 19.98, 20.97, 23.00, 23.91, 25.60, 26.74, 27.99, 36.65 and 50.22 are characteristic peaks of the sericite [10]. Further, H1 and A1 samples were also showed similar diffraction peaks with slight change in *d*-values. It was clearly observed that the samples H1 and A1 showed a little positive *d*-value difference; particularly to the 001 plane reflection having the difference of 0.0227. This indicated that the interlayer of the sericite was propped up with a little but some extent. These results were in a line to the previous findings where sand sample was modified with manganese impregnation [11], or the sericite was modified with aluminium and HDTMA or AMBA as to obtain the inorgano–organo-sericite [17].

SEM images of sericite and organo-sericite are shown in Fig. 3(a, b and c), respectively, for the sericite, H1 and A1 solids. These images clearly show that sericite is having very compact ordered layered structure and hardly possesses micro- or meso-pores on it. However, the organo-modified sericite samples possess with heterogeneous and disordered structure having small but some pores on it. Hence, the accessible surface area is apparently increased up to some extent.

3.2. Effect of initial phenol concentration

The sorbate concentration dependence data were shown in Fig. 4. It was noted that increasing the initial concentration of phenol from 1.0 to 20.0 mg/L apparently caused to increase the amount of phenol removed, respectively, from 0.156 to 0.720 mg/g by HDTMA-sericite solid. However, the similar increase in sorbate concentration from 1.0 to 20.0 mg/L of phenol was caused to decrease the percent uptake of phenol from 15.6 to 7.20%, respectively. This was explicable with the fact that at low sorbate concentrations relatively large number of active sites is available on the solid surface whereas at higher sorbate concentrations, taking a constant solid dose, relatively large number of sorbing species is available

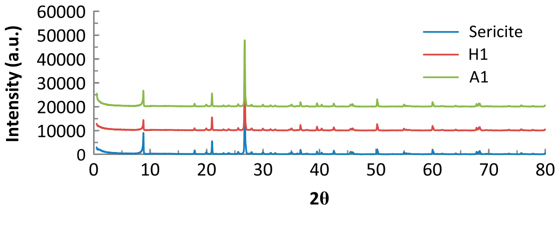

Fig. 2. XRD data for sericite and organo-sericite.

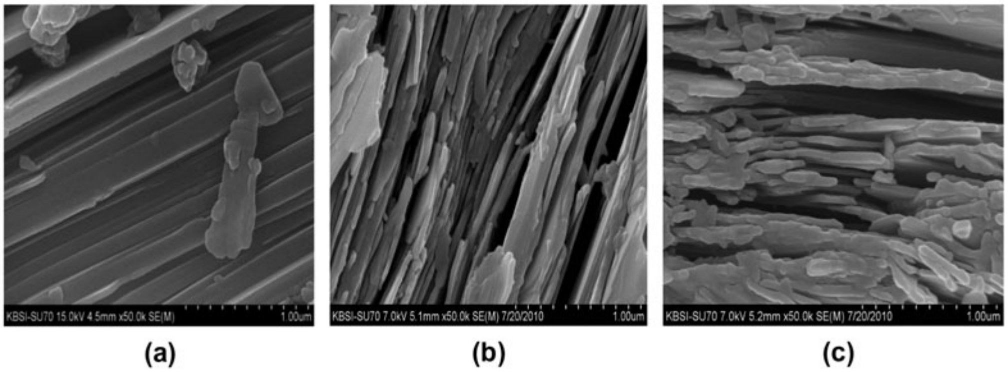

Fig. 3. SEM images of (a) bare sericite, (b) HDTMA-sericite and (c) AMBA-sericite.

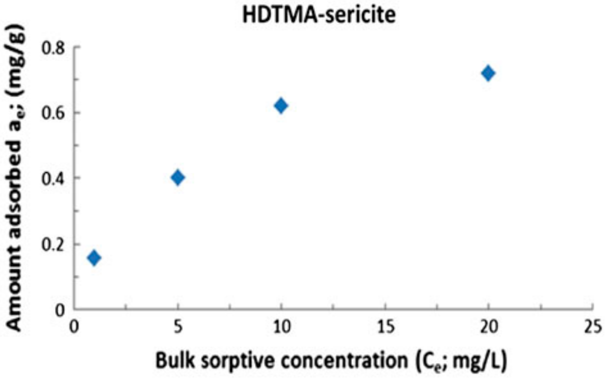

Fig. 4. Effect of initial concentration of phenol on adsorption by HDTMA-modified sericite.

for occupying the same number of active sites [18]. A significant uptake of phenol was occurred by the HDTMA-modified sericite. This is due to an enhanced hydrophobicity and organophilic nature possessed by the organo-modified sericite which could facilitate to attract the phenol by van der Walls attraction and phenol likely to partition within the interspace. The similar assumptions were suggested for the uptake of phenol and other non-ionic contaminants by the organo-modified clay materials [5,19]. Moreover, the inorgano–organo-sericite showed two distinct sorption sites which could enable to attract inorganic and organic contaminants viz., arsenic and phenol, simultaneously [17]. Further, it was also noted that the removal of phenol by virgin sericite was almost negligible which is in accordance with the previous report indicated towards the insignificant removal of other organic impurities viz., benzene, toluene etc. by sericite [10].

The concentration dependence data were applied to modelling studies using the Freundlich adsorption model [9]. The concentration dependence sorption data were fitted well to the linear Freundlich adsorption isotherm since relatively high value of regression coefficient was obtained. The estimated values of Freundlich constants, that is, $1/n$ (adsorption intensity) and K_f (adsorption capacity) were found to be 0.368 and 0.275 mg/g, respectively. The fractional values of $1/n$ implied to the heterogeneous surface structure of solid having exponential distribution of active sites [17,18]. Moreover, relatively high value of K_f showed reasonably fair sorption capacity of HDTMA-sericite in the attenuation of phenol.

3.3. Effect of pH

The pH dependence data in the removal behaviour of organo-sericite towards phenol were obtained and presented graphically in Fig. 5. Fig. 5 clearly demonstrated that increasing the pH from 2.0 to 10.0 the amount of phenol removal was decreased respectively from 0.39 to 0.14 mg/g by HDTMA-sericite (e.g. for 0.5 CEC sample). Similarly, the removal of phenol for a similar increase in pH, that is, from 2.0 to 10.0 caused to decrease in from 0.38 to 0.32 mg/g, respectively, for AMBA-sericite (e.g. for the 0.5 CEC sample). Similar, observations were obtained for different CEC organo-modified sericite samples.

Significantly high uptake of phenol obtained by organo-modified sericite at lower pH values could be ascribed with the fact; sericite interlayer which contained with organo-cations having the large alkyl group could possess with enhanced organophilic and reduced hydrophilic nature caused to attract the phenol. This could, therefore, favour the partitioning of the phenol at the organic end of the surfactant molecule. The driving force is likely to be the van der Waals attraction operative between the phenol and the organic cation available within the interspace. It was already reported previously that the clays modified by quaternary ammonium cations, that is, $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$, where R is a large

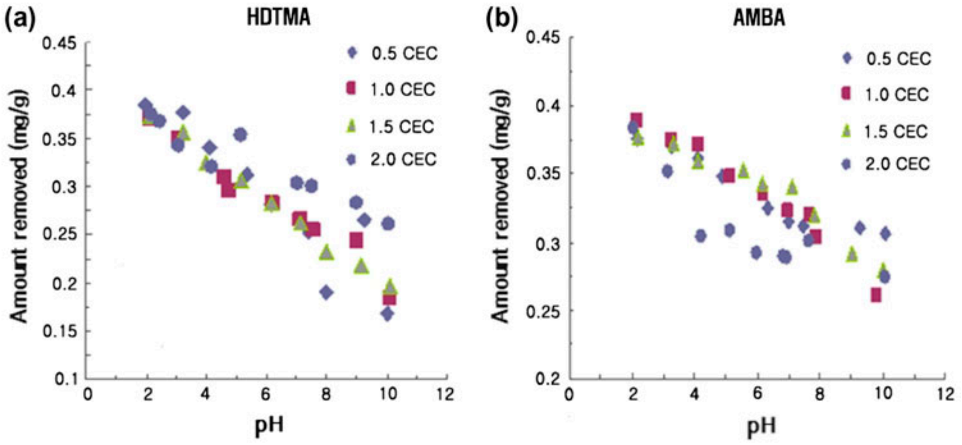

Fig. 5. Effect of pH as a function of amount of phenol removed using (a) HDTMA-sericite and (b) AMBA-sericite with various CEC values.

alkyl hydrocarbon, yielded with organo-clay which showed an enhanced organophilic nature with reduced hydrophilicity of clay materials [20].

Further, increasing the solution pH caused for gradual decrease in phenol uptake from aqueous solutions by these solids. Phenol exists in its neutral form when pH is lower than 2 units of its pK_a 9.89, whereas it is deprotonated completely higher the 2 units of its pK_a. As the pH is increased above or around the pK_a value, the deprotonated or anionic form of phenol is possessed with low partitioning coefficient than the neutral form of phenol hence caused for extreme low phenol removal. The similar decrease in deprotonated phenol or chlorophenol or DICAMBA is reported by different organo-modified clay materials [21–23]. The significant decrease in penta chlorophenol is reported by HDTMA-modified clay. They found that almost 3–4 times the uptake was decreased by increasing the pH from 4 to 8 [23]. However, the gradual decrease of phenol removal started even at low pH value, that is, pH 2.0 as obtained here, that is, with HDTMA- or AMBA-sericite, which is much before the pK_a value of phenol. This may be explained as increasing the solution pH, possibly, caused for gradual removal of organo-cation from the interlayer space of sericite and hence giving a decrease in phenol removal. Earlier report also demonstrated that a sharp and gradual decrease of phenol occurred by the organo-modified *rectorite* increasing the pH beyond 6.0 [24].

4. Conclusions

The HDTMA- and AMBA-modified sericite is obtained by wet exchange process. The IR data demonstrate that organic molecules are introduced within the interspace of sericite. The XRD data show that the interlayer of organo-modified sericite is propped up to some extent. The SEM images indicate that organo-modified sericite is possessed very disordered surface structure having some micro pores on it. Further, in the remediation of phenol containing wastewater, it is observed that the introduction of HDTMA and AMBA made the sericite mineral more organophilic and hydrophobic in nature, hence effective and efficient materials for the low level removal of phenol from aqueous solutions. HDTMA- or AMBA-modified sericite possess comparable removal behaviour towards phenol at wide range of pH. Increasing the pH from 2.0 to 10.0 caused for gradual decrease in phenol removal. Moreover, the concentration dependence data is fitted well to the Freundlich adsorption isotherm. The sorption capacity is found to be 0.368 mg/g for HDTMA-sericite sample. The possible mechanism is the partitioning of phenol within the interspace of sericite provided by the organic end of organo-cation.

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