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Thermodynamic Properties of Chromium Adsorption by Sediments of River Watari, Kano State

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ABSTRACT

The adsorption of Chromium from aqueous solution using river Watari sediment as an adsorbent was modeled. The influence of initial pH, solution temperature, adsorbent and adsorbate concentrations on the adsorption efficiency was investigated using batch equilibrium assays. From the results obtained for the adsorption envelop experiments, a good adsorption potential was recorded at initial pH of 2 and a temperature of 25^{o}C. The experimental data obtained was subjected to different adsorption isotherm models including; Linear, Langmuir, Freundlich and Temkin to establish the mechanism of chromium adsorption onto the sediment. Amongst the four models tested, Langmuir gave the best fit with regression values ranging from 0.6494 to 0.7459 for 25^{o}C, 30^{o}C, 40^{o}C and 50^{o}C respectively which suggests a homogeneous surface for the sediment. The isosteric heat (ΔH_r) of adsorption and enthalpy change (ΔH) did not change with temperature also indicating a homogeneous sediment surface. Based on the values of entropies, activation energies and Gibb's free energies obtained, the adsorption was found to be spontaneous at all temperatures.

Keywords: Adsorption, Chromium ion, Equilibrium isotherms, and Sediment.

INTRODUCTION

Transport of reactive solutes through the soil profile into ground water is a major environmental concern. Models that can predict the transport of reactive solutes through the soil profiles are needed. Such models must include the reactions of the solutes in the soil, especially retention/release reactions with soil surfaces (Amacher *et. al.,* 1988). Over the last 30 or so years numerous researchers have attempted to quantify the processes governing the interactions of various solutes with soils (Amacher *et. al.,* 1988). A summary of various solutes reactions and transport models was presented by Travis and Etnier (1981). A general purpose model that describes the reactions of a wide variety of soil solutes would be a valuable predictive tool. Soil sorption controls the persistence, activity and movement of these solute chemicals. When a runoff occurs they are transported from the field in both dissolved and soil adsorbed forms. During the erosion process, the finer soil particles which have the greatest surface/volume ratio are selectively transported as heavier particles settle out, producing sediment that has a higher amount of surface per unit weight than the parent soil. Thus three inter related processes occur during transport (and continue later in channel flow)- sediment loading, solute adsorption/desorption onto the sediment and enrichment in adsorbed solute as heavier sediment particles are left behind (Wauchope and Mc Dowell, 1984).

Dhungana andYadav (2002), observed the determination of chromium in tannery effluent using adsorption of Cr (VI) on saw dust and charcoal from sugarcane bagasses Spectrophotometric method using diphenylcarbazide as a colour developing reagent has been used to analyze the chromium content in tannery effluent located in Bara and Parsadistricks of Nepal. According to Cavaco and Fernandes (2007) who observed the determination of chromium in industrial effluent using removal of chromium from electroplating industry effluents by ion exchange resins, effluent discharged from the chromium electroplating industry contains large number of metals, including chromium, copper, nickel and zinc. The ion exchange process is an alternative technique for application in the treatment of industrial waste water containing heavy metals.

Awan *et al.* (2003), studied the removal of heavy metals (Pb, Cr, Cu and Zn) from their aqueous solutions, using ordinary sand as adsorbent, at 20^{0}C. The amount of metal adsorbed to form monolayer on sand was in the order Pb>Cr>Cu>Zn. The heavy metal sand adsorption phenomena can be illustrated on the basis of the interaction between surface functional group of silicates (sand) and the metals ions.

Xianghua *et al.* (1998), have successfully described metal ion adsorption on pure mineral materials. However, such methods have rarely been applied to model adsorption on natural materials. Three typical versions of the surface complexation model were used: the experimental data of the adsorption edges were used to verify the performance of the models. Lee and Meisel (1982) showed that several negatively charged dyes were investigated for their possible adsorption on the surface of silver and gold colloidal particles. Those dyes that were found to adsorb on the particles were then checked for surface enhancement of Raman scattering. The result showed that the dye was probably aggregated on adsorption.

The objectives of this paper are to describe the mechanism of the adsorption of chromium onto the River Watari sediment and to provide insight into the relative ability of the sediment to act as sinks for water runoff chromium.

MATERIALS AND METHODS

Chemicals of analytical grade purity and de-ionised water were used for the preparation of the reagents. All apparatus were thoroughly washed with detergent solution, tap water and finally rinsed with distilled water.

Sediment Sampling

The sediment samples involved in this work were collected beneath Janguza –bridge along Gwarzo road, Kano State, Nigeria. The samples were collected using an Ekman dredge to a depth of 20cm and 100cm apart along the river course (Wauchope and McDowell, 1984; Wen *et. al.*, 2002).

Sediment Pre-treatment

The samples were mixed, air dried and screened to pass through a 1mm analytical sieve to remove stones, plant root and other large particles. The sieved sample was labeled and stored in air tight poly-ethene bags. Before usage, the sediment samples were subjected to washings with acetone, ethanol, 0.5M NaOH solution and 0.5M HCl solution in order to remove any metal(s) or oxyanion(s) present on the surface of the sediments, and finally with distilled water to stabilize the pH to 7.

Adsorption Envelope

Adsorption experiments was carried out in batch systems to determine the chromium adsorption envelopes (amount of chromium adsorbed as a function of solution pH at fixed total chromium concentration). Sample of sediment was added to 50ml polypropylene centrifuge tubes and equilibrated with 25ml of $NaNO_3$ (1.0M) solution and shaken for 24 hours on a reciprocating shaker at 25^0C. Solid suspension density was 10g/L for the sediment. The equilibrating solution contained 1.0M of $Cr(NO_3)_3$, while the solution was adjusted to the desired pH value (2, 4, 7, 9 and 11) with 0.5M HCl or NaOH using a pH meter. After reaction, the samples were centrifuged at a relative centrifugal force of 7800 x g for 20 minutes. The decantates was analysed for pH, then filtered through filter paper to determine the concentration of adsorbed chromium. The chromium concentration was determined by difference between the amount added and that remaining in the supernatant at equilibrium. The sorption analysis was carried out in triplicate (Su and Suarez, 2000; Goldberg, 2002).

Adsorption Isotherm

Adsorption isotherms of chromium by sediments was evaluated using batch equilibrium assays. Effects of initial pH, adsorbent (sediment) dosage, adsorbate (chromium) dosage, temperature, electrolyte strength and possibly contact time were taken into consideration.

Sediments (1.0 and 2.0g) were weighed into a 25ml corex centrifuge tubes, along with 18ml of water and 2ml of $NaNO_3$ (1.0M) to produce a given ionic strength. The initial pH of the sediment suspension was adjusted to the optimum of 2 (obtained from adsorption envelope) using 0.1M HCl solutions. Equilibrating the sediment suspension took 24 hours. Chromium stock solution as nitrate was then added using a micro syringe to produce an initial chromium concentrations of 1.0M and 2.0M respectively. The contents in the tube were mixed on a rotator for 4 hours at 25, 30, 40 and 50^0C of temperature. The liquid and solid phases were separated by centrifugation at 8000 rpm (RCF=7649 x g) for 10 minutes after measuring the pH of the solution at equilibrium. The chromium concentration was determined by difference between the amount added and that remaining in the supernatant at equilibrium. The sorption analysis was carried out in triplicate (Sheng *et al.*, 1999).

RESULTS AND DISCUSSION

Effect of Initial pH (Adsorption Envelope)

In order to evaluate the effect of initial pH on removal of chromium from aqueous solution, several experiments were performed at initial pH values ranging from 2, 4, 7, 9 and 11 at 25^0C.The amount of the sediment taken was 10g/L. The percentage adsorption was found to increase with decrease in test solution absorbance value. It was also observed that increase in initial pH resulted to a decrease in percentage chromium adsorption onto the sediment with the optimal adsorption occurring at pH of 2 (Table 1). This could be associated to the reason that; of the three most common forms of chromium; Cr(II), Cr(III) and Cr(VI), the Cr(VI) is more common at low pH in form of CrO_4^{2-}. With the protonated hydroxyl groups present on the surface of the sediment, the negatively charged CrO_4^{2-} can easily be adsorbed by the positively protonated sediment surface, thereby increasing the adsorption tendencies of Cr(VI) to the sediment surface as pH drops.

Table 1: Percent adsorption of Chromium at various pH

Adsorption (%)	pH
81	2
72	4
68	7
59	9
39	11

Adsorption Isotherm

The adsorption experimental data were used to describe linear, Freundlich, Langmuir and Temkin isotherm models. The goodness of fit of the experimental data was measured by determining correlation coefficient, R^2 at 25°C, 30°C, 40°C and 50°C respectively. At all the temperatures tested, Langmuir showed better fit followed by linear adsorption isotherm model as shown in Table 2 below. This signifies homogeneity of the sediment surface such that all sites of adsorption have equal energies forming a monolayer and that there is no interaction between the adsorbed chromium ions.

Table 2: Adsorption isotherm at various temperatures

Adsorption isotherm model	Temperature			
	25°C	30°C	40°C	50°C
	R^2			
Linear	0.5912	0.5410	0.4580	0.0370
Freundlich	0.2562	0.7120	0.0880	0.0022
Langmuir	0.7459	0.7217	0.6494	0.0022
Temkin	0.0064	-	0.5044	0.3327

Effect of Temperature

The linear form of the Arrhenius equation $\ln k = \ln A - E_a/RT$ was used to test the effect of temperature on the systems subjected to adsorption experiments. It was found that the percentage adsorption of chromium decreased with increase in temperature, but increased with increase of either the adsorbent mass or chromium concentration. This may be for the reasons that at higher temperature, since the adsorption is physical, results into an increase in entropy weakening the adsorptive forces between the active sites of the adsorbent and the adsorbed species. This may result in the adsorbed molecules desorbing into the aqueous system and therefore decreasing percentage adsorption.

Thermodynamic Parameters

The changes of Gibb’s free energy, enthalpy, entropy and isosteric heats of adsorption were all calculated using the data generated from the experiments and was presented in Tables 3a and 3b respectively. From Table 3a, it can be observed that the values of ΔG were mostly negative, indicating that the adsorption process is spontaneous, while the positive values of ΔS indicated the increase in the randomness of the solid/liquid interface during the sorption of chromium ions onto the sediment. This also favors spontaneity with lower values of ΔH in most of the systems tested and moderate values of the isosteric heat of adsorption (Table 3b), the whole adsorption process can be suggested to be spontaneous and exothermic.

Table 3a: Thermodynamic Parameters (kJ/mol) of Adsorption of Chromium by River Watari Sediment at Different Temperatures

Thermodynamic Parameter(Mass of Sediment/Concentration of Chromium)	25^{o}C	30^{o}C	40^{o}C	50^{o}C
ΔG (1.0g, 1.0M)	-2998	-302.3	-6584	-5935
ΔG (1.0g, 2.0M)	-4014	-4560	-1119	-1155
ΔG (2.0g, 1.0M)	595	2141	-4112	-3142
ΔG (2.0g, 2.0M)	-4484	-5668	156	4458
ΔS (1.0g, 1.0M)	31	30	60	195
ΔS (1.0g, 2.0M)	33	-30.3	-40	-46.1
ΔS (2.0g, 1.0M)	-2.02	-7.1	13	10
ΔS (2.0g, 2.0M)	121	115.1	130	139

Table 3b: Thermodynamic Parameters (kJ/mol) of Adsorption of Chromium by River Watari Sediment at Different Adsorption Systems

Thermodynamic Parameter	Adsorption Systems (Mass of Sediment/Concentration of Chromium)			
	(1.0g, 1.0M)	(1.0g, 2.0M)	(2.0g, 1.0M)	(2.0g, 2.0M
ΔH*	-12.093	-13.743	-8.314	-40.53
A*	1.0492	1.0618	1.0284	1.0387
ΔH_r*	78.89	78.73	78.52	80.02

Average for the four temperatures

CONCLUSION

The maximum removal efficiency of Cr(VI) ion occurs at initial pH of 2 and solution temperature of 25^{o}C.The removal efficiency of Cr(VI) ion increased with increase in adsorbents dosage and Chromium concentrations respectively. The equilibrium removal of Cr(VI) ion decreased as the temperature of solution increases, because the adsorption was physical. The removal of Cr(VI) ion by the River Watari sediments is an exothermic and a spontaneous process.

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