

Adsorption of Phenol from Wastewater Using Modified Layered Double Hydroxide Clay

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Phenol and its derivatives are some of the organic pollutants found in wastewater and they pose health risks to human beings and animals if left untreated. This work investigates the use of modified Layered Double Hydroxide clay as an adsorbent for removal of phenol from wastewater. High exchange capacities, capability to be modified with surfactants and through calcination, and the ability to regenerate are some of the properties of the clay reported in literature which make it an ideal adsorbent for phenol removal from wastewater. Modification of neat clay with silane increased the adsorption percentage from 6 % to 19 %, however the extent of adsorption was reduced from 87 % to 35 % when calcined clay was coated with a silane material. Calcination of the clay increased its BET surface area from 8.71 m²/g to 29.74 m²/g. The adsorption kinetics were best fitted by the pseudo second order model. The equilibrium isotherms which best fitted the adsorption data were the Freundlich isotherm and the Three Parameter Langmuir-Freundlich isotherm. The maximum adsorption capacity of 59.1 mg/g was observed using the Three Parameter Langmuir-Freundlich isotherm.

1. Introduction

Phenol and its derivatives exist in water bodies because of the discharge of polluted wastewater from industrial, agricultural and domestic activities. These compounds are known to be toxic and inflict both severe and chronic effects on animals and human beings. The interaction of phenolic compounds with micro-organisms, inorganic and other organic compounds can result in toxic compounds which are as toxic as the original phenolic compounds (Gami et al., 2014). The removal of phenolic compounds from waterbodies is of utmost importance to safeguard and preserve the lives of human beings and aquatic species from these toxic chemicals. The use of appropriate technologies for effective removal of these compounds will eliminate problems of possible harm associated with pollutants and reduce waste disposal. These technologies include photocatalytic degradation (Jay and Chirwa, 2018), ozonation (Cheng et al., 2017), microbial and enzymatic degradation (Kulkarni and Kaware, 2013), membrane-based separation (Acero et al., 2005) and adsorption (Ulibarri et al., 1995) processes. Amongst the methods available for removal of phenol from wastewater, adsorption has been proven to be more appropriate due to its operational simplicity and economic viability. Activated carbon has been used in most processes due to its massive adsorption capacity. However, low cost adsorbents such as clays (natural and synthetic) can be utilised for adsorption of pollutants from water. This is because they are cheap, accessible and efficient, universal sorbents, and they have higher adsorption capacity, resistance to environmental influences and can serve as excellent carriers for mounting on the surface of various components at their modification (Butenko et al., 2014).

Layered Double Hydroxides (LDHs) are synthetic clays that consist of brucite type mixed metal hydroxides layers and exchangeable interlayer anions (Chen et al., 2009). LDHs and their derivatives find their applications in various processes such as ion exchange, basic catalyst of organic synthesis, antacids and antipeptins in medicine, halogen scavengers, flame retardants and PVC stabilizers in polymer technology, photocatalysis and adsorbents in wastewater treatment (Moyo et al., 2008). LDHs can be modified by various techniques to enhance their structural and chemical characteristics. Modification can be done with a surfactant in which the interaction between the clay and surfactant will either be adsorption or intercalation. Adsorption will occur when interaction is limited to aggregation of the surfactant on the outside of the clay particle while intercalation happens when the surfactant molecules additionally aggregate inside the galleries. Calcination of the clay at

moderate temperatures between 450 to 650 °C will result in the clay being converted to a mixed metal oxide with an increased specific surface area compared to the precursor hydrotalcite (Peng et al., 2015). The mixed metal oxide can be reconstructed in aqueous solution to regain its layered structure with different anions intercalated in the galleries (Chen et al., 2009). This makes LDH clays and their derivatives ideal adsorbents for removal of pollutants from wastewater. Silane coupling agents are silicon-based chemicals that contain two types of functional groups i.e. inorganic and organic in the same molecule. A typical general formula is $(RO)_3SiCH_2CH_2CH_2-X$, where RO is a hydrolysable group such as methoxy, ethoxy or acetoxy and x is an organo-functional group such as amino, methacrylaxy, epoxy (Padhiyar and Shah, 2013). Silane coupling agents can form a durable bond between organic and inorganic materials. The result of reacting an organ-silane with a substrate ranges from altering the wetting or adhesion characteristics of the substrate, utilizing the substrate to catalyse chemical transformations (Goud and Rao, 2013). This includes the ability to cause a covalent bond between organic and inorganic materials. Therefore, they can be used as surfactants on clays to reduce its surface tension, increase clay's adsorption capacity and enhance adsorption of pollutants from wastewater. The aim of this investigation was to determine the feasibility of using LDH clay for removal of phenol from wastewater. The clay material was modified by coating with various silane materials and through calcination. Kinetics of ion exchange sorption of phenol were also studied.

2. Materials and methods

2.1 Materials

Sorbacid 944 clay was supplied by Clariant. It is an Aluminium-Magnesium-Zinc- Carbonate-Hydroxide Hydrate clay. Its neat BET specific surface area is 8.71 m²/g and it has a d₅₀ of 1 µm. Silane materials which were used to coat the clay prior adsorption tests were gamma-mecaptopropyltrimethoxy silane (A189) and trichloromethyl silane (A1120), and they were supplied by Merck Chemicals. The surface area coverage for the silane materials are 348 m²/g and 358 m²/g for A189 and A1120 respectively. Synthetic solutions of phenol with various concentrations were prepared using phenol supplied by Merck Chemicals.

2.2 Methods

2.2.1 Material Characterisation

The Perkin Elmer 100 Spectrophotometer with a MIRacle ATR attachment with Zn/Se plate was used for FTIR analysis. The spectra were recorded between 4000 cm⁻¹ and 600 cm⁻¹ at a resolution of 2 cm⁻¹. XRD analysis was done using PANalytical X'pert Pro Powder diffractometer in θ - θ configuration with an X'celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-K α radiation ($\lambda = 1.789\text{\AA}$). Micrometrics Tristar BET (USA) was used for determination of specific surface area of the powders. Powder samples were viewed on a Zeiss Crossbeam 540 FEG SEM.

2.2.2 Silane Coating

The silane-ethanol treatment solutions were prepared by adding the mass of silane required to coat 20 g of clay (with 25% excess) to an equivalent mass of distilled water, and then ethanol was added to this mixture until the total mass was 20 g (Wang & Jin, 2004; Van Ooij *et al.*, 2005 quoted by Tichapondwa, 2012). The amount of silane required was calculated according to equation 1 below. Twenty (20) g of clay was then added to the silane-ethanol solution. The slurry was stirred for 8 h with a magnetic stirrer. The solids were recovered by centrifugation, washed with acetone and left to dry in open air for 24 h.

$$\text{Silane required (g)} = \frac{\text{mass of clay (g)} \times \text{clay specific surface area} \left(\frac{\text{m}^2}{\text{g}}\right)}{\text{silane minimum coverage area} \left(\frac{\text{m}^2}{\text{g}}\right)} \quad (1)$$

2.2.3 Phenol adsorption studies

Phenol adsorption experiments were conducted through batch equilibrium technique at ambient temperature. The residence times were varied up to 24 h. One (1) g of clay was dispersed in 0.1 L of phenol solution containing about 40 mg/L phenol. The mixture was stirred continuously with a magnetic stirrer over a specific residence time. Upon completion of the adsorption test, the suspension was centrifuged at 5000 rpm for 15 minutes. The resulting cake was dried in open air and stored while the centrate was further filtered with Millipore (0.22 µm) to remove any suspended solids. The filtrate was then taken for phenol analysis using High Performance Liquid Chromatography (HPLC).

3. Results and discussion

3.1 Clay characterization

The BET surface areas for the neat and calcined clay materials were found to be $8.71\text{m}^2/\text{g}$ and $29.74\text{ m}^2/\text{g}$ respectively. The increase in specific surface area on the calcined clay is due to the clay layers being broken and the formation of mixed metal hydroxide. XRD analysis on the neat LDH clay show a sharp and intense diffraction peaks (003 and 006) at low 2θ values and small symmetric peaks at high 2θ as displayed in Figure 1. These peaks are typical reflection from LDH metal layers. The diffraction peaks at low 2θ values disappear after calcination indicating that the layered structure was broken. The diffraction peaks reappear after the clay had contacted the aqueous solution during adsorption process indicating that the layered structures were restored through the “memory effect” of LDH. SEM analysis in Figure 2 show platelets like morphology which is typical of Magnesium and Aluminium based LDH clays in Figure 2 (a) and Figure 2 (b). The size distribution of particles depends on the synthesis conditions and varies from a few hundred nm to a few μm in lateral dimensions (Kumar et al., 2012). Figure 2 (c) shows the oxide particles which are much smaller and shapeless after calcination of LDH clay. The particles became more aggregated and well-structured when the calcined clay was coated with silane material as shown in Figure 2 (d). The FTIR spectra on the neat clays (coated and uncoated) reveal bands characteristics of hydrotalcite-like compounds as indicated in Figure 3. The broad and strong bands centred at 3400 cm^{-1} are due to the stretching of the OH bond of the hydroxyl groups and H_2O molecules. They further display the bands at 1360 cm^{-1} , 800 cm^{-1} and 650 cm^{-1} which can be attributed to antisymmetric stretching, weak non-planar bending and angular bending modes of carbonate respectively. This implies that there was no displacement of the hydroxide and carbonate in the clay galleries by silane materials during coating process. The hydroxyl and carbonate bands are not visible on the calcined clays because of thermal dihydroxylation and breaking of the clay’s double layers

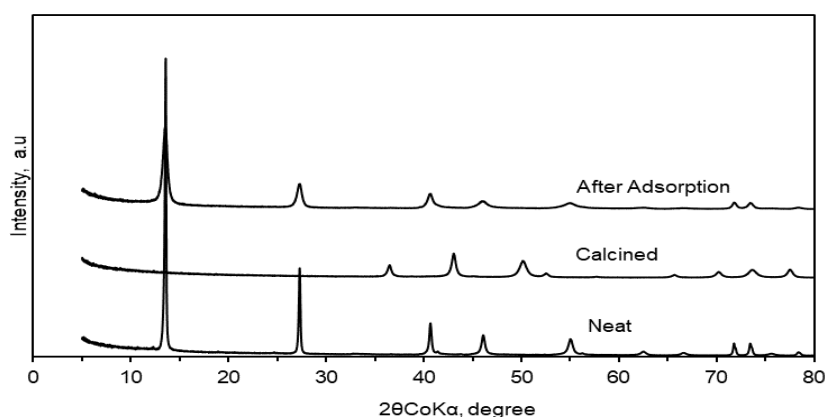


Figure 1: XRD patterns of the Neat clay, Calcined clay and Clay after Adsorption

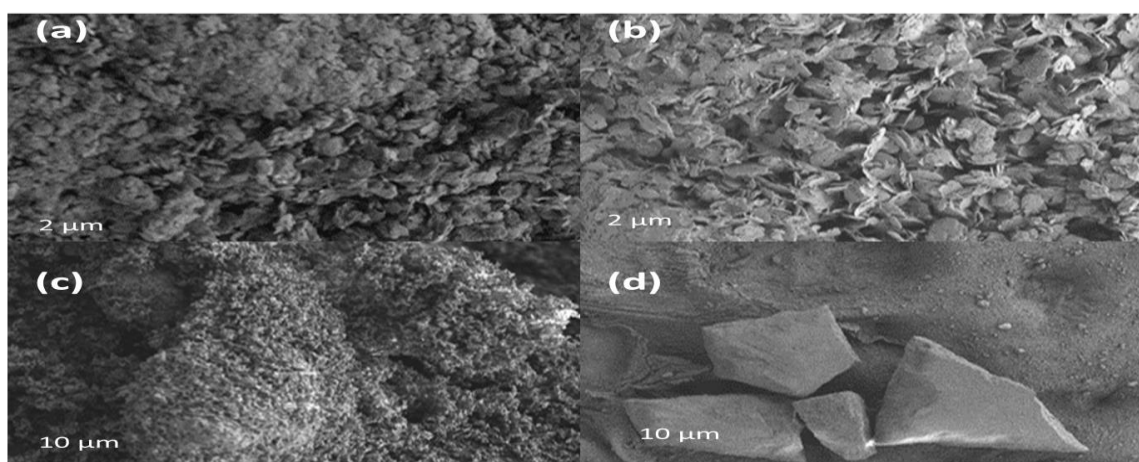


Figure 2: SEM Micrographs of (a) Neat clay, (b) Neat and Coated, (c) Calcined, (d) Calcined and Coated

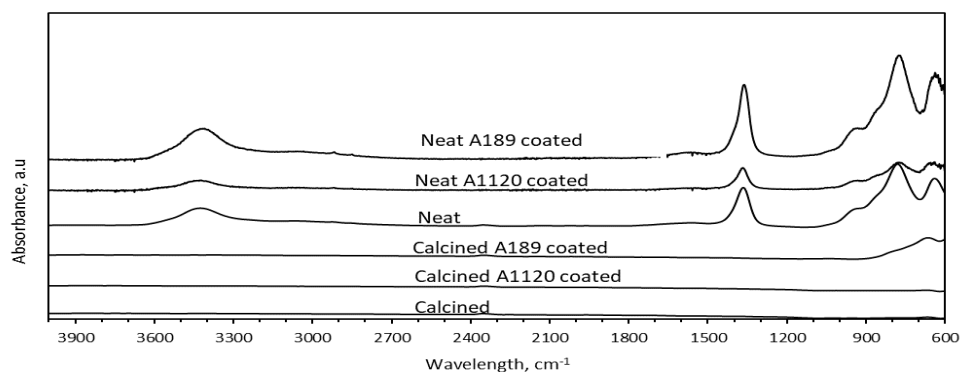


Figure 3: FTIR Spectra for various clays

3.2 Adsorption studies

The adsorption results show low adsorption efficiency of 6 % on the neat clay. There was a slight improvement in adsorption efficiencies up to 19 % and 13 % when the neat clay was coated with silane A189 and A1120 respectively. This increase in adsorption efficiencies can be due to improved surface adhesion on the clay after coating with silane. A higher adsorption efficiency of up to 87 % was observed when using calcined clay as an adsorbent. This can be explained by a higher surface area which was obtained when the clay layers were broken during calcination to produce mixed metal oxide. The adsorption efficiencies were observed to have decreased to 35 % and 5 % when the calcined clay was coated with silane A189 and A1120. This decrease in adsorption efficiencies can be explained by the reconstruction and aggregation of the clay during coating and thereby reducing the active sites of the clay. The extent of phenol adsorption for various clays is shown in Figure 4.

The adsorption efficiency at a clay loading of 5 g/L was found to be 68%. This is low when compared to 83% adsorption efficiency when 10 g/L clay loading was utilised. There was no significant change in adsorption when clay loading was increased to 15 g/L and 20 g/L as they reached 86 % and 88% respectively. This means that clay was under-utilised at the latter loadings which can be explained by aggregation at higher clay loadings hence 10 g/L was taken as the optimum clay loading. The extent of phenol adsorption at various clay loadings is displayed in Figure 5.

The adsorption capacity of the calcined clay was examined by conducting a series of equilibrium adsorption tests at ambient temperature over a 24 h period. The concentration of phenol was varied from 20 mg/L to 200 mg/L. The equilibrium adsorption data are displayed in Figure 6. Three isotherm models were evaluated i.e. Langmuir isotherm, Freundlich isotherm and the Three Parameter Langmuir-Freundlich Isotherm as shown by Equation 2, 3 and 4. The adsorption data were found to be best fit on the Three Parameter Langmuir-Freundlich and Freundlich isotherms with the parameters shown in Table 1. The maximum adsorption capacity of the calcined clay was found to be 59.1 mg/g which is five times more than the real adsorption capacity of 10.6 mg/g at the equilibrium concentration of 98 mg/L.

The pseudo second order rate equation was used to model the kinetics of phenol adsorption by calcined clay as shown in equation 5 and displayed in Figure 7. The parameters were found to be: equilibrium concentration (C_e)= 4.3 mg/L and a rate constant (K_{ad}) of 0.0369 L/mg.h at a coefficient of determination (R^2) = 0.9904. The established rate constant is low when compared to that which was determined by Chen et al (2009) of 0.351 L/mg.h and 0.154 L/mg.h for adsorption studies at pH= 5 and pH= 10 respectively. Therefore, adsorption kinetics can be enhanced by operating at elevated pH as the probability of intercalation increases.

$$q_e = \frac{Q_L K_L C_e}{1 + K_L C_e} \quad (2)$$

$$q_e = K C_e^m \quad (3)$$

$$q_e = Q \frac{(b C_e)^{1/n}}{1 + (b C_e)^{1/n}} \quad (4)$$

q_e (mg/g) is the adsorption amount on clay at equilibrium; C_e (mg/L) is equilibrium concentration; Q_L (mg/L) and K_L (L/mg) are Langmuir constants related to the loading energy and adsorption; K (mg/g). $(L/mg)^{1/m}$ and m are Freundlich temperature dependent constants; Q (mg/g) is the maximum adsorption amount; b (L/mg) and n are constants related to adsorption strength.

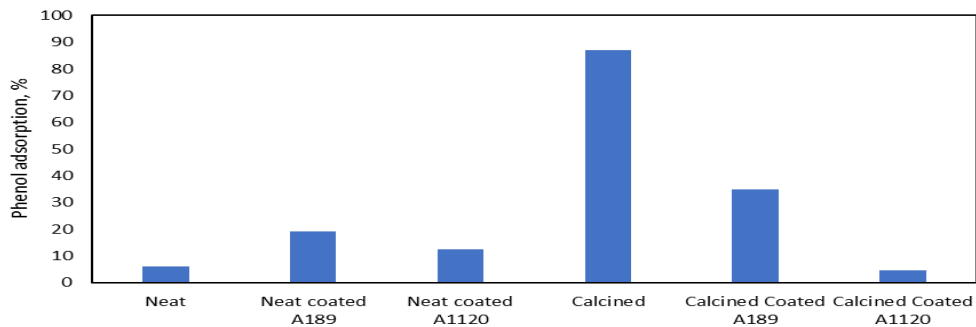


Figure 4: Phenol Adsorption efficiencies for various clays

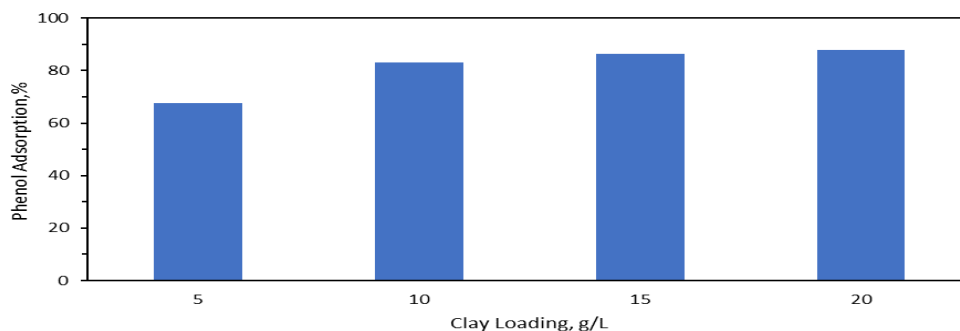


Figure 5: Phenol adsorption for various clay loading

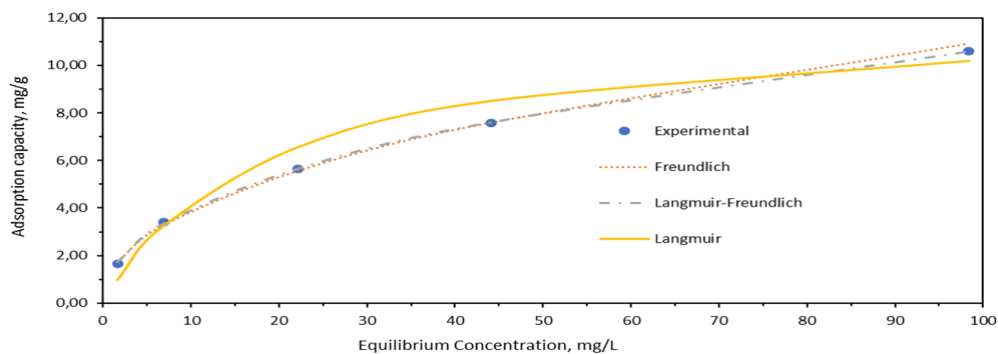


Figure 6: Various adsorption isotherms

$$\frac{t}{q_t} = \frac{1}{K_{ad}q_e^2} + \frac{1}{q_e}t \tag{5}$$

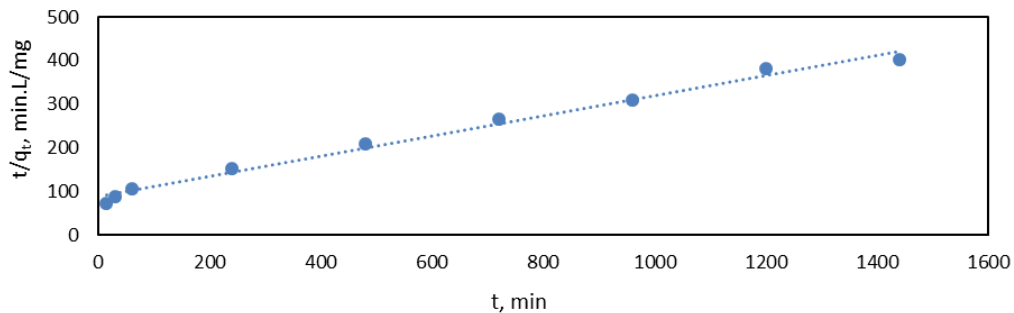


Figure 7: Phenol adsorption kinetics modelling

Table 1: Fitting parameters for various isotherms

Parameter	Langmuir-Freundlich	Freundlich	Langmuir
Q (mg/g)	59.09	-	-
b (L/mg)	0.000446	-	-
n	2.055	-	-
K	-	1.36	-
m	-	2.207	-
Q _L	-	-	12.14
K _L	-	-	0.053
R ²	0.9878	0.9979	0.9694

4. Conclusion

Mixed metal oxide derived from LDH clay is a potential adsorbent for remediating wastewater contaminated with phenol. The adsorption capacity of calcined clay was found to be 59.1 mg/g at ambient temperature. The adsorption kinetics were best fitted with the pseudo second order model while the Freundlich and Three Parameter Langmuir-Freundlich isotherms gave better fits for adsorption isotherm. Phenol adsorption was found to be reaching equilibrium after 24 hours with more than 80% phenol adsorption when operating with a clay loading of 10 g/L and an initial concentration of 40 mg/L. coating the clay material with silanes improved the phenol adsorption slightly when coating was done on a neat LDH. Phenol adsorption decreased tremendously from more than 80 % adsorption to below 40 % adsorption when silane coating was done on calcined clay. XRD analysis showed that the clay double layers were broken during calcination and restored after adsorption because of the clay's "memory effect".

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