



## ADSORPTIVE REMOVAL OF CHROMIUM FROM SIMULATED INDUSTRIAL WASTEWATER USING KAOLIN-BASED ADSORBENT



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**Abstract:** In this study, an adsorbent was developed for the treatment of industrial wastewater using the kaolin sourced from Bauchi, Nigeria. The derived adsorbent was employed in the removal of chromium metal from simulated industrial wastewater. Some batch adsorption experiments were conducted for the treatment of wastewater after which the effects of pH, adsorbent dosage, contact time and initial concentration on adsorption were investigated. The finding from the studies indicated that kaolinite clay is a promising adsorbent for the removal of chromium from wastewater due to its high adsorption capacity. The adsorption process was found to be strongly dependent on the pH of the metal solution and the maximum chromium adsorption was observed at pH 6. In the assessment of concentration effects, 99.77% was found to be the highest removal efficiency. Relatively, required adsorbent dose of 0.20 g. The contact time for effective chromium removal was 30 min.

**Keywords:** Chromium, adsorption, wastewater, kaolin, adsorbent

### Introduction

Heavy metal is one of the important pollutants in water and especially in industrial wastewater, and this has become a public health concern because of its non-biodegradable and persistent in nature. The toxicity of these metals is enhanced through accumulation in living tissues and consequent biomagnification in the food chain (Jiang, 2010). There have been studies on the removal of heavy metals from water and wastewater using chemical precipitation, physical treatment such as ion exchange, solvent extraction, reverse osmosis and adsorption among them, reverse osmosis, although is very effective, it is a cost-prohibitive process as the membranes get easily spoiled requiring frequent replacement (Jiang *et al.*, 2012). Chemical precipitation however is not very suitable when the pollutants are present in trace amounts and a large amount of sludge is produced. Ion exchange is expensive and sophisticated. Solvent extraction or electrolytic processes are also available, but they are cost-effective only for more concentrated solutions (Jiang, 2010).

Natural clays which is readily available have received much attention on heavy metals sorption from contaminated water. Clay minerals have different adsorption capacities for metal ions such as mesoporous silica and montmorillonite clay for Hg(II), which depend on the absorption conditions as they have been found to be very effective, economical, versatile and simple. The removal of metal ions using kaolinite clay is based on ion exchange and adsorption mechanisms and kaolinite has a relative low cation-exchange capacity and smaller surface area ranged from 10-20 m<sup>2</sup>/g (Jiang *et al.*, 2010). A few studies concerning use of kaolinite clay to remove heavy metals from aqueous solution have been reported. Kaolinite clay used to remove Pb(II), Cd(II) and Ni(II) in aqueous medium through the process of adsorption under a set of variables. Similarly, kaolinite has been used as adsorbents for the removal of Fe(II), Co(II) and Ni(II) in aqueous medium and for removal of Cu(II) and Pb(II). In addition, modification of clay minerals can be achieved by either impregnation or grafting of organic/inorganic molecules on its surface to improve its properties, for example, kaolinite clays were modified with orthophosphate and tri-polyphosphate, and 2-mercaptobenzothiazole. Impregnated clay surface was used for the removal of some heavy metal ions from water samples (Jiang, 2010).

Water pollution caused by heavy metal is a serious environmental problem which also has and that employs the use of spent activated clay (Padmavathy *et al.*, 2016) use magnetite injurious effect on health. Hence, the need to

develop a cost-effective means of eliminating or reducing these metals. Many research works have been attempted in identifying some potential material good for the adsorption of this metal. Some of the works are Chih-Huang *et al.* (2007) Nanoparticles; Samson *et al.* (2016) used modified groundnut hull, and other works.

In this study the feasibility of using kaolinite clay as low-cost adsorbent for the removal of chromium (VI) ion from a simulated industrial wastewater was investigated. Also, the work evaluates parameters such as pH, concentration, contact time and varying dosage on the adsorption of chromium ion using kaolin from Bauchi.

### Materials and Methods

The ones used in this research are 0.5 molar concentration of sodium hydroxide, 500 g of Kaolin from Bauchi, De-ionized water, Chromium salt and 2 bags of 0.5 kg sodium chloride (common salt).

The ones employed during course of this experiment are plastic bowl, 15 samples of plastic bottles, a bucket, analytical weighing balance, 125 mm diameter filter papers, 250 mm diameter sieve, jeans material, Edwards BS-2408-G high vacuum pump, 5 x 250 mL beakers, SB 162 STUAT magnetic stirrer, buchner funnel, syringe, stop-watch, Pyrex 250 mL measuring cylinder, pH meter, Thermo Fisher Scientific Heliot<sup>TM</sup> Zeta UV spectrometer.

### Sampling and beneficiation

Bulk sample of the kaolinite clay was collected from Bauchi. Clay lumps was crushed and dispersed in a large volume of water to remove or oxidize any colored organic and inorganic matter in the clay, the suspension was agitated and allowed to stand for 24 h. The clear supernatant liquid was decanted, and the clay re-suspended in a large volume of H<sub>2</sub>O. The process of agitation, decantation and suspension continued for about 3 weeks. The decanted suspension was sieved using a 250 mm mesh and all were followed by re-decantation for 24 h and decanted again. The solute was then almost completely dehydrated using a clear and clean white jeans material for a day. Finally, the clay was spread by air drying. The air-drying process was completed after four days. It was then crushed into fine particle size (Umar, 2014).

### Characterization of clay

The chemical analysis of the beneficiated kaolin was carried out using X-ray fluorescence.

### Ion exchange of Bauchi kaolin with Na<sup>+</sup> (From NaCl)

500 g of Bauchi kaolin (beneficiated sample) was measured, 500 mL of super saturated solution of common salt was

prepared with de-ionized water in a white clear plastic bowl, the kaolin was turned in to the super saturated solution and stirred, re stirred after an hour repeated after 3 h. 20 h later, 1000 mL of the super saturated solution was added and stirred to increase it separation speed. On the 1 h after the volume of the solution was increased, the mixture was stirred later after 3 h. the solution was decanted and replaced with another freshly prepared 1000 mL of the super saturated solution. This step was repeated for 2 rounds before air drying and crushing to get a finely crushed sodium kaolinite.

**Batch equilibrium study**

This technique is applied for the investigation of the different variables on the sorption of chromium ion by Bauchi kaolinite clay. The wastewater was shared into four places for four different analysis which are pH, dosage, adsorption time and concentration where the effect of the parameters on adsorption process were evaluated using the factors' levels presented in Table 1. 0.1 mol of NaOH was used to adjust the pH of the wastewater samples while de-ionized water was used to vary the concentration in % (Shokoohi *et al*, 2009).

Table 1: Factor level for the parametric studies

Factor	Unit	Level	Level	Level	Level	Level
		1	2	3	4	5
Adsorption time	Min	30	60	90	120	-
Dosage	g	0.50	0.10	0.15	0.20	-
pH	-	5.0	6.0	6.6	7.5	9.0
Waste concentration	mg/L	0	25	50	75	100

The adsorption or removal efficiency was calculated using equation (1):

$$\% \text{ removal} = \frac{\text{initial concentration} - \text{final concentration}}{\text{initial concentration}} \times 100\% \quad (1)$$

The adsorption capacities were calculated using equation (2):

$$q_e = \frac{(C_o - C_e)V}{w} \quad (2)$$

**Where:**  $q_e$  = adsorption capacity at time  $t$  (mg/g);  $C_o$  = Concentration of metal before interaction with the beneficiated kaolin (mg/l);  $C_e$  = Concentration of metal after interaction with the beneficiated kaolin (mg/l);  $V$  = Volume of the effluent (ml);  $W$  = Weight of the beneficiated kaolin (g)

The amount of adsorbed metal ions per unit weight of adsorbent at equilibrium concentration is presented in equation (3):

$$q = \frac{(C_o - C_f)V}{w} \quad (3)$$

**Where:**  $q$  = amount of heavy metal (mg/g);  $C_o$  = initial liquid phase concentration (mg/L);  $C$  = final liquid phase concentration (mg/L);  $V$  = volume of the solution (mL);  $W$  = weight of the beneficiated kaolin (g)

The data generated was then used to plot a graph of the percentage removal of chromium against time, dosage, pH and concentration.

**Results and Discussion**

The results of the experiment conducted on the feasibility of Bauchi kaolin is presented in this section.

**Chemical composition of Bauchi kaolin**

The results obtained for the XRF analysis of the Bauchi beneficiated kaolin in Table 2 indicated the chemical composition of kaolin. From which it was identified that that alumina and silica oxides form a larger fraction of the kaolin composition which was found to be similar to the reported by Salahudeen *et al* (2015) kaolin sample collected from Kankara in Katsina State while an insignificant amount of oxides was found for other oxides when compared relatively.

Table 2: Chemical composition of beneficiated Bauchi kaolin

Element	Concentration (wt %)
Na <sub>2</sub> O	0.115
MgO	0.423
Al <sub>2</sub> O <sub>3</sub>	41.086
SiO <sub>2</sub>	53.429
P <sub>2</sub> O <sub>5</sub>	0.344
SO <sub>3</sub>	0.260
Cl	0.000
K <sub>2</sub> O	0.168
CaO	0.074
TiO <sub>2</sub>	2.978
Cr <sub>2</sub> O <sub>3</sub>	0.017
Mn <sub>2</sub> O <sub>3</sub>	0.005
Fe <sub>2</sub> O <sub>3</sub>	1.073
ZnO	0.011

Moreover, Table 3 shows the initial concentration of Cr(+6) in wastewater as 0.0043 mg/L which was the initial aqueous phase concentration.

Table 3: Initial concentration of heavy metal in wastewater

Heavy metal	Initial concentration (mg/L)
Cr(+6)	0.0043

Investigation of parameter effects on the adsorption process

**(a) Effect of initial chromium concentration**

The effect of the concentration of chromium in wastewater is presented in Fig. 1. It indicates that as the concentration increases, the level of chromium removal increases. It can also be said that as the wastewater concentration and chromium removal showed a direct relationship. Fig. 1 presents the effect of the adsorbate concentration on the adsorption of chromium. It is seen that initially, there was a rapid increase in the percentage of chromium ion adsorbed as the concentration of the adsorbate increases from 0 to 100 mg/L. The highest sorption efficiency was found to be 99.77 %.

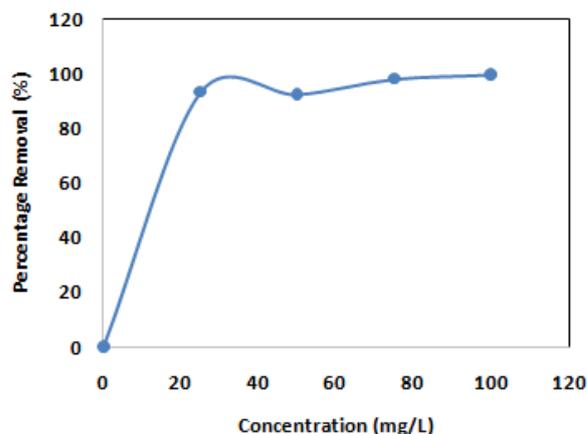


Fig. 1: Effect of initial adsorbate concentration on the adsorption of chromium

According to Sen and Ghosh (2007), this increase in chromium adsorption was due to the large number of sites available for adsorption. And this resulted into a diffusive transport where the chromium ions from region of high concentration in a wastewater solution into the kaolin pores of low concentration. Further increase in the wastewater concentration indicates a decrease to 92.56% at 50 mg/L,

since the kaolin pores becomes more concentrated. In line with the report of Khansaa and Fawwaz (2018), the sorption efficiency that increases with increase in metal concentration to about 99.77% efficiency will imply the process strongly depends on the concentration and other working conditions.

**(b) Effect of contact time**

The effect of change in the contact time on the chromium metal removal in wastewater is presented in Fig. 2 which equally shows that increase in contact time (min) will result in a higher level of heavy metal removal. It can also be said that contact time has a direct relation with the chromium removal rating.

The results in Fig. 2 indicates that increase contact time will always result to an increase in the rate of chromium removal or chromium adsorption which was observed to also increases rapidly. This finding agreed with the reports of Shokoohi *et al.* (2009) and Sen & Dastidar (2010) that indicates increase in contact time yield a significant improvement in the removal efficiency.

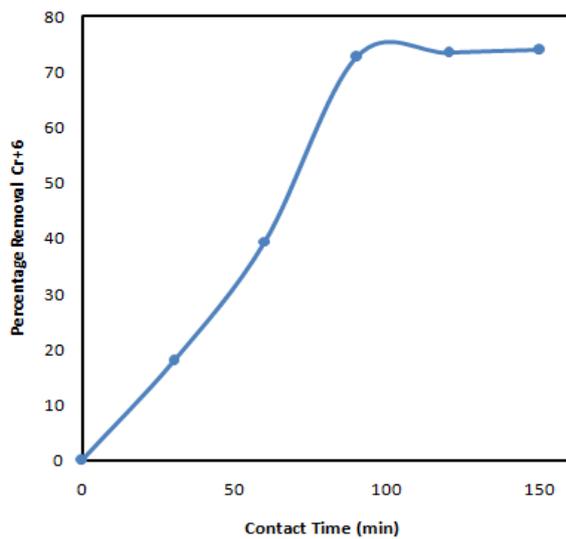


Fig. 2: Effect of contact time on the adsorption of chromium from wastewater

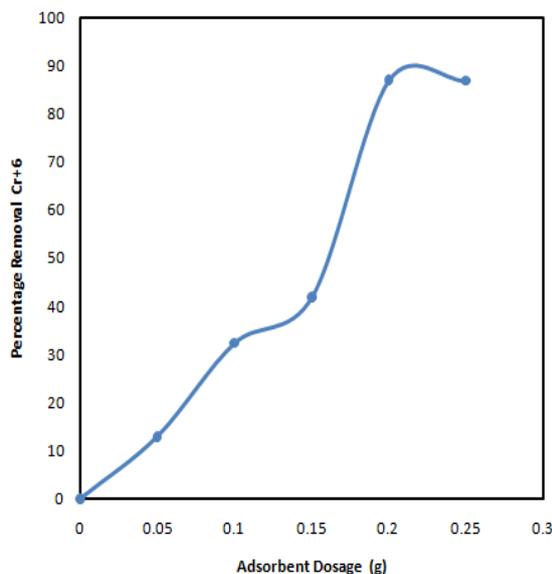


Fig. 3: Effect of adsorbent dose on the adsorption of chromium in a wastewater

**(c) Effect of adsorbent dosage**

The effect of changing dosage of adsorbent was evaluated and the results obtained are presented as Fig. 3, which indicates that increase in adsorbent dosage will yield an increase in the rate of chromium metal removal. The plot equally indicated the presence of direct relation to have existed in between adsorbent dosage and chromium removal parameters. It was also found that dosage of 0.20 g was found to display the highest chromium removal indicating that minimum of 0.20 g dosage will be required to get chromium effectively removed. It seen that from 0.05 to an adsorbent amount of 0.20 g, there was a sharp increase in the percentage adsorbed and then gradual decreases occurs. The decrease in the percentage amount per unit amount of adsorbent is generally observed. This decrease was due to the higher adsorbent amount which creates particle aggregation, resulting into a decrease in the total surface area and an increase in diffusional path length both of which contribute to decrease in the amount of chromium.

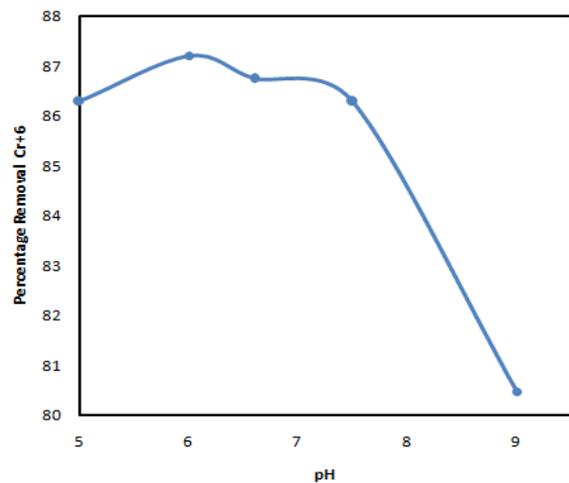


Fig. 4: Effect of pH on the adsorption of chromium in a wastewater

**(d) Effect of pH**

The effect of change in the pH of the wastewater (introduced as a result of the addition of NaOH) on the adsorption process was evaluated and the results obtained are presented in Fig. 4. It can be observed that the best pH is at 6.0 with a percentage removal of 87.20% and least favorable is pH 9 with a percentage adsorption of 80.47%. The percentage of chromium adsorbed is high at lower pH and can be extremely low at basic pH value due to precipitation of chromium hydroxide (Rai *et al.*, 2018), using activated carbon which may have varied characteristics.

**Conclusion**

Chromium adsorption on Bauchi kaolin has been tested under different working conditions including chromium concentration, adsorbent dosage, contact time and pH. The result showed that as concentration of metal ion increased, more surface sites are covered; also decrease in the percentage amount per unit amount of adsorbent is generally observed. The most favorable condition for obtaining high yield was found to be pH (6), contact time (120-150 min), and adsorbent dosage (0.2 g). The result shows that the Bauchi kaolin may be used effectively for the removal of chromium (VI) ions from industrial effluent before discharge.

**Conflict of Interest**

Authors declare that there is no conflict of interest related to this study.

**References**

- Shokoohi R, Saghi MH, Ghafari HR & Hadi M 2009. Biosorption of iron from aqueous solution by dried biomass of activated sludge, Iran. *J. Environ. Health. Sci. Engr.*, 6(2): 107-114.
- Chih-Huang W, Tsai CZ, Chu SH & Sharma YC 2007. Adsorption characteristics of copper (II) onto spent activated clay. *Separation and Purification Technology*, 54(2): 187-197.
- Jiang MQ, Jin XY, Lu XQ & Chen ZL 2010. Adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) onto natural kaolinite clay. *Desalination*, 252(1-3): 33-39.
- Jiang TY, Jiang J, Xu RK & Li Z 2012. Adsorption of Pb (II) on variable charge soils amended with rice-straw derived biochar. *Chemosphere*, 89(3): 249-256.
- Khansaa A & Fawwaz K 2018. Heavy Metals adsorption from aqueous solutions onto unmodified and modified Jordanian Kaolinite clay: Batch and column techniques. *American Journal of Applied Chemistry*. 6(1): 25-34.
- Padmavathy KS, Madhu G & Haseena PV 2016. A study on effects of pH, adsorbent dosage, time, initial concentration and adsorption isotherm study for the removal of hexavalent chromium (Cr (VI)) from wastewater by magnetite nanoparticles. *Procedia Technology*, 24: 585-594.
- Rai MK, Giri BS, Nath Y, Bajaj H, Soni S, Singh RP & Rai BN 2018. Adsorption of hexavalent chromium from aqueous solution by activated carbon prepared from almond shell: kinetics, equilibrium and thermodynamics study. *Journal of Water Supply: Research and Technology-Aqua*, 67(8): 724-737.
- Salahudeen N, Nasiru A, Ahmed AS, Dauda M, Waziri SM, Okonkwo PC & Isa MT 2015. Chemical and physical comparative study of the effect of wet and dry beneficiation of Kankara kaolin. *Nig. J. Techn.*, 34(2): 297-300.
- Samson O, Adedibu C & Tella O 2016. Removal of hexavalent chromium from aqueous solutions by adsorption on milled groundnut hull. *J. Basic and App. Sci.*, 4: 377-378.
- Sen M & Dastidar MG 2010. Chromium removal using various biosorbents. *J. Envntal. Health Sci. & Engr.*, 7(3): 182-190.
- Sen M & Ghosh Dastidar M 2007. Biosorption of chromium by resting cells of *Aspergillus* sp. *Iranian J. Envntal. Health Sci. & Engr.*, 4: 9-12.
- Umar A 2014. *Adsorption of Nickel Ion Using Bauchi Kaolin as an Adsorbent*. [www.tutorvista.com/](http://www.tutorvista.com/) lead (II)nitrate. Accessed on 15<sup>th</sup> September 2011.