

Surface modification of clay soil for heavy metals adsorption: Kinetics and isotherms

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Abstract

Environmental contamination by pollutants such as toxic heavy metals, usually as a result of anthropogenic inputs has become a thing of global concern. The global health problems arising from ingesting and absorbing these toxic metals by human necessitate the quests for designing and developing cheap and efficient materials for removing the pollutants from their respective contaminated media. Kaolinite clay sample collected from Ire-Ekiti southwestern Nigeria was modified using an anionic organic surface active agent (sodium dodecyl sulphate (SDS)) and used to adsorb lead (Pb), chromium (Cr), copper (Cu) and nickel (Ni) from their respective aqueous solution. Batch adsorption experiment was used to study the effects of concentration, pH and agitation time on the adsorption processes. Freundlich, Langmuir and Temkin isotherm models were applied to explicate the adsorption processes while Pseudo-First order, Pseudo-Second order and the Elovich kinetic models were used to predict possible mechanisms driving the adsorption processes. Overall, the results from the present study showed that the optimum condition for removal of the metals (Pb, Cu, Ni and Cr) by the SDS modified clay material was achieved by agitating for 90 min at speed of 200 rpm, concentration of 10 ppm, pH of 5 and particle size of 200 μm using adsorbent dose of 0.5 g at temperature of 298 K. The percentage removal of the metals by the modified clay soil reached the values of 98.53, 94.50, 73.82 and 80.40 respectively for Pb, Cu, Ni and Cr while the adsorption processes were driven by physical mechanisms of adsorption.

Keywords: Surface modification, Kaolinite clay, Ire-Ekiti clay soil, Adsorption kinetics, Adsorption isotherm, Heavy metals.

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Introduction

The contamination of different water bodies by the release of contaminants like heavy metals from different industries and agrochemical wastes has become a growing environmental problem of global concern [1]. Their bio-toxicological potentials, long term environmental persistence and bio-accumulation problems pose a great threat to both man and other forms of life. Concentrations of these of these metals in the aquatic environment beyond the recommendation level may constitute long-term health risks to the ecosystems and humans [2].

Several treatment techniques involving adsorption and other conventional technologies such as ion exchange, chemical oxidation, photo degradation, chemical precipitation, electrochemical treatment, and membrane filtration have been successfully used for removal of heavy metal from their respective contaminated media [3-9]. However, there has been a growing interest in exploration of adsorption technology for decontamination of pollutant laden solutions and this technology has been universally accepted as one of the most efficient and effective pollutant removal processes with other advantages such as ease in handling, low cost, low consumption of reagents, availability of several types of adsorbents as well as ease of recovery and regeneration of spent adsorbents [10-12]. Materials such as animal shells, rubber seed coat and jute fibre have been used as adsorbents for

heavy metals removal [13]. Also, diverse clay minerals, Indian rosewood sawdust, olive stones and pinewood have been reportedly used to scavenge heavy metals from aqueous their respective aqueous solutions [14-19].

Recent decades have seen clay minerals playing important roles in environmental remediation of heavy metals by acting as natural pollutant scavengers, taking up both cations and anions by different mechanisms that include pore diffusion, surface complexation, ion exchange, and direct bonding [9, 20, 21]. Clay minerals can efficiently adsorb heavy metals in their natural forms and their performance efficiencies can be enhanced by surface modification. African countries have several abundant clay deposits [22-24], which could be mined for several industrial applications but these clays are still under-utilized most especially in the areas of adsorption. For instance, Ire-Ekiti clay deposits found in Ire-Ekiti south-western Nigeria have been mined for several industrial applications but no literature has reported the use of the clay for adsorption purposes most especially in industries for treatment of wastewater or remediation of metals contaminated solutions. Also, there are still limited numbers of researches conducted up till date on the efficacy of African clays both in their raw and modified forms for adsorption purposes compared to number of clay deposits in Africa. This immensely necessitates the quest for exploring the heavy metals adsorption potentials of Ire-Ekiti clay, following an initially successful study on the clay in its raw form for heavy metals adsorption reported in earlier

literature [9]. The present study also investigates the possible mechanisms driving the adsorption processes via the kinetics and isotherm studies.

Materials and Methods

Clay sample collection and preparation

An adequate amount of clay soil was collected from Ire-Ekiti, Southwestern Nigeria. The raw clay sample was dried at room temperature for 72 hours, crushed and dispersed in deionized water. Contaminants such as debris from plants were removed by hand picking and also by decantation. The suspension was thoroughly stirred in order to allow none clay materials to further separate from the clay. The clay was recovered from water by centrifuging the suspension at 3000 rpm for 15 min. The recovered clay soil was oven dried at 105 °C for 12 hours; thereafter cooled in a desiccator. The dried sample was pulverized and sieved using a sieve with mesh size 200 µm. The sieved sample was stored in a black polyethylene bag prior to modification.

Metal salts and preparation of adsorbate (metal) solution

Analytical grade reagents (lead nitrate, potassium chromate, copper nitrate and hydrated nickel sulphate) were used to prepare each adsorbate solution. The stock solutions containing 1000 mgL⁻¹ of each metal (Ni, Pb, Cu and Cr) were prepared by dissolving known quantities of the metal salts in de-ionised water and serially diluted to prepare solutions of required concentration for the experimental work. The concentrations of metal in solution were determined by an Atomic Adsorption Spectrophotometer (Agilent AAS 55AA).

Modification of raw clay

The clay sample (350 g) to be used was modified with 0.01 M sodium dodecyl sulphate (SDS) in 0.01 M NaCl solution at pH 5 by agitating for 90 min at 200 rpm on a rotary orbital shaker. The pH of the solution was adjusted using both HCl and NaOH. After agitation, the mixture was centrifuged and the supernatant decanted to collect the residue. The residue collected was washed until the pH reached 6.0, and was dried in an oven at 105 °C for 12 hours. Thereafter, the sample was milled and sieved to obtain the desired particle size 200 µm which was labeled the modified clay material.

Batch adsorption experiments

Adsorption experiment for the modified clay was carried out in batch by adding 50 mL adsorbate solution of 10 mg/L into conical flasks containing 0.50 g of the adsorbent [9]. Each adsorbent and adsorbate mixture was equilibrated at pH 5.0 by shaking at 200 rpm in a temperature (298 K) using a rotary orbital shaker until equilibrium. The pH of each solution was adjusted using drops of HCl and NaOH when necessary. After equilibration, the mixtures were centrifuged for 15 min at 3000 rpm after which the supernatants were collected and analyzed for equilibrium concentrations of the Cu, Ni, Pb and Cr by

Atomic Absorption Spectrophotometer. Effect of pH on adsorption processes was studied at pH 3, 4, 5, 7 and 8 with equilibration time of 90 min. Effect of agitation time on the adsorption process was investigated at time varied between 10 and 80 min at pH value of 5. Also, the adsorption of Cu, Ni, Pb and Cr on the modified clay material was optimized at different concentrations (20, 40, 60, 80 and 100 ppm) with equilibration time of 90 min at pH 5.

Results and Discussion

Effect of pH on the Adsorption Process

Metal	pH	C ₀	C _e	% removal
Pb	3	10	1.783	82.17
	4	10	0.509	94.91
	5	10	0.557	94.43
	7	10	0.814	91.86
	8	10	0.963	90.37
Ni	3	10	5.773	42.27
	4	10	3.01	69.9
	5	10	3.015	69.85
	7	10	4.901	50.99
	8	10	4.644	53.56
Cu	3	10	3.462	65.38
	4	10	1.334	86.66
	5	10	1.253	87.42
	7	10	1.73	82.7
	8	10	1.735	82.65
Cr	3	10	4.715	52.85
	4	10	3.162	68.38
	5	10	1.998	80.02
	7	10	3.621	63.79
	8	10	4.334	56.66

Table 1. Adsorption parameters of the modified clay material as function of pH.

pH of a solution is known to determine the degree of ionization and speciation of metal ions in the solution and it also affects the surface charge of an adsorbent (Osu and Odoemela, 2010). From the results in shown Figure 1 and Table 1, the Optimum adsorption of Cu, Ni and Cr on the adsorbent was achieved at pH of 5.0 while that of Pb was obtained at pH 4.0. These results showed that optimum adsorption could be achieved in acidic media (at pH condition usually greater than 2.0) without chemical precipitation of the hydroxide form of the metals on the surface of the adsorbents. Similar results to these findings have been reported by Erdemoglu et al. and Chaari et al.

Effects of Agitation Time on the Adsorption Process

Metal	Time (Min)	C ₀	C _e	% removal
Pb	10	10	1.243	87.57
	20	10	0.817	91.83
	30	10	0.563	94.37
	40	10	0.621	93.79
	50	10	0.622	93.79
	60	10	0.621	93.78
	70	10	0.621	93.79
	80	10	0.621	93.79
Ni	10	10	5.831	41.69
	20	10	4.16	58.4
	30	10	3.826	61.74
	40	10	3.678	63.22
	50	10	3.474	65.26
	60	10	2.998	70.02
	70	10	2.998	70.03
	80	10	2.998	70.02
Cu	10	10	2.776	72.24
	20	10	2.223	77.77
	30	10	1.149	88.51
	40	10	1.05	89.51
	50	10	1.05	89.5
	60	10	1.05	89.5
	70	10	1.05	89.5
	80	10	1.05	89.5
Cr	10	10	4.726	52.74
	20	10	4.14	58.6
	30	10	3.815	61.85
	40	10	3.321	66.79
	50	10	2.859	71.41
	60	10	2.85	71.5
	70	10	2.455	75.55
	80	10	2.455	75.55

Table 2. Adsorption parameters of the modified clay material as function of agitation time.

Equilibration time for maximum adsorption of Cu and Pb was fast and achieved within 30 and 40 min respectively (Table 2) and the adsorption trend tended to be constant for 80 min. The fast adsorption rate of the metals was probably due to the higher number of available vacant sites for metal binding at the beginning of the adsorption process which became saturated with time.

Saturation of the active sites on the adsorbent's surfaces by the metals accounts for the stability in adsorption rate. Maximum adsorption of Ni and Cr was observed at 60 and 70 min respectively and tended to be stable after this period as there appear not to be available vacant sites for metal binding.

Senthil et al. explained that the progressive increase in adsorption and, consequently, the attainment of equilibrium adsorption may be as a result of limited mass transfer of the adsorbates from solution to the external surface of the adsorbent. Similar results were observed in studies conducted by Bosco et al. and Jaiswal et al.

Effects of Adsorbate Concentrations on the Adsorption Process

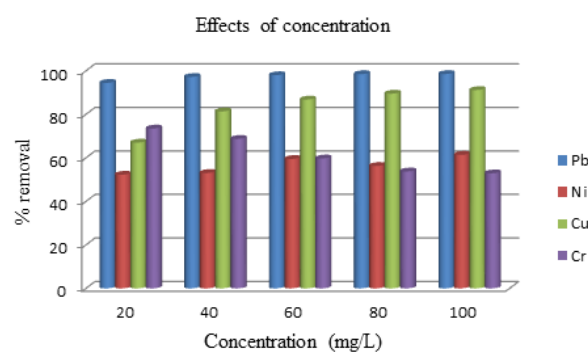


Figure 1. Adsorption trend with increase concentration for Ni, Pb, Cu and Cr.

Metal	C ₀	C _e	% removal
Pb	20	1.111	94.44
	40	1.138	97.16
	60	1.202	97.98
	80	1.233	98.46
	100	1.476	98.52
Ni	20	9.552	52.24
	40	18.789	53.03
	60	24.321	59.47
	80	35.005	56.24
	100	38.655	61.35
Cu	20	6.642	66.97
	40	7.469	81.33
	60	7.924	86.79
	80	8.411	89.49
	100	8.883	91.117
Cr	20	5.307	73.47
	40	22.247	68.72
	60	16.647	59.72
	80	37.01	53.73

	100	48.133	52.87
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Table 3. Adsorption parameters of the modified clay material as function of adsorbate concentration.

Parameters in Table 3 and represented showed equilibrium adsorption trend for of the metals. The results of this study showed increased adsorption of Ni, Pb and Cu with increased concentration. It was observed that increasing the concentration of the metals in their respective solution resulted in higher adsorption of the metals until equilibrium was achieved. This trend was attributed to the fact that when concentration of metals in solution is increased, the trans-boundary movement will be re-initiated, thereby resulting to increased adsorption. Similar findings have been reported in literature for similar and other pollutants adsorption. The effect of concentration on Cr adsorption onto the modified clay showed decreased adsorption of the metals with increased concentration. In support of this result, Akpomie et al. have earlier shown that at low concentrations, more of chromium ions would be removed by the abundant active sites on adsorbents.

Adsorption isotherms

Langmuir adsorption isotherm: The adsorption nature is unfavourable if RL is greater than 1, it is linear if $RL = 1$, irreversible if $RL = 0$, and favourable if $0 < RL < 1$. A negative RL value indicates that the adsorption process does not fits the Langmuir isotherm, hence, cannot be explained by the Langmuir isotherm. This showed that the adsorption processes does not fits the Langmuir isotherm. On the other, the KL value for Cr on the modified clays is 26.88 L/mg. Also, RL value in the range of 3.7×10^{-5} - 1.9×10^{-4} was also obtained for Cr adsorption on the modified clay material. The RL value for chromium adsorption on and modified clay is greater than 0 but less than 1 which implies a favoured Langmuir isotherm; the positive KL values is indicative that the adsorption processes correlates to the Langmuir isotherm. The R2 values for the Cr, Pb, Cu and Ni adsorption onto the modified clay are 0.9538, 0.5119, 0.9215 and 0.9864 respectively. The positive KL values of Cr and other data obtained from all isotherms, showed that chromium adsorption on the modified clay is in best compliance and correlates to the Langmuir isotherm as the negative KL values (Table 2 of other metals showed their unfitness to the isotherm. These results imply a monolayer adsorption of Cr on the clays' flat surfaces. The correlation was not only determined by the (coefficient of determination linear regression coefficient parameter but also the KL value as the R2 value is not enough to describe the fitness and correlation of an adsorption process to Langmuir isotherm.

Linear regression parameter is used to determine the fitness of kinetics and isotherm models. The values of $1/n$ are greater than 1 for Cr, Pb and Cu adsorption by the modified clay material. This indicates that the adsorption processes are cooperative while the adsorption of Ni is more favoured. The R2 values of 0.9895 and 0.9806 were obtained for the Cu and Ni respectively from the Freundlich adsorption isotherm plot.

The adsorption processes of the Cu and Ni on the modified clay fits best to the Freundlich isotherm than other tested adsorption isotherms. This implies that the adsorption process describes a heterogeneous system characterized by multi-layer adsorption on the rough surfaces of the clay material.

	Pb	Ni	Cu	Cr
R2	0.966	0.8927	0.97	0.8648
B	52.11	3.53	26.9	1.546
bT	47.87	7.44×10^2	92.7	1.6×10^3
AT	0.943	1.231	0.16	0.591

Table 4. Temkin isotherm parameters for the modified clay soils.

The following values shown were estimated for the adsorption of Pb on the modified clay: AT = 0.943 L/g, bT = 47.87 and B = 52.11 J/mol. The parameters obtained from all the tested isotherms showed that Temkin plot is the best fitting isotherm for the adsorption of Pb onto the modified clay with R2 value of 0.9655. This implies a monolayer adsorption of the Pb particles in layers on the modified clay whereas the heat of adsorption decreased linearly rather than logarithmic with coverage.

Adsorption kinetics

Pseudo-first-order kinetics: The model was used to show that physical adsorption mechanism was responsible for the metals' adsorption on the modified clay material. Where q_e represents the amount of metal adsorbed at equilibrium, q_t (mg/g.min) represents the amount of metal adsorbed on the surface of the adsorbent at any time t (min and K_1 min⁻¹ represents the equilibrium rate constant of pseudo-first-order adsorption kinetics as given by Lagergren. The rate constant K_1 , was determined from the slope of $\log(q_e - q_t)$ versus time t for plots in which straight lines were obtained. An obtained straight line graph of the plot of $\log(q_e - q_t)$ versus time t obtained as well as closeness in values of q_{eCal} to q_{eExp} , suggests the applicability of the model.

The results of this study showed that straight line graphs were obtained for metals' adsorption on the modified clay material but the values of q_{eCal} were not close to those of q_{eExp} . This suggests that the adsorption processes cannot be explained by the pseudo-first order kinetics model.

Conclusion

The present study has investigated the possible adsorption mechanisms and processes of Cu, Cr, Ni and Pb uptake from their respective aqueous solution using isotherm and kinetic models. Effects of some adsorption parameters on the adsorption process of these metals on the modified clay material were also understudied to understand the nature of the adsorption and for possible applications of the clay material for both industrial and domestic purposes. Findings from this study showed that the adsorption processes of the metals on the

clay material were driven by physical mechanisms which would enhance the regeneration of the adsorbent and possible reuse. The outcome of this study further showed good adsorption efficiency and high rate of removal of the metals by the organically modified clay and hence its applicability for both domestic and commercial purposes for remediation of contaminated aqueous solutions of the investigated metals. We there by recommend further studies on the use of this modified form of clay for removal of other toxic metals from their respective contaminated medium.

Competing interests

The authors declare that there are no competing interests.

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