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Adsorption of Cr (VI) and Cu (II) Ions onto Kaolinite Clay

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Abstract :
The sorption of Cr (VI) and Cu (II) ions onto Kaolinite Clay was studied with the aim to compare the affinity of Cr (VI) and Cu (II) ions onto Ahoko Nigeria Kaolinite Clay. The potential of Ahoko Nigeria Kaolinite clay was studied with variation of initial concentration, adsorbent dosage and time. The percentage of removal of Cu (II) and Cr (VI) ions increases with increase temperature and adsorbent dosage. The Langmuir, Freundlich and Temkin isotherm model fitted to the data with Langmuir having the most appropriate fit. The kinetic study shows that it follows the pseudo-second-order model with the adsorbent having better affinity for Cu (II) ion to Cr (VI) ion.

Keywords - *Adsorption, Ahoko Nigeria Kaolinite clay, Isotherms, Kinetics, Pseudo-second-order*

I. INTRODUCTION

The last few decades has witness increased releases of heavy metallic ions to the ecosystem because of rapid industrialization, this has resulted in many adverse effects and obvious concerns globally; principally because of its harmful and deleterious effects in the health and psychology of living organisms especially human being [1]. The utilization of chromium and copper has prevailing industrial applications as antifouling agent in cooling towers, chrome-plating, pigment, textile, and wood preservation, and the by-products and effluents have resulted to pollution of the ecosystem [2]. Cr (VI) is toxic and is believed to be carcinogenic, with adverse effects on circulatory system (Lung), kidney, and the nasal cavity, hence the permissible limit of Cr (VI) in water is 0.05 (mg/L) while it concentration in industrial wastewaters varies from 0.55 to 275 mg/L [3]. Cu (II) ion leads to necrotic alteration in the liver and kidney, gastrointestinal irritation and lung cancer. The permissible limit of Cu (II) in water suitable for drinking should be1.3 mg/dm^3 according to the Safe Drinking Water Act [4].

Many methods and mechanism have been adopted for the removal of deleterious metallic ions from the environment; these include precipitation, co-precipitation, [5, 6], solvent extraction, sedimentation [7], coagulation-flocculation, ion exchange [8], Ultrafiltration, wet oxidation, and adsorption [9]. Adsorption have been utilized as a method of uptake of deleterious heavy metals using activated carbon, molecular sieve carbon [10], zeolites, nanoparticles [4] and other composite adsorbents [11] that have improved capacity for adsorption over a wide range of adsorbates, however, their high cost of preparation and activation process presents a great limitation to their application. Hence there is a need of utilization of materials that have low-cost and are abundant in nature yet possesses excellent properties for adsorption as the above mentioned adsorbents [12]. The application of kaolin for adsorption is because of its low-cost, availability, abundance, shape-selective properties, and pore size has made it an excellent material for adsorption. Kaolinite clay is considered as a good material for adsorption of deleterious metallic ions [5].

II. MATERIAL AND METHOD

A. Kaolinite Clay Collection and Treatment

The kaolinite clay was obtained from Ahoko, Kogi State, Nigeria and was sieved using 250 µm mesh sieve in order to remove some unwanted materials of organic, metallic, and geological origin. 300 g of the kaolinite clay was suspended into a 1500 ml beaker containing distilled water for 6 hours and Moore and Reynolds technique of soil minerals purification was utilized to treat the kaolinite clay. The pre-treated kaolinite clay was allowed overnight after which the supernatant was decanted. The wet clay was then dried in an oven at 373 K.

1000 mg/l of stock solution of copper (II) and chromium (VI) ions were prepared from their respective salts by dissolving them separately in 1dm^3 with deionized distilled water (DDW). The solutions of metal ions of three different concentration of 100, 200, and 400 mg/L were prepared and 0.1 mol/dm^3 of NaOH was used to adjust the pH to about 6.0±0.2.

B. Batch Studies of Chromium (VI) and Copper (II) ion Adsorption Experiments

The adsorption studies were carried out on a batch mode technique at 298 K using different initial concentration of 400, 200, and 100 mg/L of chromium (VI) and copper (II) solutions with 3.0g of chemically-modified kaolinite. 5.0 ml of aliquots of Cu (II) and Cr (VI) at different time interval was centrifuged for 5 min at 5000 rpm. The equilibrium concentrations of both metallic ions at different time interval were analyzed using Atomic Absorption Spectrometer (AAS). The above procedures were repeated at temperatures of 298, 308 and 323 K at different initial concentration of the metallic ion onto the chemically-modified kaolinite clay, to study the effect of temperature on chromium (VI) and copper (II) ions adsorption.

The percentage of metallic ions removal at any time was evaluated using:

$$\text{Metal \%} = \frac{C_0 - C_e}{C_0} \times 100\% \qquad 1$$

Where, Ct and Co are the equilibrium concentration at time t and initial concentration (mg/L) respectively.

The amount of chromium (VI) and copper (II) removed by kaolin was evaluated using:

$$q_e = \frac{(Co - Ce)V}{M(g)} \qquad 2$$

Where q_e represent the amount of the adsorbates removed at time t (mg/L), M is the mass of kaolinite clay (g) and V is the quantity of adsorbates (L).

III. RESULT AND DISCUSSION

A. Kaolinite Clay Characterization

X-Ray Diffraction of the Nigeria Kaolinite clay discloses various peaks which are indicative of the present of minerals in the kaolinite clay sample and a closer observation and analysis reveals that a narrow peak have a low intensity of 2θ = 12.35o (d = 7.15Å).

Detailed analysis of the kaolinite clay sample using X-Ray Diffraction further attested the presence of considerable amount of quartz present at the peak position

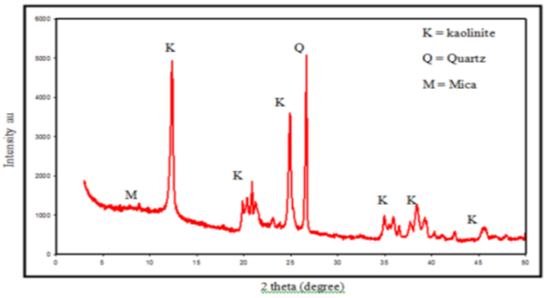

Fig 1: XRD Pattern of the Nigeria Kaolinite Clay Sample

Table 1: Chemical Composition and Physical Properties of Nigeria Kaolinite clay used in this Work

Chemical constituent	Weight %
SiO_2	72.455
Al_2O_3	18.963
TiO_2	0.985
K_2O	0.531
Fe_2O_3	0.9471
Na_2O	0.0210
MgO	0.132
MnO	0.004
LOI[a]	7.170

a Loss on Ignition.

The surface morphology of the modified Nigeria kaolinite clay was analyzed using SEM to clearly validate the effect of refinement of Nigeria kaolinite clay. The images of the Nigeria kaolinite clay sample from SEM shown in figure 2 clearly reveal the notable ordered arrangement of crystalline particles, however, in some areas in the images, there are obvious present of coarser particle fraction which indicates the presents of quartz, this further elucidates that the separation was 100% [13, and 14].

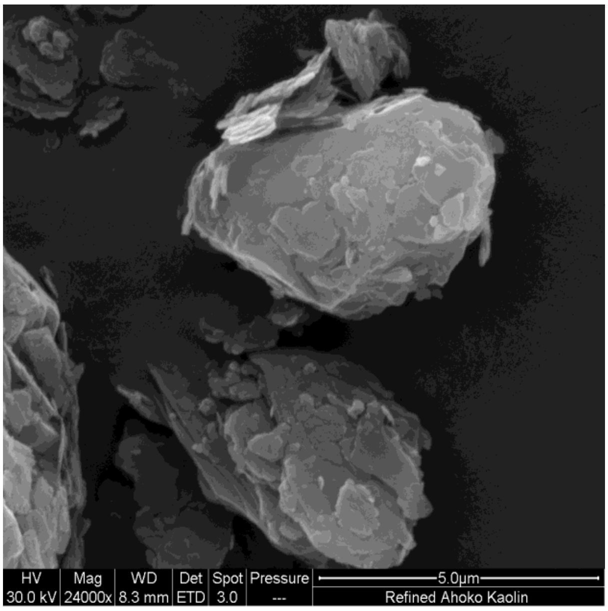

Fig 2: SEM Image of Modified Nigerian kaolinite Clay Sample

B. Sorption Study

1) Effects of Adsorbents Weights

The influence of the amount of kaolinite clay on removal of metallic ion is significant. The amount of Cr (VI) and Cu (II) adsorbed at different adsorbent (kaolinite clay) dosage per unit mass showed that the rate and percentage of the metallic ions removal increase with dosage of adsorbent. When the adsorbent loading is increased from 2 – 5 g/L, the percentage of copper (II) and chromium (VI) ions increase from 94.83 to 99.08 to % and 93.22 to 98.55 % respectively.

2) *Effect of Temperature*

The effect of temperature on Cu (II) and Cr (VI) ions uptake using Ahoko Nigeria kaolinite clay was performed varying two parameters namely: time (10, 20, 40, 60, and 80 Min) and temperature (298, 308, and 323 K) at constant concentration of 400 (mg/L), pH of 6 and adsorbent weight of 3 (g) as shown in Figure 3 and 4. Figure 3 and 4 indicates that the percentage of adsorption of Cu (II) and Cr (VI) ions increase with increase temperature. This influenced the time required to attain sorption equilibrium and indicates the sorption process to be endothermic in nature [15]

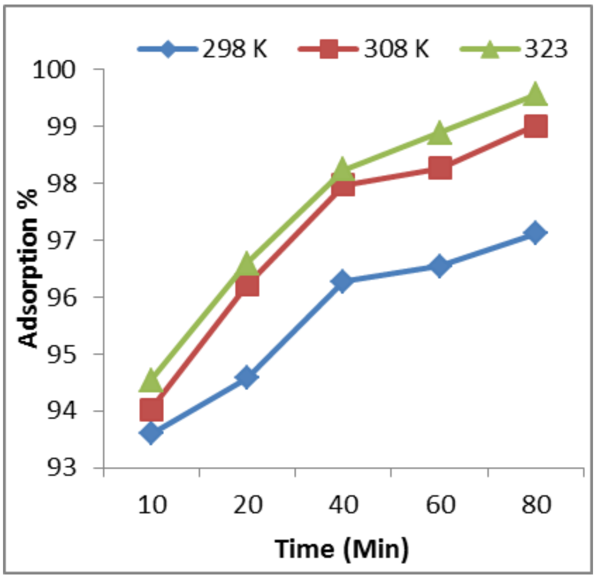

Fig 3: Effect of Temperature and Initial Concentration on Cr (VI) ion uptake onto Kaolinite Clay

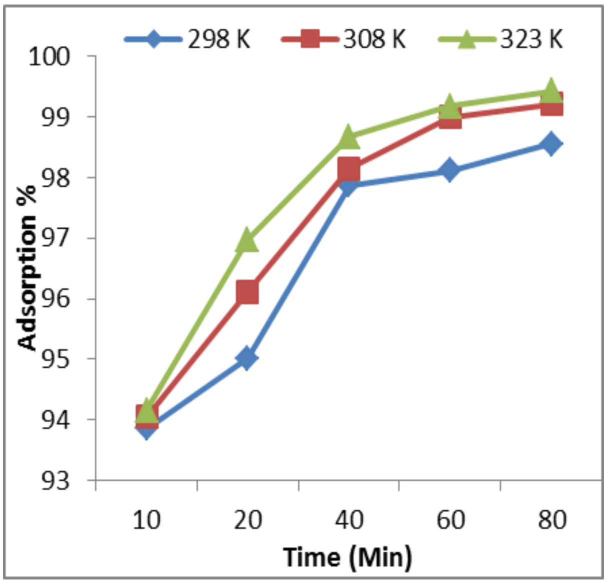

Fig 4: Effect of Temperature and Initial Concentration on Cu (II) ion uptake onto Kaolinite Clay

3) *Effect of Initial Concentration and Contact time*

The impacts of initial concentration and time on uptake of Cu (II) and Cr (VI) ions are shown in (Figure 5 and 6) by altering the contact time and initial concentration at different experimental runs. The plots indicate that the amount and percentage of Cu (II) ion adsorbed is more to that of Cr (VI) ion. Percentage removal increases from 96.64 to 98.56% and 95.22 to 97.61% for Cu (II) and Cr (VI) ions respectively with increasing initial concentration from 100 to 400 mg/g, similar results trend was found by Kovo *et al.*, [5]. The reason may be due to the nature of adsorbents used.

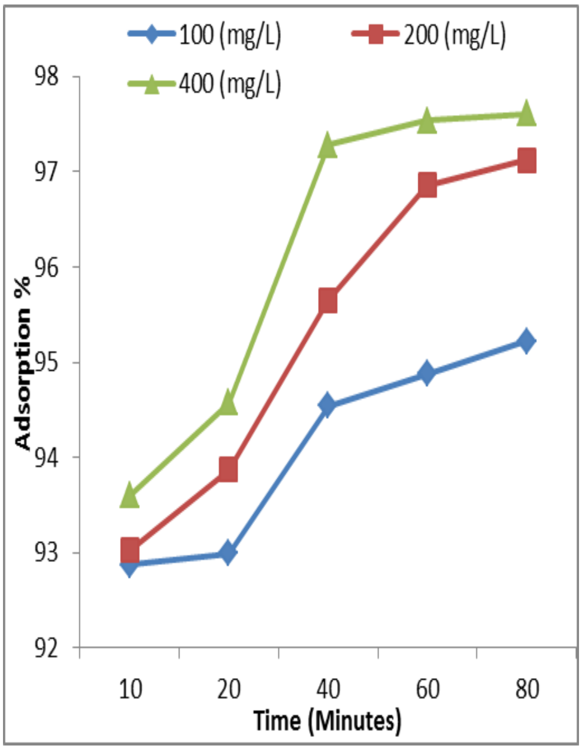

Fig 5: Effect of Initial Concentration of Cr(VI) ion and Contact Time on Adsorption onto Ahoko Nigeria Kaolinite Clay

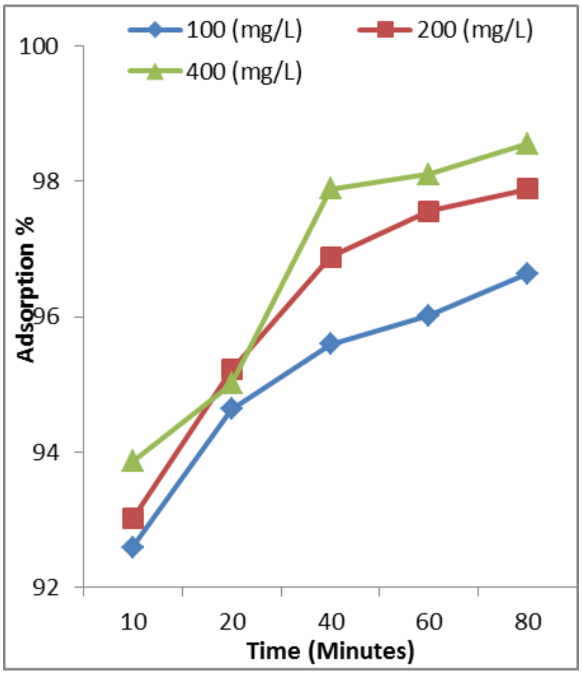

Fig 6: Effect of Initial Concentration of Cu (II) Ion And Contact Time on Adsorption Onto Ahoko Nigeria Kaolinite Clay

C. *Sorption Kinetics*

A kinetics study of adsorption is imperative because adsorption rate and mechanism can be determined from such study. Figure 7 and 8 reveals plots of the quantity of adsorbed as a function of time. The kinetic study was carried out for removal of Cu (II) and Cr (VI) ions at contact temperature of 298K, pH of 6 and mass of adsorbent of 3g with varying time and initial concentration. The rate of adsorption increase rapid in the first 10 minute after which it slows down towards attaining equilibrium, this is in compliance with results reported by [16]. Kinetic models are required to examine the kinetic of adsorption of the metallic ions [17].

After evaluating the equilibrium data, the results reveals that the pseudo-first-order model fitted very poorly to the data after the first 10.0 minutes, however, the pseudo-second-order shown a good fit for all reaction time at different initial concentration as revealed in Figure 5 and 6 for Cu (II) and Cr (VI) ions respectively.

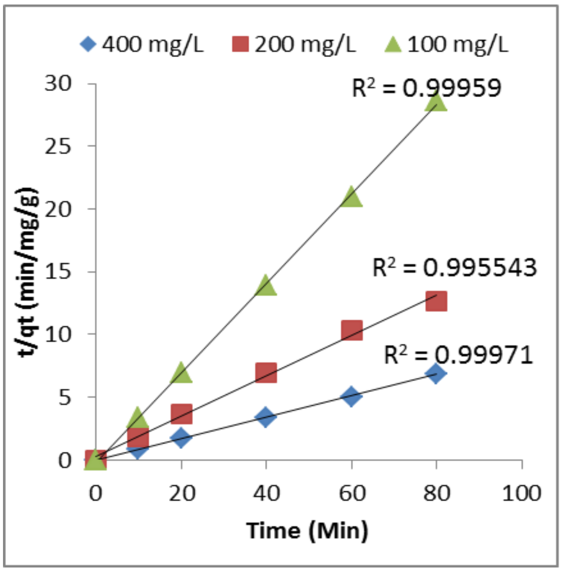

Figure 7: Second-Order Kinetic Plot for Removal Of Cr (VI) Ion onto Nigeria Kaolinite Clay at 298K

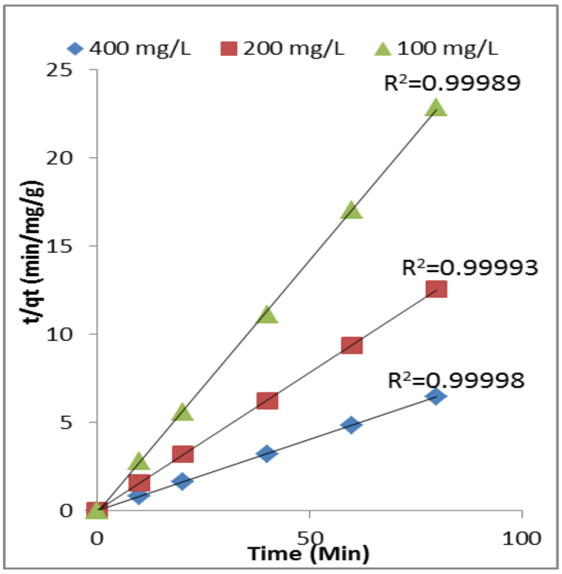

Fig 8: Second-Order Kinetic Plot for Removal of Cu (II) Onto Nigeria Kaolinite Clay at 298K

D. *Sorption Isotherms*

The isotherm study was analyzed using Freundlich, Langmuir and Temkin isotherm model at initial concentration of 400 (mg/L), pH of 6, adsorbent weight of 3 (g) and 298 K,

Table 2

Metallic Ion	Cu(II)	Cr(VI)
Langmuir		
K_L	-0.01687	-0-0045
q_m	11.6299	12.3402
R^2	0.999739	0.999595

Freundlich		
K_f	1.097604	1.099502
1/n	-0.00451	1.11465
R^2	0.22594	0.679941
Temkin		
K_f	7.8182	4.4127
B_T	0.004979	-0.1478
R^2	0.036525	0.293795

The application of the linearized form of the isotherm model of Freundlich, Temkin, Langmuir made it possible to check that these three models were applicable and that the yield of removal of Cu and Cr (VI) ions vary in the same direction with the three models, however, Langmuir have better fitting when compared to the other two. It is also noteworthy that the kaolinite clay has better affinity for adsorption of Cu (II) ion to Cr (VI) ions.

IV. CONCLUSION

The present study indicates Ahoko Nigeria kaolinite clay as a very good adsorbent for uptake of both Cu (II) and Cr (VI) ions from wastewater. The adsorption process was studied with variation of time, temperature, initial concentration and adsorbent dosage. The amount of Cu (II) and Cr (VI) ions adsorbed at different adsorbent (Ahoko Nigeria kaolinite clay) dosages per unit mass showed that the rate and percentage of the metallic ions removal increase with dosage of adsorbent. The data fitted well to all isotherm models, with the three models, however, Langmuir have better fitting compared to the other two. The kinetic study reveals that the that pseudo-first-order model fitted very poorly to the data after the first 10.0 minutes, while pseudo-second-order showed a good fit for all reaction time at different initial concentration. It is also noteworthy that the Ahoko Nigeria kaolinite clay better affinity for adsorption of Cu (II) ion to Cr (VI) ions.

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