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Investigative Study on the Detoxification of Chromium III Ion (Cr^{3+}) Polluted Water Using Neem Leaves as Adsorbent

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Abstract. This research work is being carried out in order to ascertain the presence and level of dissolved chromium III ion (Cr^{3+}) in water, vegetables and soil of farm land and to investigate the production of an adsorbent from natural source and its use for the removal of the metal ion (Cr^{3+}) from the affected water. The presence and level of dissolved chromium III ion (Cr^{3+}) in the water, vegetable and the soil samples were ascertained using simple qualitative test and AAS (Atomic leaves) respectively.

Powdered Azadiracta indica leaves (Neem leaves) were prepared and used as adsorbent as against the use of activated carbon, silica, alumina etc.

The equilibrium study was systematically carried out in a batch process covering process parameters such as agitation time, adsorbent dosage and pH of the chromium solution. The effect of the variation of equilibrium agitation time was considered by plotting % removal of Cr^{3+} against agitation time and found out that as time increases, the rate at which chromium ion is being adsorbed by the adsorbent increases, indicating a removal efficiency of 89.2% at 5min. for the water 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 adsorption from 89.2% to 89.4% as the amount of 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 increased due to the large quantity of it being used. The results 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 106µm, size adsorbent at 60min equilibrium agitation time. The results of the effect of pH variation shows that the % removal of Cr^{3+} from the water increases from 89.2% to 96.8% with 6g of 106µm adsorbent for an increase in pH from 2 to 6. Thus adsorption increases with decrease in acidity, since at low pH, H+ competes with Cr^{3+} for sites on the adsorbent.

Based on the above results which show the maximum % removal of Cr^{3+} higher adsorption of Cr^{3+} heavy metal ion on the adsorbent, there is the possibility of electrostatic interaction or attraction between the adsorbent and Cr^{3+} adsorbent. The possibility of the neem leaves powder containing higher % electronegative components and polar groups like –NH_2 –COOH, OH etc., providing negative surface and making the attraction possible is also thought in this study.

From the results of the AAS and the qualitative test on the soil and vegetable samples, the presence of (Cr^{3t}) was confirmed though at a low level of 0.000352 ppm and 0.000537 ppm respectively for each of the samples.

Keywords: Neem leaves, Chromium III, Chromium vi, Detoxification and Electrostatics

Introduction

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/adsorbent interaction (Demirbas et al., 2004).

In a physical adsorption, there is a weak vanderwaals interaction as the adsorbent 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 adsorbent. Easily liquefiable gases are readily adsorbed due to their strong vanderwaals forces near the critical temperature.

An adsorption process in which adsorbent 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 & Forster, 1994). 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 [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/i. It exists in compounds like chromium (III) nitrate Cr (NO3)3 $9H_20$, which is green, anhydrous and soluble in water, but decomposes at 100°C. The hydrate from of the chromium nitrate is red-violet with a melting point 36-37°C. It is useful in the production of alkali metal-free catalyst and in pickling (Dara, 2006).

Chromium Determination by Spectrophotometric Method

The diphenylcarbazide method involves the formation of a purple-red complex of chromium (VI) with 1,5 diphenylcarbazide in the acid medium. Its molar absorption coefficient at ƛ545 nm is 4.3×10^4. The obtained color is a result of a reaction of chromium (III) in statue nascendi, still not hydrated with water molecules, produced in the process of the reduction of Cr^{6+} with 1.5- diphenylcarbazide which is at the same time oxidized to form the diphenylcarbazone.

Oxidation of Cr^{3+} to $Cr_2O_7^{2-}$ is of key importance in the determination of chromium by this method. The following compounds are often used as oxidizing agents: sodium peroxide, hydrogen peroxide, chloric (VII) acid, bromine, sodium bismuthate (V), ammonium peroxydisulfate (VI) and potassium manganate (VII).

The acidity of the analyzed solution influences the intensity of the color, so it should be maintained at the same level. The recommended pH is about 1-2 since it ensures high sensitivity of the reaction. The color is stabilized by the presence of phosphates (V).

The diphenylcarbazide method of determination of Cr^{6+}can be considered selective. The determination is disturbed only by Fe, V. Mo and Hg ions if their amount considerably exceeds the amount of chromium. Higher amounts of Fe^{3+} are masked by the addition of orthophosphoric (V) acid or sodium versenate. It can also be separated by extraction or in the form of Fe $(OH)_3$. Vanadium should be separated prior to chromium determination if its amount is 10 times higher than the amount of chromium. After the oxidation of chromium, 8-hydroxyquinoline (pH=4) is added and vanadium is extracted with chloroform. At the same time, iron, molybdenum and copper oximes are extracted. The disturbing molybdenum is masked with oxalic acid. The addition of chlorine is bound with Hg^{2+} to form a non-dissociated $HgCl_4^{2-}$ and prevents a reaction between mercury and diphenyl carbazide. The method is very sensitive, so it can be used for the determination of very small amounts of chromium in biological samples, water, industrial waste water and minerals (Kamburowa, 1993; Mocák, Vaníčková, & Labuda, 1985).

Soil Sampling and Mineralization

The primary soil samples would be collected according to the recommended standard by means of a soil sampler from the surface layer of soil (0-20 cm). After drying them in air. laboratory samples would be prepared. Total chromium would be determined in the mineralized soil samples. Mineralization of the laboratory soil samples would he clone by the following methods;

i. *Digestion (Method A)*

0.5 g of the dried (105 °C) sample would he digested with 6 cm3 of concentrated HNO_3 and 2 cm^3 of concentrated HCI in closed polytetraf1uoroethylene (PIFE) vessels in a microwave oven. After digestion the solution with a solid phase would he placed into the $100cm^3$ volumetric flask, filled to the mark with deionized water and filtered through a filter paper to polyethylene (PE) bottle (Poznan, 1997).

ii. *Digestion Method B (wet acid digestion in an open system)*

Soil sample would be dried to constant weight at 105 °C. Then 1 g aliquot of each sample would be digested using a mixture of 12 cm^3 HNO_3 and $4cm^3$ HCI. Samples would be boiled for 2hrs in covered beakers on a hot plate. All solutions with undisclosed residual phases would then be transferred into the 100 cm volumetric flasks and filled to the mark with deionized water followed by filtration through medium filters as above to the PE bottles. In order to plot the calibration curve 0.0, 0.2, 0.4, 0.8, 1.4, 2.0,3.0,4.0, and 5.0 ml of the working Cr^{6+} solutions would be measured in turns into 50 ml flasks, which corresponded with the Cr^{6+} content in a sample ranging from 0.0 to 0.025 mg. 1.0ml of H_2SO_4 (1:1) and 0.3 ml of concentrated H_3PO_4 would be added and the solution diluted with distilled water up to the mark. After 5 minutes, 1.0 ml of 1,5- diphenylcarbazide would be added to each sample. After another 10 minute, the absorbance of the solutions would then be measured in 5 cm cells at analytically determined wavelength (say ƛ=543.5 nm) against black test. The dependence between the concentrations would be ascertained.

Determination of Cr^{3+} in Soil Samples

A similar procedure would be adopted to determine the content of chromium in the soil sample: 0.1ml of mineralized soil would be added to the flasks. Since chromium can occur in different oxidation states, ammonium sulfate (Mol ut 228.18g/mol) $(NH_4)_2\ S_2\ O_8$ would be added as an oxidizing agent, which guaranteed that chromium us present in the solutions only in the form of $Cr_2O_7^{2-\cdot}$ Since Cr^{3+} is unstable and quickly oxidized to $Cr6^{+}$. The content of chromium in the soil would then be calculated according to the following equation (Jankiewicz & Ptaszynski, 2005):

$$X = C_x \frac{1000V_1}{V_2M}$$

where x = the content of Cr in the soil [ppm]
C = the concentration of the metal read on the calibration line [mg]
Vi = the total volume of the mineralized or extracted soil sample [ml]
V2 = the volume of the soil solution used for the analysis (ml)
m = the weighed portion of soil used for mineralization

Chromium Determination by Flame Atomic Absorption Spectroscopy (FAAS) Method

Chromium could also be determined by flame atomic absorption spectrometry (FAAS) in a reducing air/acetylene flame at a wavelength of 357.9 nm. Prior to each series of measurements, a calibration line would be plotted. For this purpose, 0.00; 0.125; 0.50; 1.25 and 2.50 ml of stock standard solution of Cr^{6+} would be placed in 50 ml flasks and 10.0 ml of

5% lanthanum solution would he added (to prevent matrix effect) and the volume filled up to the mark with I M solution hydrochloric acid.

Similar procedure would be used to determine the content of chromium in soil samples. Adding 0.01 nil of 5% solution or lanthanum to the flasks containing the soil ineralizates and then adding solution of hydrochloric acid to the mark.

Atomic adsorption spectrophotometer determines the total Cr concentration (Cr^{3+} and Cr^{6+} after aqua regial (HCI: HNO_3 = 3:1) digestion of the soil samples (Soon & Abboud, 2001). The chromium (VI concentration is measured by using 1.5 diphenylcarbazide as stated above using spectrophotometer and Cr^{3+} would thus be determined by subtracting the concentrations of' Cr^{6+} from total Cr (Bartlett & James, 1993).

The type of vegetable used: Garden egg Collected from the farmland

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 (Oboh, Aluyor, & Audu, 2009; Ibrahim, 2011; Guo et al., 2008; Gomes et al., 2001; Michalski, 2005; Auranet et al., 2003; Botes & Van Staden, 2005; Wen, Du, & Tang, 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 (Kobya, 2004; Hamadi et al., 2001; Mor et al., 2006; Demerbas et al., 2004), Sugarcane bagasse (Sharma & Forster, 1994), leaf mould (Sharma & Forster, 1994), Coconut tree saw dust (Selvi et al., 2001) Eucalyptus bark (Sarin & Pant, 2005), Tamarind hull (Verma et al., 2006), the absorbents showed different degrees of versatility and selectivity for the heavy metals at various concentrations and p11 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 plataea, Division Magnoliophyta, order Sapindales, family Melianceae, Genus Azadirachta and Specy Indica.

Neem powder containing negative surface charges as a result of the presence of polar group like -NH2, -COOH, -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 Part

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. HNO_3 and lastly with distilled water.

Apparatus

The apparatus used in this work include beaker (250ml), measuring cylinder (lOmI, lOOmI), volumetric flask (100mI, 250m1, 500ml and l000ml), conical flask (250m1), glass funnels, whatman filter papers (125mm diameter), spatula, glassrod, weighing balance (mark 8055), pH meter (Jenwey 3320 model), handgtoves, and Atomic absorption spectrophotometer (AAS 210 BJ model). Soil sampler, polytetrafluroroethylene, microwave, even, volumetric flasks, hotplate, 1,5- diphenyl carbazide, digital colorimeter.

Reagents

The reagent used in this investigation includes Hydrochloric acid, sodium hydroxide, nitric acid and chromium nitrate. Con.H_3Po_4,$(NH_4)_2S_20_3$

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 106µm size and were kept in glass bottles for subsequent use.

Reagent Preparation

Preparation of O.1M $HN0_3$

3.5cm^3 concentrated HNO_3 was measured into a 500cm^3 of distilled water in a 1000cm^3 volumetric flask. After thorough shaking, the solution was made up to mark with more distilled water.

Preparation of l000mg/L of Cr (HI) Solution

This was prepared by measuring 2.73g of Cr $(NO^3)^3$ and dissolved in 100cm^3 of 0.1 M HNO_3 in a beaker. The resulting solution was then transferred into a 1000cm^3 volumetric flask and made to the mark with distilled water.

Preparation of Intermediate Stock Solution of 100mgIL

This was prepared by measuring 10cm^3 of the 1 000mg/L Cr^{3+} solution into 100cm^3 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

4.2cm^3 of concentrated HCI was measured and added to some quantity of distilled water in a 100cm^3 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 adsorbent adsorbed on the adsorbent increases, the adsorbent 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 (Rajagopal & Kapoor, 2001).

The percentage removal were elucidated from the relation,

$$\frac{C_0 - C_e}{C_o} \times 100$$

Where C_0, C_e are the initial and final adsorbent 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 100cm^3 of the l00mg/L chromium nitrate solution.

The resulting mixture was agitated for 5mm, 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 10mm, 15mm, 30mm, 45mm, 60mm and 90mm respectively. The results are shown in Table 1.

Variation of Adsorbent Mass

Adsorbent masses (2, 4, 6, 8 and log) were carefully weighed on a balance and transferred into separately labeled conical flasks. 100cm^3 of the 100mg/L chromium nitrate solution was added to each of the conical flasks. The mixtures were agitated for lhr, followed by their filtration, and the filtrates 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 adsorbent were measured and transferred into separate beakers containing 4g of adsorbent each. The mixtures were agitated for lhr, 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 HCI 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

Results

Table 1. Variation of agitation time with adsorbent concentrations

Variation of agitation time (min)	Residual cone (c/mgL^{-1})	C_o- C_o
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	1.5	8.5

Table 2. Variation of adsorbent mass

Adsorbent mass (g)	Residual cone (c/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 adsorbent concentration

Concentration (mg/L)	Residual cone ($c_1$mg/L^{-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 cone ($c_1$mg/L^{-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

Discussion

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.

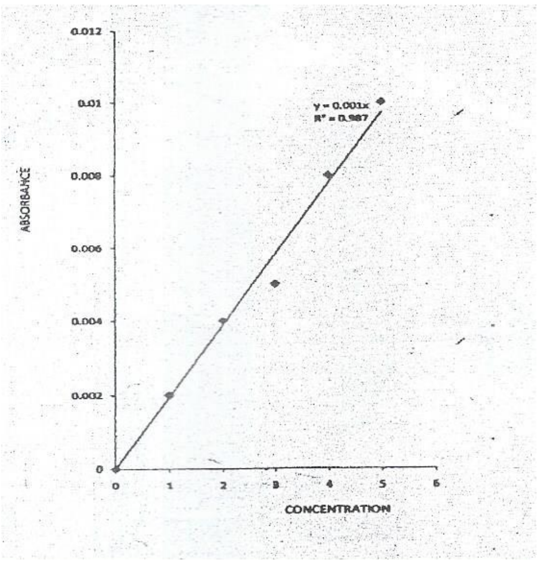

Figure 1. Calibration curve for chromium

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 Figure 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 5mm, it has a removal efficiency of 89% and a maximum of 92.5% at equilibrium time of 60mm. this is attributed due to the system's constant stirring and weak interaction between the Cr^{3+} 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).

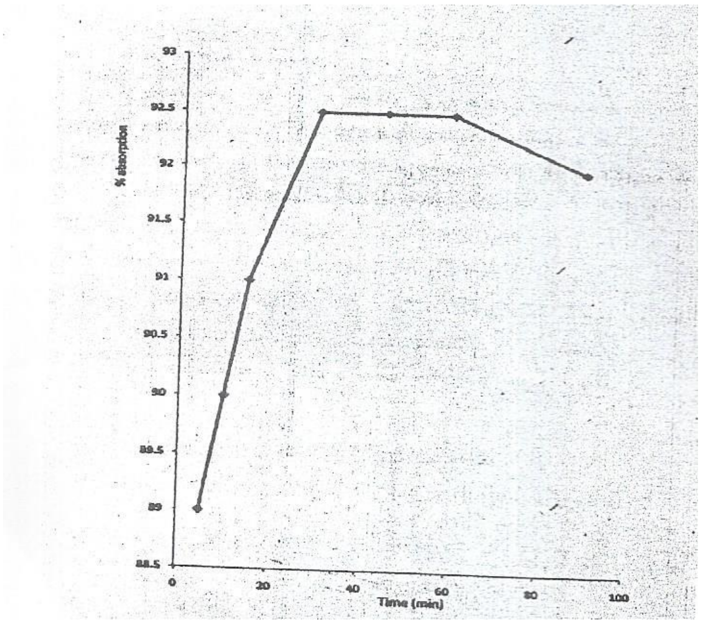

Figure 2. A graph of % adsorption against agitation time

Variation of Adsorbent Dosage

The percentage removal of chromium for the same agitation time of lhr 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 l0g as shown in figure 3. This is due to increase in active sites for adsorption of the Cr (III) ion with increasing soiption dosage. The result justified that a mass of log of the adsorbent is enough to remove a good amount of the Cr (111) 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).

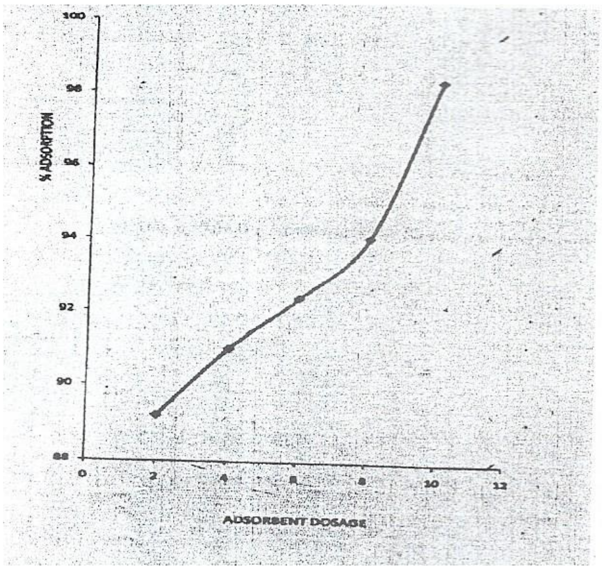

Figure 3. A graph of % adsorption against adsorbent dosage

Variation of Change in Concentration

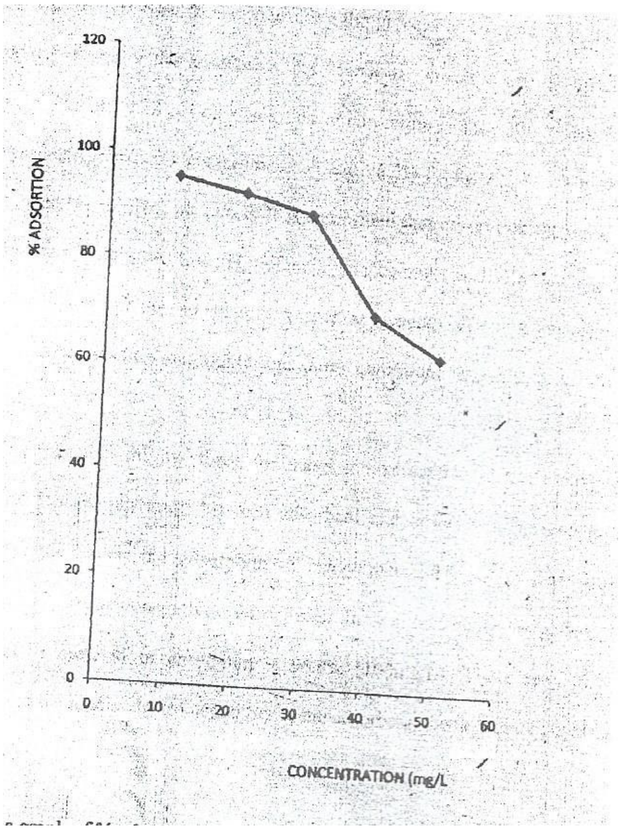

Figure 4. A graph of % adsorption against concentration

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 10pm size adsorbent at 60mm, 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 106pm 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 adsorbent. 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 cofirmed 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 arc bound to the adsorbent.

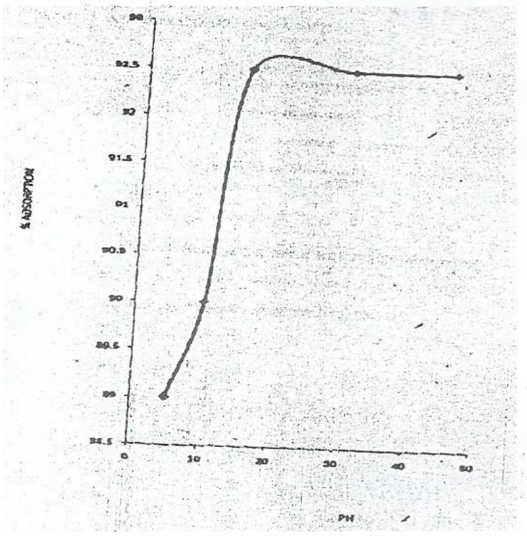

Figure 4. A graph of % adsorption against pH

The principal driving force for metal ion adsorption is the electrostatic interaction that is, attraction between adsorbent and adsorbent. 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% (100mgfL). 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 Ihr. 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 leave is a good adsorbent for the adsorption of chromium. It is therefore recommended that industries that deals with heavy metals should employ the use of neem leaf for the treatment of their effuent to remove chromium.

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