The Effect of Metallic Composition of Layered Double Hydroxide Clay on the Removal of Phenol from Aqueous Solution

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The present study focused on the evaluation of Layered Double Hydroxide (LDH) clays containing various metallic compositions as adsorbents for phenol from wastewater. Neat clays were found to have low phenol adsorption efficiencies mainly due to poor mixing and incompatibility of the inorganic clays with phenolic water. Calcination of the clays at 500 °C produced amorphous mixed metal oxides which greatly increased the Brunauer Emmett Teller (BET) surface areas by more than 200 % from 8.71 to 29.73 m^2/g. The highest phenol adsorption removal (85 %) was observed within 24 h upon calcination of the clay. The presence of a substantial amount of zinc in hydrotalcite clay was found to be the main cause of a high phenol removal. Optimisation studies showed that higher adsorption efficiencies were attainable at pH 7 and the clay was reusable for up to 3 cycles.

1. Introduction

The global supply of freshwater has recently become a major concern due to a combination of factors such as increasing population, reduced sources of fresh water and heightened pollution caused by anthropogenic activities. This has resulted in the search for alternative sources of water. Water reuse has emerged as one of the promising technologies in this regard. However, its effectiveness is highly dependent on the efficiency of the upstream conventional biological wastewater treatment processes whose effluent is received as feed in water reuse plants. Organic pollutants which have known mutagenic and carcinogenic effects were found to be present in reuse water since they are not biodegradable. There is a continual need to find efficient processes for removal of these recalcitrant organic pollutants. Various physical, biological, chemical and electrochemical treatment technologies have been used for the removal of such pollutants from water (Alqadami et al., 2018). Adsorption based processes have widely been used due to their low operational cost, simplicity, high efficiency, ease of handling, low energy demand, minimal sludge generation and the possibility of regeneration (Capra et al., 2018). Activated carbon is the most widely used adsorbent for the removal of refractory compounds due to its high surface area and hydrophobic surface. However, the production and regeneration costs of activated carbon have limited its application in wastewater remediation. This has led to the prospects of using alternative low-cost adsorbents such as clays for wastewater remediation. LDH clays in particular have been shown to possess properties which are favourable for adsorption of several pollutants in aqueous solutions. Some of the main LDH properties that give rise to good adsorption properties include surface area, crystallinity, composition and surface chemistry (Tabana et al., 2019). LDH clays can be synthesised through relatively low cost processes such as co-precipitation, regeneration, hydrothermal crystallisation urea hydrolysis and sol-gel methods. Labuschagne et al. (2018) recently developed a green, zero effluent synthesis method which produces LDH in an economic and environmentally friendly manner. LDH clays can remove impurities from aqueous solutions through several mechanisms such as surface adsorption, intercalation, adsolubilization of organics with organo-modified LDH and reconstruction of calcined clays (Tabana et al., 2019). While the use of LDH as adsorbents for various pollutants in aqueous solutions has been thoroughly articulated in literature, the effect of metallic

compositions of the LDH clays in wastewater remediation has not been well investigated to the best of our knowledge. The current study aims to evaluate the impact of metallic compositions in LDH clays for phenol removal from aqueous solution.

2. Materials and methods

2.1 Materials

Seven LDH clay materials were available for this investigation. Clay GF-450 and B44 were supplied by Greenfield Additives, DHT-4A and Alcamizer 1 were supplied by Kisuma Chemicals while Sorbacid 944, Sorbacid 911 and Hycite 713 were supplied by Clariant. Phenol used to prepare the simulated phenolic wastewater was obtained from Merck, South Africa. The technical grade acetonitrile and acetic acid, which were used as mobile phase in High-Performance Liquid Chromatography (HPLC) were procured from Sigma Aldrich. Sodium hydroxide used for pH adjustment was also procured from Sigma Aldrich, South Africa. Deionised water was used for all dilutions and standards preparations.

2.2 Methods

The composition and phases of the neat and calcined clays were analysed using a 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-Kα radiation (λ=1.789Å). Samples were prepared according to the standardised Panalytical backloading system which provides for near-random distribution of the particles. Data was collected in the angular range 5° to 80° 2θ with a step size of 0.008° 2θ and 13 s scan step time. Mineralogy was determined by selecting the best–fitting pattern from the Inorganic Crystal Structure Database (ICSD) to the measured diffraction pattern, using X'Pert Highscore plus software. The elemental composition of the clay samples was determined by X-Ray Fluorescence (XRF) analysis. A Thermo Fisher ARL Perrform'X Sequential XRF instrument with Uniquant software was used to collect the data. The Loss on Ignition (LOI) was determined by roasting the sample (placed in alumina refractory crucible) at 1,000 °C. The Brunauer Emmett Teller (BET) surface areas were determined using a Micrometrics Tristar 3000 BET analyser. All samples were degassed for 24 h at 150 °C under a 10 − 5 Torr vacuum before analysis.

Calcination of the clay was carried out in an Aluminium Electric Muffle Furnace at 500 °C. Neat clay samples weighing ca. 50 g were placed in porcelain crucibles and covered with a lid before charging them into the furnace at the pre-set temperature for 4 h. The resultant product was collected for further tests and analysis upon cooling. The first set of phenol adsorption tests compared the adsorption efficiencies of the neat clays. In these tests, 100 mL of simulated wastewater containing 40 mg/L phenol was contacted with 10 g/L of clay in a 250 mL glass beaker. The resulting suspension was stirred continuously for 108 h to allow for maximum adsorption. A sample was taken after every 24 h for four days and 12 h thereafter. The suspension was then centrifuged at 9,000 rpm for 10 min, the centrate was further polished by filtering through a 0.45 μm millipore filter. The solids remaining from centrifuging were left to dry in open air, after which they were milled and taken for further analysis. Three best perfoming clays were further modified by calcining them at 500 °C and conducting adsorption tests over a residence time of 48 h. Once the best performing clay was identified, it was used for further optimisation studies. The influence of solution pH was investigated at values of 7, 9 and 12. A 1 M sodium hydroxide solution was used to adjust the pH. It should be noted that no experiments where conducted in the acidic pH range since it is known to damage the structure of the LDH clay (Grover et al., 2019). All the samples obtained from the previously mentioned experiments were analysed using a Waters Alliance 2695 Separations HPLC Module equipped with auto sampling unit and a Photodiode Array Detector (PDA). Separations were performed on a C18 waters column using isocratic elution with 70 % acetonitrile solution (99 % (v/v) acetonitrile and 1 % acetic acid) and 30 % water (99 % deionised water and 1 % acetic acid) at a flowrate of 1 mL/min. The adsorption efficiency in terms of percentage of phenol (R) was determined as shown in Eq(1), C_o and C_t (mg/L) represents the initial phenol concentration and concentration at time=t.

$$R = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \tag{1}$$

3. Results and discussions

3.1 Characterisation results

Table 1 shows the x-ray fluorescence analysis of the clays reported from calcined samples. The analysis showed that Sorbacid 944 had higher aluminium (Al), magnesium (Mg) and zinc (Zn) contents amongst the clays. It was the only clay which had a substantial zinc oxide (ZnO) content of ca. 24 % while the ZnO content of the other

clays was below the detection limit (0.01 %). Clay B44 was the only clay which had less of Mg and more of calcium (Ca) with magnesium oxide (MgO) and calcium oxide (CaO) contents of 1 % and 35 %. This meant that B44 was a hydrocalumite while others were hydrotalcites. Clay GF-450 had a silica content of ca. 6 % while the silica content in other clays was below the detection limit.

Figure 1 shows the XRD spectra of the neat and calcined DHT-4A, GF-450 and Sorbacid 944 clays. The XRD spectra of the neat DHT-4A and Sorbacid 944 showed sharp peaks at various planes indicating high crystalline materials (Naseem et al., 2019). The neat GF-450 clay showed more peaks which were less crystalline compared to the other two clays. This can be attributed to the presence of impurities in the GF-450 clay. Calcination of the DHT-4A and Sorbacid 944 resulted in amorphous products featuring the periclase and spinel phases. This accession is in line with studies conducted by Milanovic (2016) who reported that various phases can be formed upon calcination of the clay depending on the calcination temperature.

Table 1: X-ray fluorescence analysis of the clays in the calcined phase

| Phase	Alcamizer 1	B44	DHT-4A	GF-450	Hycite 713	Sorbacid 911	Sorbacid 944
SiO_2	0.03	0.44	0.02	5.76	0.02	0.14	0.04
Al_2O_3	20.57	22.74	19.36	20.47	18.63	19.17	30.19
MgO	34.82	0.95	35.39	23.58	35.88	35.97	38.14
Na_2O	0.01	0.01	0.01	0.13	0.01	0.01	0.01
Fe_2O_3	0.00	0.04	0.01	0.14	0.01	0.01	0.01
CaO	0.03	34.58	0.03	10.40	0.20	0.32	0.23
ZnO	0.01	0.01	0.01	0.01	0.01	0.01	23.67
SO_3	0.02	0.08	0.02	0.03	0.01	0.01	0.01
LOI	44.50	41.03	45.10	38.41	45.20	44.30	7.18
Total	99.99	99.88	99.95	98.93	99.97	99.94	99.48
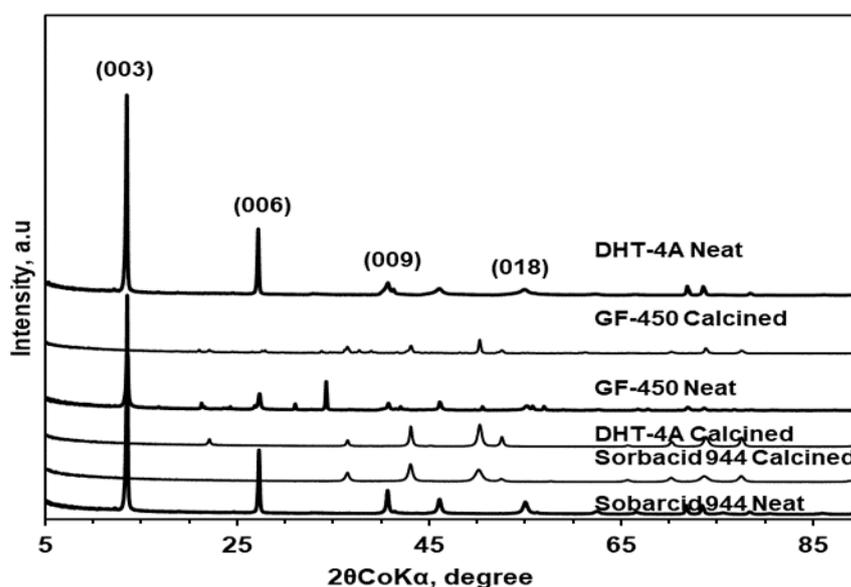
Figure 1: X-ray diffraction spectra of the neat and calcined clays.

The Brunauer Emmett Teller (BET) surface areas of neat GF-450, DHT-4A and Sorbacid 944 were 17.55, 4.28 and 8.71 m^2/g. The surface areas increased to 24.35, 15.07 and 29.73 m^2/g for GF-450, DHT-4A and Sorbacid 944 upon calcination of the clays at 500 °C. This means that DHT-4A and Sorbacid 944 had more than 200 % increase in the surface area while GF-450 increased by ca. 40 %. The increase in the surface area upon calcination is attributed to a combination of phase changes from LDH to mixed oxides as a result of temperature treatments, and the development of pores and channels which are formed when water and carbon dioxide are driven out of the clay interlayers.

3.2 Adsorption results

Figure 2 shows the phenol adsorption efficiencies of the neat clays over 108 h residence time. Clay GF-450 and Sorbacid 944 showed better adsorption efficiencies of 9 % and 6 %. Clay B44 and DHT-4A showed a phenol adsorption efficiency of ca. 3 % while other clays were below 2 %. Poor mixing and incompatibility between inorganic clays and phenolic water attributed to low adsorption efficiencies. Modifying LDH clay with organic surfactants can improve its compatibility with phenolic water and subsequently the adsorption efficiency. Clay GF-450, Sorbacid 944 and DHT-4A were investigated further as they showed better adsorption efficiencies.
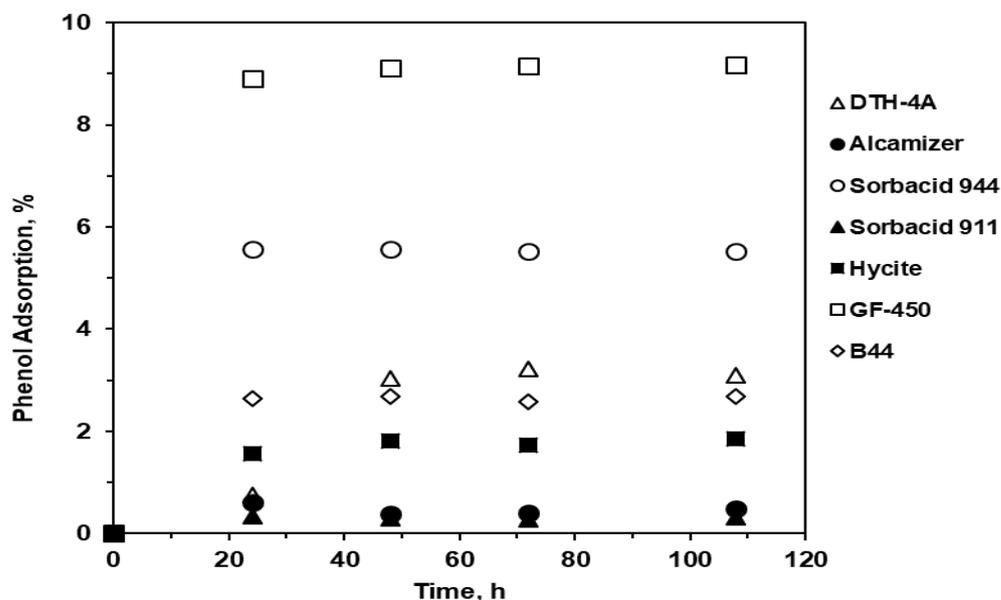

Figure 2: Phenol adsorption efficiencies of the various clays.

Figure 3 shows the adsorption efficiencies of calcined GF-450, Sorbacid 944 and DHT-4A. Calcination of Sorbacid 944 at 500 °C improved its adsorption efficiency with an increase to 85 % from 6 % (neat clay) within 24 h. This increase can be attributed to the formation of amorphous phases as discussed in section 3.1. This is in line with the results from studies conducted by Cai et al. (2010) who found excellent organic pollutant removal rates using amorphous metal oxides. The increase in adsorption efficiency of DHT-4A was visible after 48 h as it rose to 56 % from 6 %. There was no apparent improvement in adsorption efficiency of GF-450 as it remained below 10 %. It can be deduced that the presence of Zn in Sorbacid 944 improved its adsorption properties compared to DHT-4A which had no Zn. It can further be concluded that the presence of impurities such as silica in GF-450 lowered its phenol adsorption efficiency. Sorbacid 944 was utilised for subsequent experiments. The initial pH of contaminated water is an important parameter for efficient removal of pollutant using LDH clays. LDH clays can neutralise the hydrogen ions in solution with low pH while they get deprotonated in solutions with high pH (Grover et al., 2019). In this study, the effect of initial pH on the adsorption of phenol was evaluated over the 7 - 12 pH range, with pH 7 indicating simulated wastewater with no pH adjustment. A 1 M sodium hydroxide solution was used to adjust the pH. It should be noted that no experiments were conducted in the acidic pH range since it is known to damage the structure of the LDH clay. The results shown in Figure 4 indicate a low adsorption rate at high pH. This can be attributed to an increase in hydroxyl ions at higher pH values increasing the LDH reconstruction rate. Since the hydroxyl ions have high affinity for LDH compared to phenol, an increase in hydroxyl ions will lead to a decrease in intercalation of phenolate ions. The removal of phenol with calcined LDH clay was optimum at neutral pH of polluted water and the proceeding adsorption equilibrium tests were conducted at this pH.
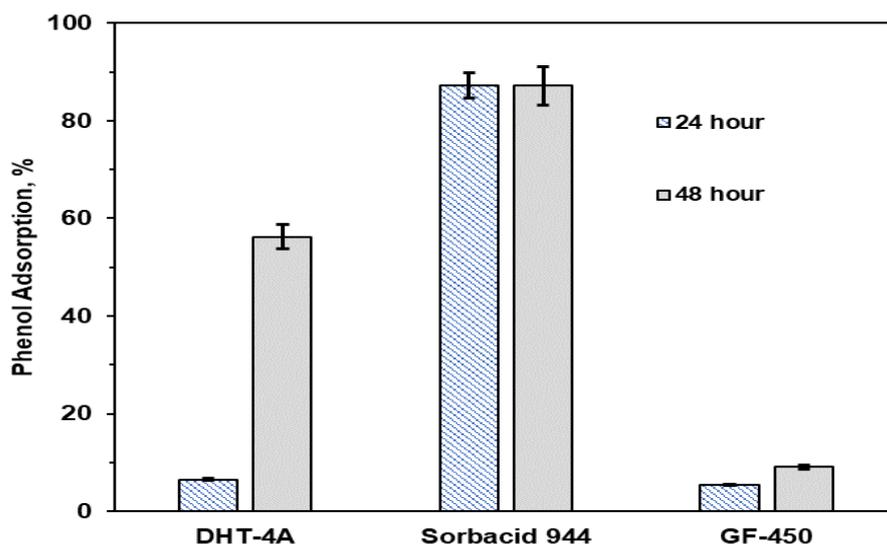
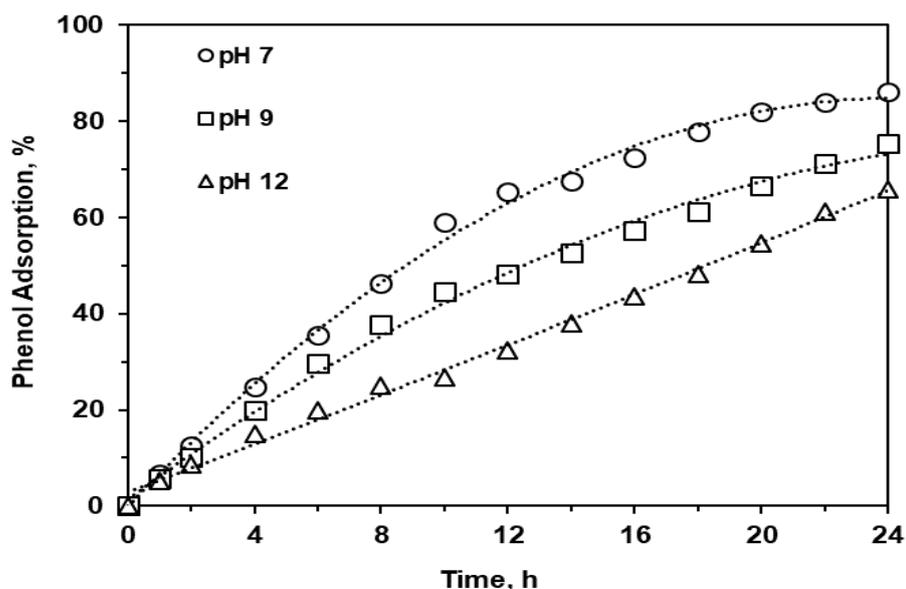Figure 3: Phenol adsorption on calcined clays.

Figure 4: Effect of pH on phenol adsorption.

Recycling and reusability of an adsorbent is an important aspect for the viability of the adsorption process. Calcined LDH clays are capable of being regenerated due to "memory effect". Phenol adsorbed on the LDH clay can be completely decomposed upon re-calcination of the spent clay, and the suspensions were recovered after completing equilibrium adsorption experiments and recalcined at 500 °C for 4 h. The adsorption efficiencies of phenol using regenerated clay after thermal recycling are shown in Figure 5. The reduction in phenol adsorption over the first 3 cycles was relatively small at 2 % (from 86 % to 84 %). There was a significant decrease in phenol adsorption efficiency of 25 % (from 86 % to 61 %) on the fourth cycle. These showed that thermal regeneration of clay for re-use was only feasible over 3 cycles after which the clay loses its sorption capacity.
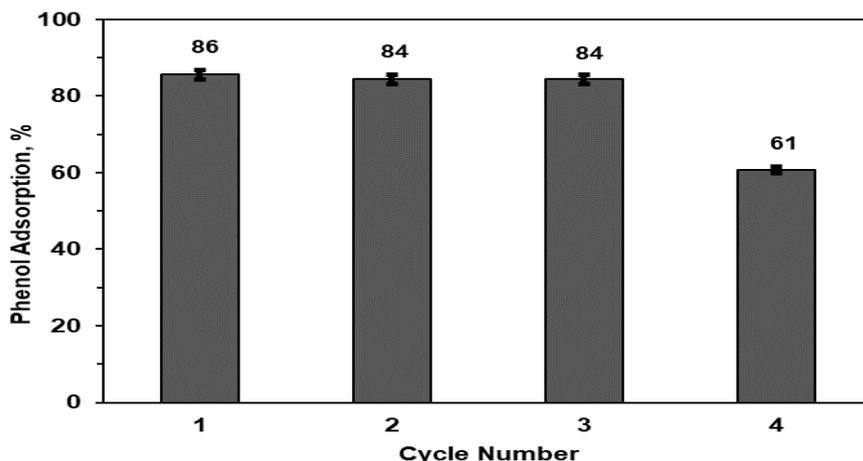
Figure 5. Phenol adsorption efficiencies on regenerated and re-used of clay.

4. Conclusions

Low phenol adsorption efficiencies (< 10 %) were achieved using neat clay due to poor mixing and incompatibility between the inorganic clays and phenolic water. It can be recommended that organo-modified LDH be synthesised to improve adsorption efficiencies of organic pollutants from wastewater. Calcination of the clays at 500 °C resulted in the formation of amorphous mixed metal oxides and an increase in BET surface area by more than 200 % for DHT-4A and Sorbacid 944. The calcined clays exhibited high phenol adsorption of ca. 85 % efficiency within 24 h. The presence of a substantial amount of Zn in Sorbacid 944 was determined to be the cause of an improved phenol adsorption efficiency. Neutral pH was found to be optimum for removal of phenol from wastewater while the clay could be reused for up to 3 cycles.

Acknowledgements

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