Thermodynamic Studies on the Sorption of Lead (II), Chromium (III) and Manganese (II) ions onto Acid-Activated Shale

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Authors' Contributions

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ABSTRACT

Shale mineral in its raw form was collected, processed, calcinated and activated using tetraoxosulphate (VI) acid. The microstructural arrangement and chemical composition of the raw, calcinated and acid-activated shale was determined using x-ray fluorescence and scanning electron microscope to verify its ability for the removal of Pb^{2+} , Cr^{3+} and Mn^{2+} from wastewater. Batch experimental method was used to study the effect of different adsorption parameters on the sorption efficiency of shale. The effect of temperature on the sorption of Pb^{2+} , Cr^{3+} and Mn^{2+} on acid-activated shale was investigated at varied temperature of 15 – 40 °C. The calculated value of enthalpy (ΔH°) was 12.50 kJ/mol for Pb^{2+} adsorption, 5 kJ/mol for Cr^{3+} and 11 kJ/mol for Mn^{2+} adsorption. The calculated values of Gibbs free energy (ΔG°) varies from -6.576 kJ/mol to 1.358 kJ/mol for Pb^{2+} adsorptions, from -2.696 kJ/mol to 0.192 kJ/mol for Cr^{3+} adsorptions, and -4.994 kJ/mol to 1.870 kJ/mol for Mn^{2+} adsorptions. The entropy (ΔS°) range is 38.68 – 60.946 kJ/mol for Pb^{2+} adsorptions, 16.69 – 24.58 kJ/mol for Cr^{3+} adsorptions, and 31.70 – 51.10 kJ/mol for Mn^{2+} adsorptions. The positive value of ΔH° shows that the adsorption of Pb^{2+} , Cr^{3+} and Mn^{2+} onto acid-activated shale was an endothermic process. The values of ΔG° are negative at temperature of 298 K and above for the three metal ions studied, which confirmed that the adsorption of Pb^{2+} , Cr^{3+} and Mn^{2+} on acid-activated shale was a spontaneous process. The decline in ΔG° with increasing adsorption temperature showed that adsorptions of Pb^{2+} , Cr^{3+} and Mn^{2+} onto acid-activated shale became better at higher temperature while the positive value of ΔS° for all metal ions studied showed the amplified arbitrariness at the solid-solution interface during the fixation of the adsorbate on the active site of acid-activated shale.

1. Introduction

The economic advancement of a country depends not only on the health status of the people but also on how free the environment is from disease [1]. One of the critical environmental pollution is the continuous discharge of untreated wastewater in our environment. Wastewater is any water, which has been adversely influenced in quality by anthropogenic activities of man. It encompasses liquid waste discharged by residential buildings, commercial estates, industries, and/or agriculture and can involve a broad variety of potential pollutants such as metal ions, which are vital for human beings at low concentrations but they are toxic or even carcinogenic at high concentrations [2].

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The discharge of untreated effluents from different industries comprising mining, fertilizer and pesticide industry has become a major issue of serious concern owing to their high level of toxicity [3-4]. Research into the effective removal of these toxic heavy metals from wastewater is fast growing and has developed into a widely studied area. There are numerous conventional technologies such as chemical precipitation, electrolytic precipitation, solvent extraction, ion exchange and reverse osmosis, have been developed to remove these heavy metals from wastewater [5]. However, these physico-chemical processes have significant shortcomings of being highly expensive and complex. In addition, the chemical by-products from some of this technology can be disruptive to the environment causing harmful effects to plants, animal and even humans [6-7].

Attempts have been made by different scholars to develop alternate low-cost techniques for heavy metal removal [8-11]. Among them, the treatment of wastewaters with activated carbon is considered an effective technique for the removal of metal ions from wastewater [12-17]. An investigation into the performance of cassava peel as adsorbent for wastewater treatment was conducted and reported by Ilaboya et al. [12]. In their study, activated carbon from cassava peel was prepared and characterized for different physico-chemical properties, namely, volatile matter, moisture content, iodine number, methylene blue number, surface area, fixed carbon, micropore as well as total pore volume. The effect of various adsorption parameters such as contact time, adsorbent dosage, and adsorption temperature in addition to the pH were considered to optimize the conditions for the maximum adsorption. The adsorption mechanism was studied with the aid of selected kinetic models (Elovich, pseudo-first order, and pseudo-second order model) while the equilibrium relationship between the amount of lead and copper adsorbed and the amount left in the system was investigated using the popular Langmuir, Freundlich and Temkin isotherm models. To understand the thermodynamics of the adsorption process, the value of the enthalpy (ΔH°), entropy (ΔS°) and the Gibbs free energy (ΔG°) were calculated using simple mathematical equations. Results indicated that the adsorption of copper and lead ions onto activated cassava peels is endothermic in nature owing to the positive value of ΔH° . The computed values of ΔG° were observed to be negative at 298 K and above as anticipated for spontaneous process. The decreasing value of ΔG° with increasing adsorption temperature indicates that the adsorption became better with increasing temperature. The positive value of ΔS° shows the increased variability at the solid-solution interphase during the fixation of the adsorbate ion (copper and lead) on the active site of the adsorbent.

In this paper, adsorption thermodynamic study was done to understand the type and nature of reaction that accompanied the sorption of Pb^{2+} , Cr^{3+} and Mn^{2+} onto acid-activated shale. The objectives were to find out if the reaction was endothermic or exothermic, and spontaneous or non-spontaneous coupled with the degree of randomness associated with the adsorption process. To compute the thermodynamic parameters such as ΔH° , ΔS° and ΔG° , the effect of temperature on the sorption of Pb^{2+} , Cr^{3+} and Mn^{2+} on acid-activated shale was investigated under varied temperature of 15 – 40 °C.

2. Methodology

2.1. Sample Collection and Preparation

Shale was collected from its deposit at Okada (see Fig. A1, Appendix A), Edo State, Nigeria. First, the shale was soaked with 5 % hydrogen peroxide in a plastic container to get rid of any carbonaceous matter, which can interfere with the metal adsorption ability of the shale. Then, it was washed with distilled water before being dried in hot air oven at 50 – 70 °C for 8 h. The dried shale was cut to fine particles and screen sieved with a sieve size of 212 μm before usage [18]. For calcination, 500 g of the processed shale was put in a furnace at 550 °C for 10 h and thereafter placed in a desiccator to cool before use.

For acid-activation, 200 g of the calcinated shale was mixed with 1 liter of 0.25 M sulfuric acid. The mixture was heated at 105 °C for 30 min, slowly cooled, filtered and washed free of acid using distilled water as indicated by a pH meter. The shale was dried at a temperature of 100 °C for 30 – 45 min, ground using mortar and pestle, sieved to 212 μm and stored in a desiccator before use. The acid activated shale was then characterized using scanning electron micrograph (SEM) and x-ray fluorescence (XRF). The list of equipment used in sample preparation and characterization has been described in previous study [19].

2.2. Characterization of Adsorbent

The surface microstructure of the shale was observed using SEM (APEX 3020 PSEM 2). The chemical composition of shale was analyzed using XRF APEX 3022. A mixture (1:1) of 0.025 M solution of hydrochloric acid and nitric acid was prepared. Then, a mixture (1:10) of the solid adsorbent to acid solution was taken and stirred for 30 min. The resulting solution was filtered and the filtrate was utilized for the analysis [20].

2.3. Preparation of Aqueous Solution

The chemicals utilized were analytical grade. Stock solution of lead and manganese were prepared by dissolving correct amounts of $\text{Pb}(\text{NO}_3)_2$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in a liter of distilled water. All working solutions were obtained by diluting the stock solution with distilled water and the concentration of metal ion present in solution was analyzed by the Atomic Absorption Spectrophotometer (AAS).

2.4. Adsorption Analyzes

Adsorption study was performed to determine the effect of adsorption temperature on the sorption of studied metals ions onto acid-activated shale using batch adsorption method. The experiment was carried out at varied adsorption temperatures (288, 298, 303 and 313 K). A 250 ml conical flask containing the adsorbent and 50 ml solution of the aqueous media containing the metal ion was stirred at 150 rpm by a mantle fitted with magnetic stirrer. The pH value of the aqueous media was kept at optimal value for each metal. The separation of the adsorbent from the aqueous media containing the heavy metal was carried out by filtration using 150 mm Whatman filter paper [19]. The filtrate was then stored in a sample can and placed in a refrigerator before analysis. The residual metal ion concentration was deduced using the AAS. The mass balance equation was used to determine the amount of heavy metal ions removed during the series of batch examination as [21]:

$$q = \frac{v}{m} [C_0 - C_e] \quad (1)$$

Where, q (mg/g) defines the metal uptake, C_0 (mg/l) and C_e (mg/l) are the initial and equilibrium metal ion concentrations, v (ml) is the aqueous sample volume and m (g) is the mass of adsorbent used.

2.5. Thermodynamic Studies

Thermodynamic study was done to understand the nature of the reaction, the degree of randomness and the spontaneity of the process involved in the sorption of lead, chromium and manganese ions onto shale. Thermodynamic parameters employed are presented in Table 1. Thermodynamic parameters (ΔG^0 , ΔH^0 and ΔS^0) for Pb^{2+} , Cr^{3+} and Mn^{2+} adsorption onto acid-activated shale were computed from equations presented in Table 1.

Table 1 Definition of selected thermodynamic parameters.

Parameter	Equation	Reference
K_c	$K_c = \frac{K_1}{K_2} = \frac{C_L}{C_s}$	[22]
ΔH^0	$\ln K_c = \left[\frac{-\Delta H^0}{RT} \right]$	[23]
ΔG^0	$\Delta G^0 = [-RT \ln K_c]$	[23]
ΔS^0	$\Delta S^0 = \left[\frac{(\Delta H^0 - \Delta G^0)}{T} \right]$	[22,23]

Where, K_c (gm/g-min) is the adsorption equilibrium constant, K_1 (gm/g-min) is adsorption rate constant, K_2 (gm/g-min) is desorption rate constant, C_L (mg/l) is equilibrium concentration of metal ion in solution, C_s (mg/g) is residual metal ion concentration, R (J/gmol-K) is the gas constant, and T (°C) is the adsorption temperature

3. Results and Discussion

3.1. Adsorbent Characterization

Result of the microstructural and chemical analysis of the raw shale, calcinated shale and acid-activated shale are presented in Fig. 1 and Table 2. SEM result can provide adequate information on the morphology and topological presentations of the shale. Such presentations can also give possible explanations of the solid behavior [20]. SEM was taken to confirm the presence of microspores in the shale structure. It was observed from Fig. 1 that the surface features of the shale materials change severely with calcination as well as acid treatment with the acid-treated shale shows a better irregular porous surface structure. The explanation is that calcination followed by acid treatment tends to open up the pore spaces better than calcination alone. The larger number of microporous structures seen with acid-activated shale indicates a higher surface area. It was observed from Table 2 that silicon oxide and aluminum oxide are the dominant oxides present in shale. The alumina composition of the raw shale was observed to be 21.33 wt%, it increases to 24.41 wt% for the calcinated shale and decreases to 18.13 wt% for the acid-activated shale apparently due to the acid dealumination of the shale resulting from the effects of acidification as relates to the works of [21].

Table 2 Result of Chemical Composition.

Oxides	Raw Shale (Wt. %)	Calcinated Shale (Wt. %)	Acid-Activated Shale (Wt. %)
SiO ₂	49.53	54.47	57.19
Al ₂ O ₃	21.33	24.41	18.13
TiO ₂	1.36	1.18	2.17
Fe ₂ O ₃	2.74	2.09	0.28
MgO	1.73	1.14	1.63
MnO	0.06	0.05	0.04
CaO	2.23	2.03	1.64
Na ₂ O	2.21	1.87	1.56
K ₂ O	2.11	2.26	2.03
P ₂ O ₅	0.54	1.23	0.32
Si/Al ₃	1.581	2.231	3.154

(a)

(b)

(c)

Fig. 1 SEM (a) raw shale (b) calcinated shale (c) acid-activated shale.

3.2. Adsorbent Characterization

The influence of temperature on the sorption of Pb^{2+} , Cr^{3+} and Mn^{2+} on acid activated shale investigated under varied condition of 15 – 40 °C is analyzed in Figs. 2 – 4, respectively.

Fig. 2 Influence of temperature on the sorption of Pb(II) ion onto acid-activated shale at pH of 8, dose 1 g, agitation 150 rpm, and initial metal ion concentration of 5 mg/l.

Fig. 3 Influence of temperature on the sorption of Cr(III) ion onto acid-activated shale at pH of 6, dose 1 g, agitation 150 rpm, and initial metal ion concentration of 5 mg/l.

Fig. 4 Influence of temperature on the sorption of Mn(II) ion onto acid-activated shale at pH of 8, dose 1 g, agitation 150 rpm, and initial metal ion concentration of 5 mg/l.

Results of Figs. 2 – 4, show that temperature variation influenced the amount of Pb^{2+} , Cr^{3+} and Mn^{2+} adsorption, respectively. At high temperature, the diffusion of metal ions through the adsorbent pores was faster and can advance to a greater extent as reported by [11]. The equilibrium constant for the sorption of Pb^{2+} , Cr^{3+} and Mn^{2+} adsorption onto acid activated shale were computed at different temperatures for equilibrium adsorption time of 120 min and result is presented in Table 3. The variation of equilibrium constant with temperature for Pb^{2+} , Cr^{3+} and Mn^{2+} ions adsorption onto acid activated shale is presented in Fig. 5. Results of Fig. 5 showed that adsorption K_C increases with increase in adsorption temperature for Pb^{2+} , Cr^{3+} and Mn^{2+} adsorption thus implying a consolidation of the adsorbate-adsorbent interactions with rising adsorption temperature. Values of ΔH^0 were calculated from the slope of the linear variation of $\ln K_C$ against the reciprocal of adsorption temperature ($1/T$) presented in Fig. 6.

Table 3 Equilibrium constant (K_C) computation for Pb^{2+} , Cr^{3+} and Mn^{2+} adsorption.

Adsorbate	Temp. (K)	C_o (mg/l)	C_e (mg/l)	$(C_o - C_e)$ (mg/l)	$F = \frac{C_o - C_e}{C_o}$	$(1 - F)$	$K_C = \left(\frac{F}{1-F}\right)$	$\ln K_C$
Pb^{2+}	288	5.0	3.19	1.81	0.362	0.638	0.567	-0.567
	298	5.0	2.14	2.86	0.572	0.428	1.336	0.290
	303	5.0	0.63	4.37	0.874	0.126	6.937	1.937
	313	5.0	0.37	4.63	0.926	0.074	12.514	2.527
Cr^{3+}	288	5.0	2.60	2.4	0.48	0.52	0.923	-0.080
	298	5.0	2.09	2.91	0.582	0.418	1.392	0.331
	303	5.0	1.44	3.56	0.712	0.288	2.472	0.905
	313	5.0	1.31	3.69	0.738	0.262	2.817	1.036
Mn^{2+}	288	5.0	3.43	1.57	0.314	0.686	0.458	-0.781
	298	5.0	2.66	2.34	0.468	0.532	0.880	-0.128
	303	5.0	1.89	3.11	0.622	0.378	1.646	0.498
	313	5.0	0.64	4.36	0.872	0.128	6.813	1.919

Fig. 5 Variation of K_C with temperature for Pb^{2+} , Cr^{3+} and Mn^{2+} adsorption onto acid-activated shale.

Fig. 6 Variation of $\ln K_C$ against the reciprocal of adsorption temperature.

Result obtained from the computation of thermodynamic parameters (ΔG^0 , ΔH^0 and ΔS^0) for Pb^{2+} , Cr^{3+} and Mn^{2+} adsorption onto acid activated shale is shown in Table 4.

Table 4 Thermodynamic variables (ΔH^0 , ΔG^0 and ΔS^0) for lead, chromium and manganese ion adsorption onto acid activated shale.

Adsorbate	Temperature (K)	Thermodynamic Parameters		
		ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/k.mol)
Pb^{2+}	288	12.5	1.358	38.680
	298		-0.718	44.357
	303		-4.880	57.358
	313		-6.576	60.946
Cr^{3+}	288	5.0	0.192	16.690
	298		-0.820	19.530
	303		-2.280	24.020
	313		-2.696	24.580
Mn^{2+}	288	11.0	1.870	31.701
	298		0.317	35.849
	303		-1.255	40.444
	313		-4.994	51.098

The positive value of ΔH^0 observed in Table 4 shows that the adsorption of Pb^{2+} , Cr^{3+} and Mn^{2+} onto acid-activated shale was an endothermic process. The values of ΔG^0 are negative at temperature of 298 K and above for the three metal ions studied which confirmed that the adsorption of Pb^{2+} , Cr^{3+} and Mn^{2+} onto acid-activated shale was a spontaneous process. The decline in ΔG^0 with rising adsorption temperature revealed that adsorption of Pb^{2+} , Cr^{3+} and Mn^{2+} onto acid activated shale became better at higher temperature [24]. The positive value of ΔS^0 for all metal ion studied revealed the enlarged variability at the solid-solution interface during the fixation of the adsorbate on the active site of acid-activated shale. Results deduced from this study is in line with the works of Qadeer and Hanif [22], which reported a positive of ΔS^0 for the adsorption of zirconium ions on activated charcoal from aqueous solution.

4. Conclusion

The study was conducted to investigate the potential of using shale as adsorbent for Pb^{2+} , Cr^{3+} and Mn^{2+} adsorption. Results of this study have shown that shale, particularly acid activated and calcinated shale are highly effective for the treatment of wastewater containing Pb^{2+} , Cr^{3+} and Mn^{2+} . The relative abundance of shale within our local environment makes it even better. These will help in addressing the health hazards caused by the occurrence of these metals as well as the difficulties of preparing commercial activated carbon by indigenous industries involved in wastewater treatment. The positive value of ΔS^0 for the three metals ions studied showed the increased randomness at the solid-solution interface during the fixation of the adsorbate ion while the negative values of ΔG^0 at higher temperature showed the spontaneous nature of the process and the dependence of adsorption on temperature.

Appendix A

Fig. A1 A Large Deposit of Shale in Okada.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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