

INVESTIGATIVE STUDY ON THE USE OF NEEM LEAVES IN THE ADSORPTION OF CHROMIUM (III) IONS (Cr^{3+}) CONTENT OF INDUSTRIAL WASTE WATER

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Abstract

This research work is being carried out in order to investigate the production of an adsorbent from natural source for the removal of heavy metal ion (Cr^{3+}) contained in an industrial waste water effluent in the Lambun Sarki polluted water in Katsina. In this study, powder *Azadirachta indica* leaves (Neem leaves) have been prepared and used as against the use of activated carbon, silica, alumina etc. as adsorbents for such method of moving heavy metals from industrial effluent such as chemical precipitation, membrane separation, ion exchange which are not only expensive, nor readily available. The equilibrium study were systematically carried out in a batch process covering process parameters such as agitation time, adsorbent dosage, pH of the chromium solution. The effect of the variation of equilibrium agitation time was considered by plotting % removal of Cr against agitation time and found out that as time increases, the rate at which chromium ion is being absorbed by the adsorbent increases indicated a removal efficiency of 89% at 5min and a maximum of 92.5% at equilibrium time of 60min probably due to weak interaction between Cr^{3+} and the adsorbent with constant stirring. The result of varying the adsorbent dosage to give the idea of the percentage removal of Cr^{3+} in 60min agitation time indicated an increase in adsorbent dosage from 89.2%

to 89.4% as the amount of the neem powder increases from 2g to 10g. This is probably due to an increase in surface area of attachment of the Cr^{3+} to the adsorbent whose surface area has been increase due to the large quantity of it being used. The result of the effect of variation of concentration indicate a decrease in % removal of Cr^{3+} from 95.3% to 62.2% as the initial concentration of Cr^{3+} increases from 10mg/L to 50mg/L for 10g of 106 μm size adsorbent at 60min equilibrium agitation time. The result of the effect of pH variation shows that the % removal of Cr^{3+} from the effluent increase from 89.2% to 96.8% for 6g of 106 μm adsorbent with an increase in pH from 2 to 6. Thus adsorption increases with decrease in acidity, since at low pH; H^+ competes with Cr^{3+} ions for sites on the adsorbent.

Based on the above results which shows the maximum % removal of Cr^{3+} as 96.8% (100mg/L), and indication of a higher adsorption of Cr^{3+} heavy metal ion on the adsorbent, there is the possibility of electrostatic interaction or an attraction between the adsorbent and the Cr^{3+} adsorbate. The possibility of the neem leave powder containing higher % of electronegative components and polar groups like $-\text{NH}_2$, $-\text{COOH}$, $-\text{OH}$ etc. providing negative surface charge and making the attraction possible is also thought of in this study.

An Adsorption process is a spontaneous process that is accompanied by a decrease in free-energy ΔG , decrease in randomness of molecules. It is an exothermic process involving an adsorbent/adsorbate interaction (Demirbas, et al., 2004).

In a physical adsorption, there is a weak vanderwaals interaction as the adsorbate molecule become attracted towards the adsorbent molecules. The process is characterized by very low activation energy; it is exothermic, reversible and occurs at lower temperature. The extent of adsorption is said to depend on the nature of the adsorbate. Easily liquefiable gases are readily adsorbed due to their strong vanderwaals forces near the critical temperature.

An adsorption process in which adsorbate molecules bond to the surface of an adsorbent by chemical bonds is called chemisorption. It is a slow process with high activation energy and is an irreversible process. The extent of a chemisorption process increases with an increase in temperature and high specificity (Sharma and Forster, 1994b). And adsorption process can be affected by temperature, pressure, surface area, activation of adsorbent.

Chromium

Chromium is a transition element atomic number 24, in group 6, period 4 and in d-block element, with an atomic mass of 51.99g/mol, electronic configuration $[\text{Ar}] 3d^5 4s^1$, its common oxidation states are +2, +3 and +6, and are used as a powerful oxidant. (Dara, 2006).

Ingestion of chromium into the gastric system causes harmful effects such as nausea, vomiting, severe diarrhea, skin corrosion, respiratory tract and lung carcinoma. It is hazardous to health when its limit in portable water exceeds 0.5mg/l. It exists in compounds like chromium (III) nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, which is green, anhydrous and soluble in water, but decomposes at 100°C . The hydrate form of the chromium nitrate is red-violet with a melting point $36\text{-}37^\circ\text{C}$. It is useful in the production of alkali metal-free catalyst and in pickling (Dara, 2006).

Water Pollution: The presence of *toxic substance* in river, ocean, lakes, and stream cause water pollution as they can get dissolved or lie suspended, or deposited on the bed. This affects the quality of the water by way of deteriorating. Some common sources of water pollution are city sewage and industrial wastes.

Industrial Effluent: An industrial effluent is a form of waste water from an industrial chemical process which can contain low to medium levels of heavy metals. This effluent is often encountered in metal plating facilities, electroplating, mining, battery manufacturing, fertilizers, dyestuffs, electronic device manufacture etc. Industrial effluent can contain specific and readily identifiable chemical compounds.

Heavy Metals: Heavy metals such as pb, Cr, Cu and Zn that are known to be present in industrial effluents in aqueous solution form have been variously studied, and have been removed by processes such as chemical precipitation, membrane separation, ion-exchange, and biomaterial, sawdust, lignin etc. and adsorbed using adsorbents such as activated carbon, silica, alumina which are expensive (Innocent et al 2009, Ibrahim (2011), Guo et al (2008), Gomes et al (2001), Rajmond 2005, Auran et al (2003), Botes and Vanstaden (2005), Xianghua et al (1998). Heavy metals like chromium has been reportedly removed from waste water at various pH and agitation times and different maximum uptake values by adsorbents such as coconut jute carbon (Chand et al, 1994), activated carbon from different materials (Koby, 2004, Hamadi et al, 2001, Mor et al, 2006, Demerbias et al, 2004), Sugarcane bagasse (Sharma and Forster, 1994a), leaf mould (Sharma and Forster, 1994b), Coconut tree saw dust (Selvi, et al, 2001) Eucalyptus bark (Sarin and Pant, 2005), Tamarind hull (Verma, et al, 2006), the adsorbents showed different degrees of versatility and selectivity for the heavy metals presence at various concentrations and pH and various degrees of uptake for the metals.

Neem Leaf: *Azadirachta indica* or neem is grown in India, Pakistan, Bangladesh and Nigeria. It is called Dogon yaro or bedi by the Hausa speaking people of Northern Nigeria. Its fruit and seed are the source of neem oil. The neem plant belongs to the kingdom plantae, Division Magnoliophyta, order Sapindales, family Meliaceae, Genus *Azadirachta* and Specy *Indica*.

Neem powder containing negative surface charges as a result of the presence of polar group like $-\text{NH}_2$, $-\text{COOH}$, $-\text{OH}$ etc. from niacin, praline, glutamic acid, aspartic acid, glutamine, tyrosine and alanine, which then contributes a low electronegativity value of about 35.1% to the neem leaf.

Experimental

Materials

Chemicals of analytical grade purity and distilled water were used for the preparation of the reagents. All apparatus were thoroughly washed with detergent solution, tap water, dil. HNO₃ and lastly with distilled water.

Apparatus

The apparatus used in this work include Beaker (250ml), measuring cylinder (10ml, 100ml), volumetric flask (100ml, 250ml, 500ml and 1000ml), conical flask (250ml), glass funnels, whatman filter papers (125mm diameter), spatula, glassrod, weighing balance (mark 8055), pH meter (Jenway 3320 model), handgloves, and Atomic absorption spectrophotometer (AAS 210 BJ model).

Reagents

The reagent used in this investigation includes Hydrochloric acid, sodium hydroxide, nitric acid and chromium nitrate.

Method (1)

Collection of Adsorbent

The mature neem leaves used in this work collected from available neem trees at the Federal College of Education, Katsina.

Preparation of Adsorbent

The neem leaves were washed thoroughly with water to remove dust and any water soluble impurities that may be present on the leave and were dried until the leave become crisp.

The dried leaves were powdered and further washed with distilled water until the washings were free of color and turbidity. The powder was then dried and sieved to 106 μ m size and were kept in glass bottles for subsequent use.

Reagent Preparation

Preparation of 0.1M HNO₃

3.5cm³ concentrated HNO₃ was measured into a 500cm³ of distilled water in a 1000cm³ volumetric flask. After thorough shaking, the solution was made up to mark with more distilled water.

Preparation of 1000mg/L of Cr (III) solution.

This was prepared by measuring 2.73g of Cr (NO₃)₃ and dissolved in 100cm³ of 0.1M HNO₃ in a beaker. The resulting solution was then transferred into a 1000cm³ volumetric flask and made to the mark with distilled water.

Preparation of Intermediate stock solution of 100mg/L

This was prepared by measuring 10cm³ of the 1000mg/L Cr III solution into a 100cm³ volumetric flask, and then made up to the mark with distilled water. Working standards of 1, 2, 3, 4 and 5mg/L were prepared by serial dilution.

Preparation of 0.5M hydrochloric acid.

4.2cm³ of concentrated HCl was measured and added to some quantity of distilled water in a 100cm³ measuring cylinder, and the resulting solution made up to the mark using distilled water.

Batch Studies

In batch (static) adsorption studies, the same solution remains in contact with a given quantity of adsorbent. As the amount of adsorbate adsorbed on the adsorbent increases, the adsorbate concentration in the solution reduces. The driving force for the adsorption decreases with time and accompanied by a reduction in the adsorption capacity. The adsorption process continues until equilibrium between the adsorbent being adsorbed and the adsorbent per unit weight of adsorbent is reached. The equilibrium established is static in character, as it does not change further with time (Rajgopal and Kapoor, 2001).

The percentage removal were elucidated from the relation,

$$\frac{C_o - C_e}{C_o} \times 100.$$

Where C_o , C_e are the initial and final adsorbate concentrations (in mg/L) respectively (Bhattacharya et al., 2008).

Variation of Agitation Time.

The variation of agitation time was conducted by weighing about 2g of Neem leaf powder into a conical flask, followed by the addition of 100cm³ of the 100mg/L chromium nitrate solution.

The resulting mixture was agitated for 5min, and the content was filtered. The filtrate was analyzed for residual chromium using AAS. The procedure was repeated with fresh mixtures for agitation periods of 10min, 15min, 30min, 45min, 60min and 90min respectively.

The results are shown in Table 1.

Variation of Adsorbent Mass.

Adsorbent masses (2, 4, 6, 8 and 10g) were carefully weighed on a balance and transferred into separately labeled conical flasks. 100cm³ of the 100mg/L chromium nitrate solution was added to each of the conical flasks. The mixtures were agitated for 1hr, followed by their filtration, and the filterates analyzed as in 2.6.1. The results are shown in Table 2.

Variation of increase in concentration.

10,20,30,40 and 50mg/L of the adsorbate were measured and transferred into separate beakers containing 4g of adsorbent each. The mixtures were agitated for 1hr, after which they were filtered and the filterates analyzed as in 2.6.1 and 2.6.2 above the result are shown in Table 3.

Variation of pH.

The pH variations were studied by measuring 100cm³ of 100ppm chromium solutions adjusted to pH 2, 4, 6, 8 and 10 using 0.5M HCl and NaOH and transferred into separate volumetric flasks each containing 4g of the adsorbent. The mixtures were filtered and the filterates were then analyzed using AAS. The results are shown in Table 4.

Results and Discussion

Result

Table 1: Variation of Agitation Time with Adsorbate concentrations.

Agitation time (min)	Residual Conc. (c _t /mgL ⁻¹)	C _o - C _e
0	10	10
5	4	6
10	2	8
15	1.8	8.2
30	1.5	8.5
45	1.5	8.5
60	1.5	8.5
90	1.6	8.4

Table 2: Variation of Adsorbent Mass

Adsorbent Mass (g)	Residual Conc. (c _t /mgL ⁻¹)	C _o - C _e
2	2.16	17.84
4	1.80	18.20
6	1.52	18.48
8	1.18	18.82
10	0.32	19.68

Table 3: Variation of increase on Adsorbate concentration

Concentration (mg/L)	Residual Conc. (c _t /mgL ⁻¹)	C _o - C _e
10	0.47	9.53
20	1.50	18.50
30	3.30	26.70
40	11.84	28.16
50	18.65	31.35

Table 4: Variation of change in pH

pH	Residual Conc. (c _t /mgL ⁻¹)	C _o - C _e
2	2.16	17.84
4	1.54	18.46
6	0.64	19.36
8	1.16	18.84
10	1.90	18.10

3.2 DISCUSSION

3.2.1 CALIBRATION CURVE

The calibration curve is obtained by making 0, 1, 2, 3, 4, 5 mg/L of the chromium solution from the stock solution using serial dilution. The absorbances of these solutions were measured using AAS.

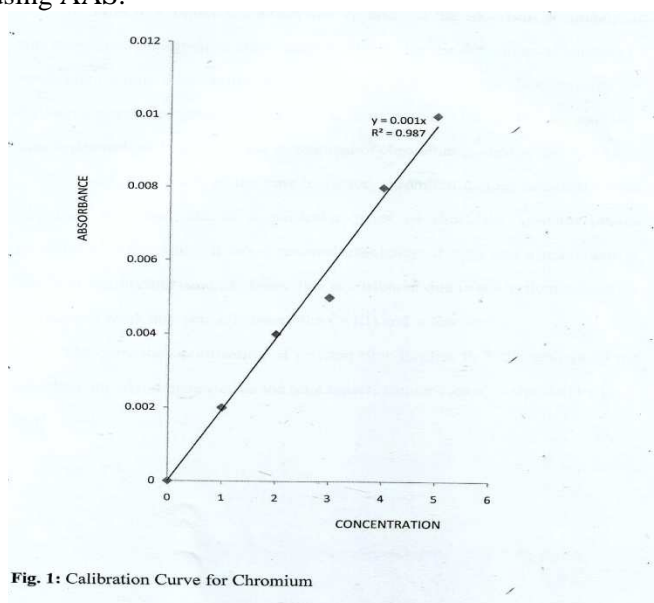


Fig. 1: Calibration Curve for Chromium

Variation of Agitation Time

In order to estimate the adsorption capacity of the adsorbent accurately, it was very much important to allow significant time for the experimental solution to attain equilibrium. Equilibrium agitation time is defined as the time required for the heavy metal concentration to reach a constant value. The equilibrium agitation time is determined by plotting the % removal of chromium against agitation time.

From fig. 2 below, as the time increases, chromium getting adsorbed by the adsorbent increases, but at a particular point of time, the solution attains equilibrium. After 5min, it has a removal efficiency of 89% and a maximum of 92.5% at equilibrium time of 60min. this is attributed due to the system's constant stirring and weak interaction between the Cr (III) and adsorbent.

Therefore the optimization of resident time implies that, the amount of the adsorbent metal ion increased as the time lapses, similar case was reported by Garg *et al.*, 2004.

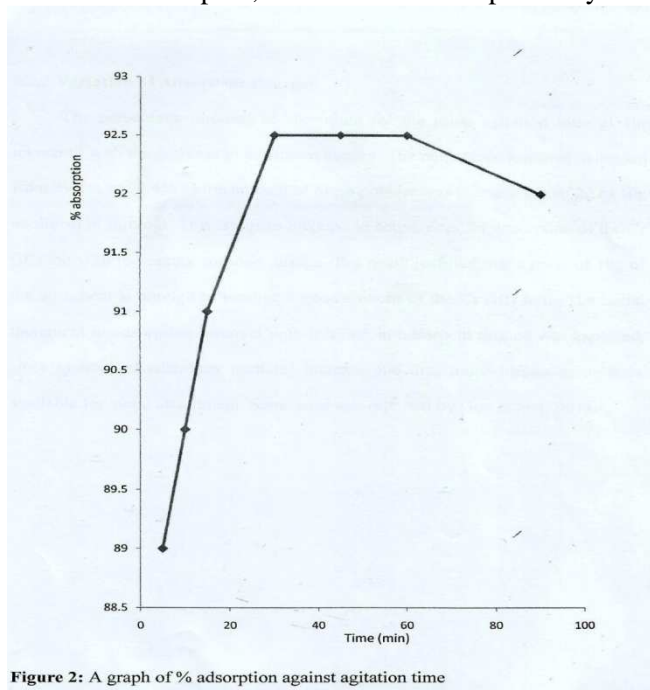
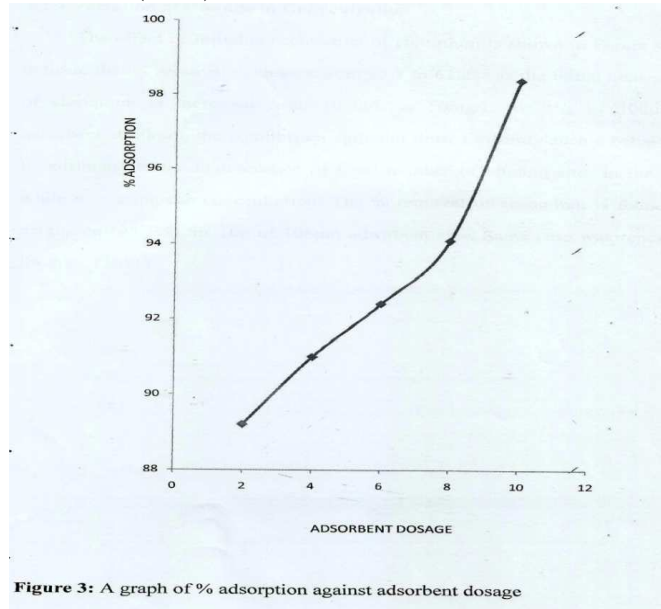


Figure 2: A graph of % adsorption against agitation time

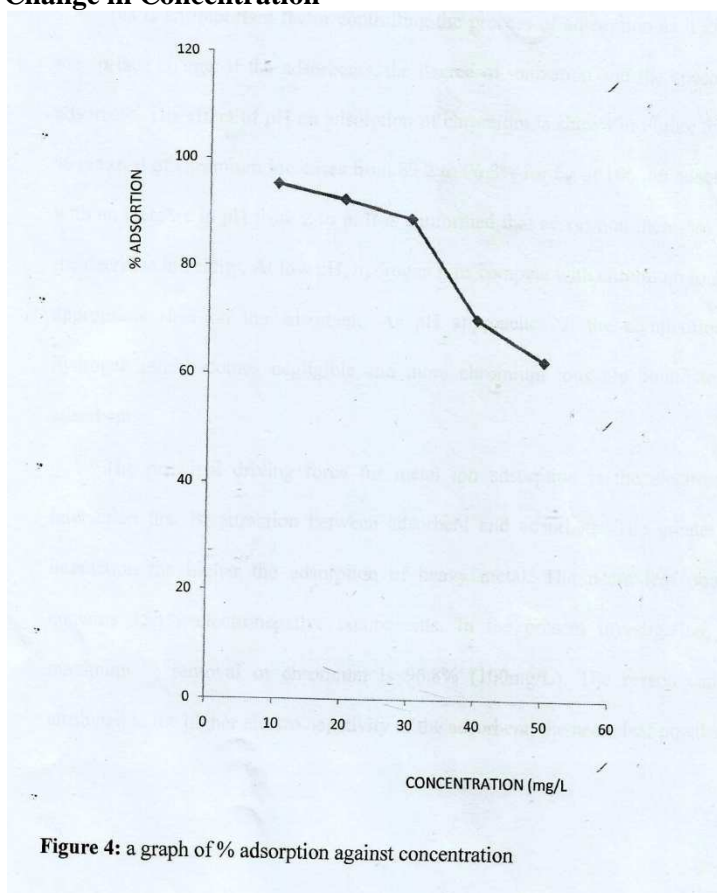
Variation of Adsorbent Dosage

The percentage removal of chromium for the same agitation time of 1hr increased with the increase in adsorbent dosage. The percentage removal increased from 89.2% to 98.4% as the amount of neem powder was increased from 2g to 10g as shown in figure 3. This is due to increase in active sites for adsorption of the Cr (III) ion with increasing dosage. The result justified that a mass of 10g of the adsorbent is enough to remove a good amount of the Cr (III) ions. The initial increment in adsorption removal

with increase in adsorbent dosage was expected, since number of adsorbent particles increase and thus more surface areas were available for metal attachment. Same case was reported by Guo *et al.* (2001).



Variation of Change in Concentration



The effect of initial concentration of chromium is shown in Figure 4 which indicates that % removal decreases from 95.3 to 62.2% as the initial concentration of chromium is increased from 10mg/L to 50mg/L for 10g of 106µm size adsorbent at 60min, the equilibrium agitation time. Evidently such a behavior can be attributed to the maintenance of fixed number of binding sites in the dosage while increasing the concentration. The % removal of chromium is found to be maximum (95.3%) for 10g of 106µm adsorbent size. Same case was reported by Ibrahim, (2011).

Variation of Change in pH:

PH is an important factor controlling the process of adsorption as it affects the surface charge of the adsorbents, the degree of ionization and the species of adsorbate. The effect of pH on adsorption of chromium is shown in Figure 5. The % removal of

chromium increases from 89.2 to 96.8% for 6g of 106 pm adsorbent with an increase in pH from 2 to 6. It is conformed that adsorption increases with the decrease in acidity. At low pH, hydrogen ions compete with chromium ions for appropriate sites on the adsorbent. As pH approaches 7, the competition of hydrogen ions becomes negligible and more chromium ions are bound to the adsorbent.

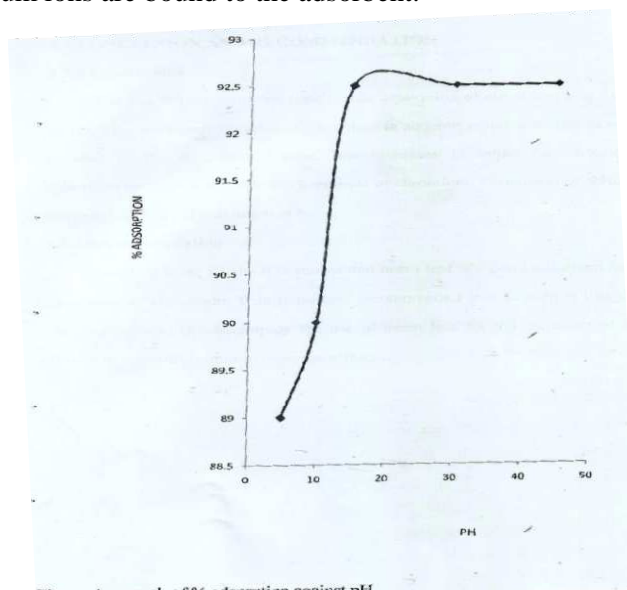


Figure 4: a graph of % adsorption against pH

The principal driving force for metal ion adsorption is the electrostatic interaction that is, attraction between adsorbent and adsorbate. The greater the interaction, the higher the adsorption of heavy metals. The neem leaf powder contains 35.1% electronegative components. In the present investigation, the maximum % removal of chromium is 96.8% (100mg/L). The reason can be attributed to the higher electro negativity of the adsorbent, the neem leaf powder.

Conclusion and Recommendation

Conclusions

The equilibrium agitation time for the adsorption of chromium was found to be 1hr. The percentage removal of chromium in aqueous solution increased with an increase in the adsorbent dosage. The increases in initial concentration of chromium result in a decrease in % removal of chromium. % removal of chromium increased up to a pH maximum at 6.

Recommendation

Based on these results it is shown that neem leaf is a good adsorbent for the adsorption of chromium. It is therefore, recommended that industries that deals with heavy metal should employ the use of neem leaf for the treatment of their effluent to remove chromium from the effluent.

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