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STUDY OF SORPTION OF CHROMIUM ON MAIZE COBS IN AQUEOUS SOLUTIONS

Nale Biki Yusuf, Saidu Simon, Siaka Stephen, Victoria A. Alex, Nwankwere Emeka Thompson and Shebi Joshua Goje.

KeyWords

Activated Carbon, Adsorption, Chromium, Maize cobs.

ABSTRACT

Investigation has been carried out on the potential of a locally sourced maize cob for the removal of chromium ion from aqueous solution using batch equilibration technique. The maximum uptake of Chromium is 4.507mg/g maize cob. The separation factor R_L for Chromium ion (0.32) is less than unity indicating that maize cob biomass is an excellent adsorbent. The Fourier transform infrared (FT-IR) techniques has provided evidence for chromium fixation on to the surface of the maize cob. The sorption mechanism appears to follow Langmuir adsorption isotherm model. The Langmuir constants b and Q_0 (mass of Cr^{6+} required to form monolayer on the entire surface of maize cob) were 0.0677l/mg and 5.767mg/g respectively. It was also observed that the adsorption of $Cr(VI)$ was pH dependent and the optimum removal was observed in the acidic pH range.

INTRODUCTION

Hexavalent chromium, Cr(VI), is recognised as a human carcinogen [1]. Workers in many different occupations are exposed to hexavalent chromium. Occupational exposures occur mainly among workers who handle dry chromate-containing pigments, spray chromate containing paints and coatings operate chromate plating baths weld cut or grind, chromium-containing metals such as stainless.

A number of treatment processes for the removal of heavy metal ions from aqueous solutions have been reported, mainly ion exchange, electrochemical reduction, evaporation solvent extraction, reverse osmosis, chemical precipitation, membrane filtration, adsorption etc. Depending on the nature of the aqueous effluents flow rates and metal ion concentrations, the industrial application of these process is restricted by the operating costs or by the inefficiency of the technique [2]. Adsorption is by far the most effective and widely used technique for the removal of toxic heavy metals from waste water. The use of activated carbon (AC) for the adsorption of heavy metals was first proposed by *Watonabe and Ogawa* [3]. In recent years several investigators have concentrated their work on low cost, non-conventional adsorbents to achieve the economically feasible and effective treatment of wastewater containing Cr(vi). Various industrial solid wastes agricultural by-products and similar materials have adsorption infinity for heavy metals [4]. AC derived from coconut shells for Cr(vi) removal was reported by [5]. *Mohammed et al.*, [6] have utilized saw dust as adsorbent for the removal of Cu(II) from waste water. The present study is undertaken to evaluate the efficiency of a carbon adsorbent prepared from maize cob for the effective removal of Cr(vi) from solution by varying contact time, Cr(vi) concentration, and pH.

MATERIALS AND METHODS

The maize cob was collected from the Ahmadu Bello university Agricultural research farm Shika, Zaria, Nigeria. These materials are low-value agricultural by-products that at present have no commercial value. All the chemicals used were of AnaLaR grade. Stock solution of Cr(vi) ions was prepared by dilution/dissolution of $K_2Cr_2O_7$.

Preparation of Activated Carbon

Activated carbon was prepared from the agricultural by-products using the methods described by *Gimba and Bahago* [7] at optimum conditions of temperature and time for activation. The activated carbon was then washed with deionised water and soaked in 1% $NaHCO_3$ solution to remove any remaining acid. The samples were further washed with deionised water until no acidity was left and then dried at $105^\circ C$ for 5 hours [8]. The dried material was ground and sieved to obtain the particle size of $300-850\mu m$ [9] and [10] and stored in airtight container for further experiments.

Characterization of the Activated Carbon

pH Determination

The pH of the carbon was determined by the method of *Akporhonor and Egwaikhide* [11]. This was done by immersing 1.0g sample in $100cm^3$ of deionised water and stored for 1 hour before measuring pH.

Bulk Density

$$\text{Bulk density (g/ml)} = \frac{\text{Wt. of dry material (g)}}{\text{Volume of Carbon in cylinder}} \quad (1)$$

This was determined using the method of *Ahmadna* [12]. A $25cm^3$ measuring cylinder was filled to a 10ml volume with granular activated carbon that was dried in an oven $80^\circ C$ over night. The cylinder and its contents was tapped for at 1 minutes to compact the carbon. The volume on the cylinder was marked before being weighed.

Ash Content Determination

$$\text{Ash\%} = \frac{\text{weight after ashing}}{\text{Original Carbon weight}} \times 100 \quad (2)$$

About 2g of granulated activated carbon was placed into weighed ceramic crucibles, oven-dried at $80^\circ C$ over night and then reweighed to obtain the dry carbon weight. The samples were then heated in a furnace at $400^\circ C$ for 3 hours and cooled in a desiccators. The remaining solids (ash) were then reweighed [12].

Moisture Content Determination

Moisture content of sample was determined using the method of *Allen et al.* [13]. A portion (1g) of sample was placed in the pre-weighed crucible and weighed again after which it was placed in an air circulated oven at $105^\circ C$ for 8 hours and then cooled in a desiccators followed by reweighing.

$$\text{Moisture\%} = \frac{\text{Loss in weight on drying}}{\text{Initial sample weight}} \times 100 \quad (3)$$

Percentage Carbon Yield

A portion (2g) of maize cob was weighed into a crucible of known weight. The sample was placed at a temperature of 300°C for 40 minutes to achieve carbonisation. The percentage yield was calculated as:

$$Yield\% = \frac{\text{final weight}}{\text{Initial Sample weight}} \times 100 \quad (4)$$

Optimisation of particle sizes of activation carbon Derived from maize cob

The activated carbon from maize cob was ground using mortar and pestle and sieved through a set of test sieves model equipped with a bottom pan with the following sizes 300µm, 355µm, 425µm, 500µm and 850µm attached to an Endecott mechanical test shaker.

Determination of Surface area

The surface was determined by methylene blue absorption test (MBT) method as described by *Santamarina et al.* [14].

$$S_S = \frac{M_{MB} A_V A_{MB}}{391.87 \times M_s}$$

Where M_{MB} is the mass of the adsorbed MB, at the point of complete cation replacement, M_s is the mass of activated carbon, S_s is the specific surface area, A_V is Avogadro's number (6.02×10^{23}) and A_{MB} is the area covered by one MB molecule (assumed to be 130\AA^2).

Fourier Transform infrared spectrophotometer (FT-IR) Analysis

The activated carbon produce was characterised for its functional groups using FT-IR analysis. For this, the activated carbon samples were brought to the constant weight in a drying oven at 50°C for 24 hours and kept in the desiccators. Then 1mg dried activated carbon was mixed with 100mg KBr, which was initially dried at 110°C in the sample disk. The FT-IR spectra was in the range of 450-4000 cm^{-1} .

Adsorption studies of Metal ions using batch Equilibrium Technique

Adsorption studies were performed in 100ml flasks where solutions of Chromium ions (25ml) with different initial concentrations (5-20mg/l) were placed equal mass of 0.2g of maize cob for a particle size 355µm was added to metal ions solution and each sample was kept in shaker for 180 minutes at room temperature of 30°C [15] to reach equilibrium. The flasks were then removed from shaker and final concentration of metal ions in the solution was analysed by Atomic Absorption spectrophotometer at a desired wavelength of each metal ions. The adsorption capacity at equilibrium q_e (mg/g) was calculated by

$$q_e = \frac{(C_i - C_e)V}{M} \quad (5)$$

Where C_i and C_e (mg/l) are the liquid phase concentrations of metal ions at initial and equilibrium concentration respectively. V is the volume of the solution (L) and M is the mass dry adsorbent used (g). The effect of initial concentration, contact time, and pH were studied. Adsorption Kinetic and Adsorption Isotherm were applied to equilibrium data.

RESULTS AND DISCUSSION

Characteristics of Activated Carbon

Physicochemical characteristics of activated carbon prepared from maize cob are given in table 1.

Parameter	Maize cob
Ash content (%)	8
Moisture (%)	3
Bulk density g/m^3	0.4500
Yield (%)	16.67
pH aqueous solution	6.47
Surface area (m^2/g)	599.42

FTIR Analysis for Maize Cob

The functional group on the surface of activated carbon analysed by FT-IR demonstrated, the existence of carboxyl, hydroxyl and amines group. The carbon-oxygen functional groups are by far the most important structure in influencing the surface characteristics and surface behaviour of the adsorbent. The functional groups suggested most often in AC are (i) carboxyl group, (ii) phenolic hydroxyl groups (iii) carbonyl group (e.g quinone-type) and (iv) lactone group e.g Fluorescein-type [16]. The FTIR spectra of the blank and metal loaded Activated Maize cob (AMC) is shown in table 2. The figure demonstrates that after the adsorption the shifting

occurs both to higher and lower wave numbers. These clear band shift could be observed at 3750.26, 3455.76, 2921.37, 1952.67, 1561.07 and 1037.01 cm^{-1} for Cr-laden activated carbon. This shift indicated that there were binding processes taking place on the surface of activated carbon [17]. The functional groups involved in the adsorption were as follows: Broad band 3750.26-3455.76 cm^{-1} representing bonded OH groups and NH groups [18], 2921.37-1952.67 cm^{-1} the aliphatic C-H groups, 1952.67-1561.07 cm^{-1} , the C = O stretching group and 1037.01 cm^{-1} , P-O-C stretching in chain. These functional groups could act as chemical binding agents where carboxyl, hydroxyl and amine groups could dissociate negatively charged active surface. This means that these functional groups could attract the positive charge objects such as heavy metal ions [19].

Table 2: Summary of FT-IR Results from chromium laden activated carbon.

FTIR Peak	Original adsorption	Cr(VI) Loaded AC Diff	Assignment
1	3750.26	3735.19 + 15.07	Bonded-OH
2	3455.76	3405.31 + 50.45	Bonded-NH
3	2921.37	2921.68-0.31	Aliphatic-CH grp
4	1952.67	1945.80 + 6.87	Aliphatic-grp for anhydride C = O stretching.
5	1561.07	1561.07 + 0.00	C = O stretching
6	1037.01	1036.21 + 0.80	P-O-C Stretching

Equilibrium Sorption Studies of Maize Cob

In the present study two Kinetic models are tested in order to predict the adsorption data of Cr(VI) as function of time using a Pseudo-first-order and Pseudo-second-order Kinetic model. Good R^2 values were obtained from 0.9495-0.9859 and from 0.9992-0.9996 respectively (Table 3). Analysis of variance (ANOVA) showed significant difference between the R^2 values of the two models at 99% confidence level.

Table 3: Pseudo first order and Pseudo second order model constants.

Initial Conc. Of Cr(VI) (mg/l)	Pseudo-First-order model K_1 (min^{-1}), R^2	Pseudo-Second-order model ($\text{gK}_2/\text{mg.min}$), R^2
5	0.0115, 0.9858	0.4556, 0.9996
10	0.0170, 0.9495	0.1137, 0.9992
15	0.0159, 0.9859	0.0768, 0.9994
20	0.0267, 0.9840	0.0377, 0.9996

Based on the high R^2 values, it is concluded that adsorption of Cr(VI) onto the activated maize cob can be described by both models. Nevertheless the R^2 values also indicated that the sorption Kinetics of Cr(VI) is better expressed by the second order reaction rates. Compliance to the second-order-Kinetic model strongly suggests chemical adsorption or chemisorption between the adsorbent and adsorbate.

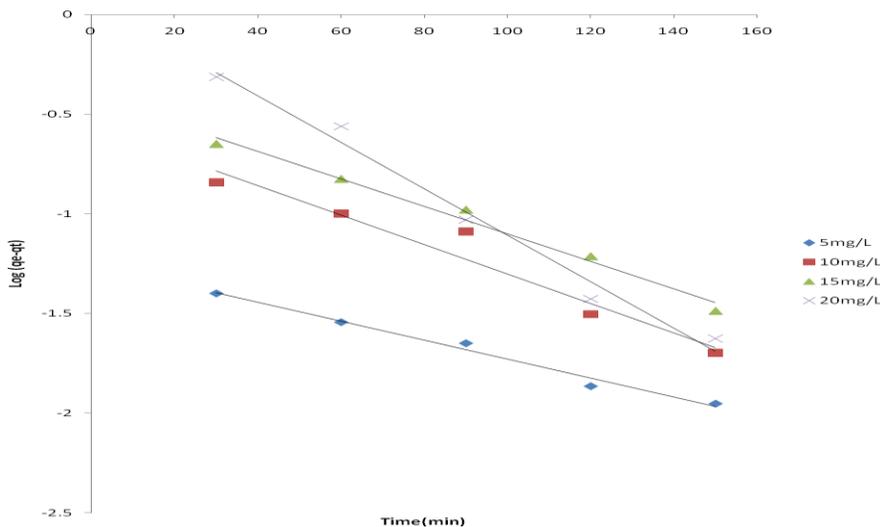


Figure 1: Pseudo first order Kinetic plot at different initial concentrations: pH 2.0; Volume, 25ml; agitation speed 180 min,

adsorbent dosage 0.2g/l; and temperature 30°C.

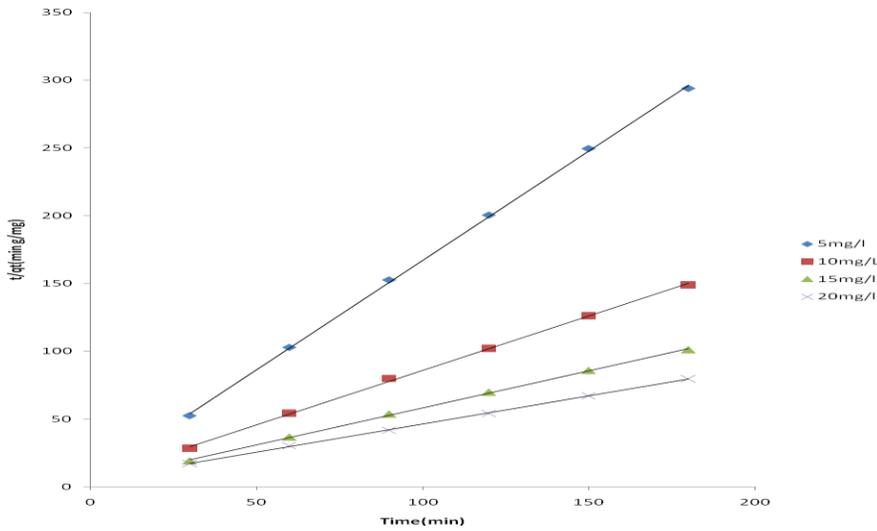


Figure 2: Pseudo second order Kinetic plot at different initial concentration: pH 2.0, volume 25ml; agitation speed 180 min, adsorbent dosage 0.2g/l and temperature 30°C.

Sorption Isotherm Studies

The sorption isotherms of chromium (VI) on the sample were studied at a constant temperature of 30°C. When C_e/q_e was plotted against C_e , straight line with slope $1/Q_0$ was obtained as shown in (fig 3) indicating that the adsorption of adsorbates on activated carbon follows the Langmuir isotherm. The Langmuir constants 'b' and Q_0 were calculated from this isotherm and their values are given in Table 4. The adsorption capacity, Q_0 which is a measure of the maximum adsorption capacity for Cr(VI) 5.767mg/g. The adsorption co-efficient, b is 0.0677/mg. This observation showed that the energy of adsorption is favourable to Cr(VI) due to its small

ionic radius. Hence all binding sites are available to Cr(VI) [20],[21]. The extent of adsorption of Cr(VI) ion on the maize cob biomass was tested using the Langmuir isotherm model, expressed in terms of a dimensionless constant called separation factor, R_L

$$C_e/q_e = \frac{1}{Q_0 \cdot b} + \frac{C_e}{Q_0} \tag{6}$$

$$R_L = \frac{1}{1 + bC_i} \tag{7}$$

Where b is the Langmuir isotherm constant, C_i is the initial metal ion concentration. The separation factor for Cr(VI), was found to be 0.3299. Hence, the value was found less than unity indicating that maize cob biomass is an excellent adsorbent for the chromium ions.

Table 4: Sorption Isotherm Constants and Coefficients of maize cob for chromium

Langmuir Constant			Freundlich Constant			
Qmax (mg/g)	b(L/mg)	R ²	R _L	K _f (mg/g)	n	R ²
5.767	0.0677	0.9729	0.3299	0.3982	1.2757	0.9938

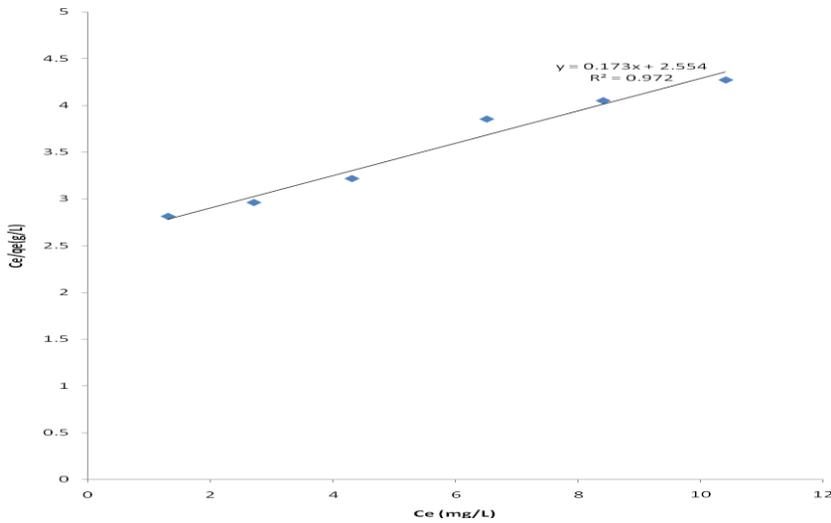


Figure 3: Langmuir isotherm plot for Cr

The Freundlich model is often used for heterogeneous surface energy systems. The linear form is given as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

Where K_f and n are constant in incorporating all parameters affecting the adsorption process. The linear logarithmic plots of q_e versus C_e show that the adsorption followed Freundlich model (fig 4). It also indicates that the average energy of adsorption decreases with increasing adsorption capacity values of K_f and n was calculated from the intercept and slope and given in Table 4 along with the Langmuir constants. The values of n between 1 and 10 represent good adsorption of the adsorbate onto the adsorbent [22]. Values of Q_e predicted by models, as well as the experimental values are in fig.3 and 4 for chromium ions. These also show that the Langmuir model fitted the result slightly better than Freundlich model.

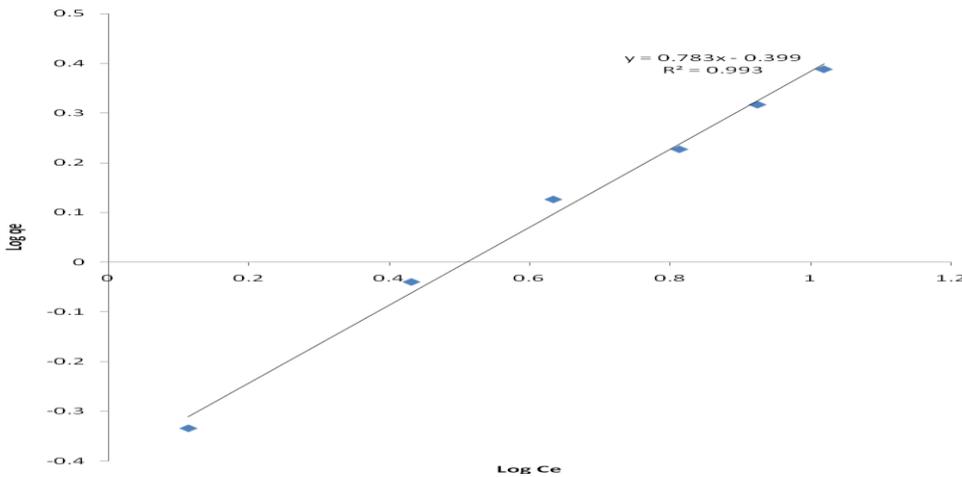


Fig. 4 Freundlich isotherm plot for Cr.
Effect of Constant Time

Fig 5 reveals that the uptake of adsorbate species is fast at the initial stages of the contact period and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. The adsorption capacity of chromium increased rapidly in the beginning of the reaction and reached equilibrium in about 120 min. A long contact time necessary to reach equilibrium indicates that the predominant mechanism is physical adsorption while a short contact time indicates chemisorptions is the predominant mechanism. The contact time obtained in this study indicates that physisorption may be involved [23].

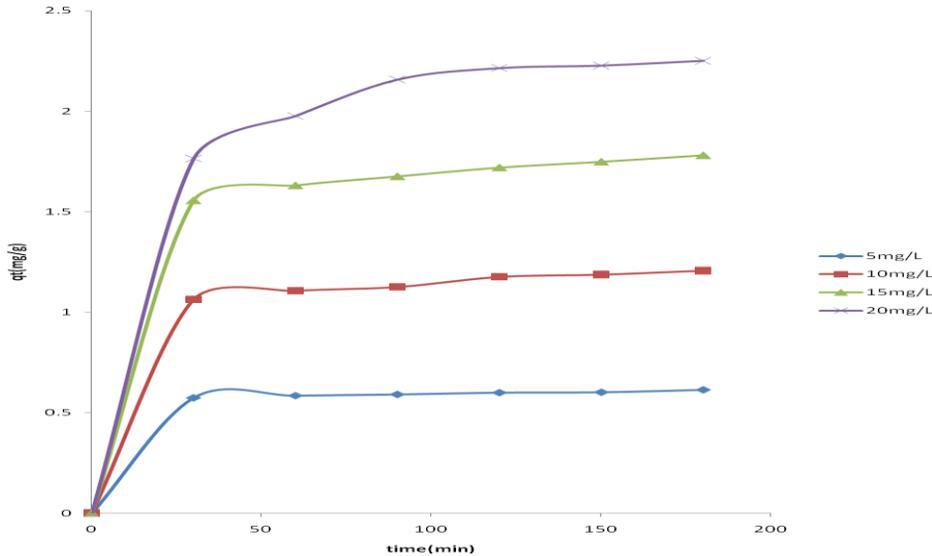


Fig. 5: Effect of contact time for metal ion (chromium)

Effect of Initial Concentration

The effect of initial concentration on the adsorption of Cr(VI) metal ion onto maize cob at $m = 0.2g/l$ is shown in Fig 6. It was evident that metal ion removal decreased with an increase in initial concentration. This indicates that there exists a reduction in immediate solute (metal ion) adsorption owing to the lack of available active sites required for the high initial concentration of metal ions [24]. The actual amount of metal ions adsorbed per unit mass of maize cob increased with increase in initial concentration. These increase because the resistance to the uptake of metal ions from the solution decreases with an increase in metal ions concentration [25].

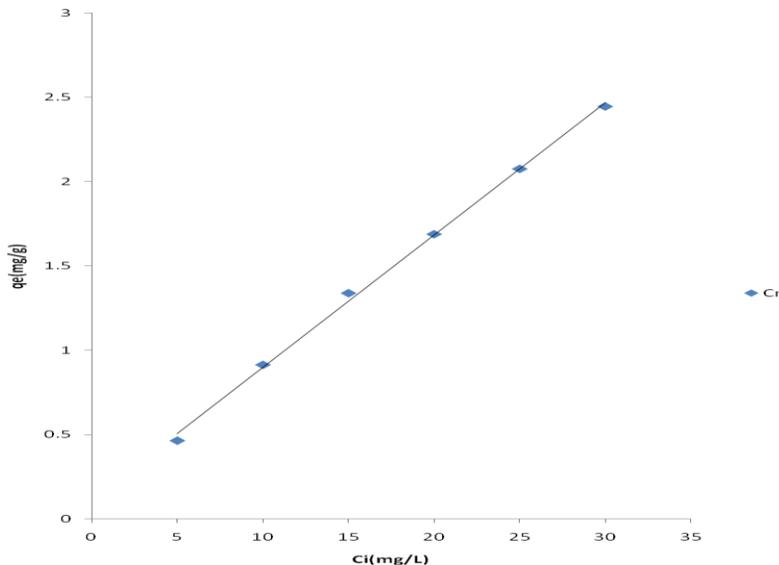


Fig. 6 Effect of initial ion concentration

Effect of pH

The removal of metal ions in aqueous solution by adsorption is related to the pH of solution as the latter affects the surface charge of adsorbents, the degree of ionisation and species of adsorbate in Fig 7 showed that for metal ion removal was significantly high under the influence of acidic pH (pH 1 to 2). At this pH range, the predominant Cr(VI) was HCrO_4^- and therefore, electrostatic attraction occurred between the positively charged adsorbent and negatively charged HCrO_4^- . However, the decrease in Cr(VI) removal at higher pH values was apparently due to the competitiveness of another Cr(VI) species (CrO_4^{2-}) and OH^- ions in the bulk [26]. pH 2.0 was adopted as optimum condition for further adsorption study.

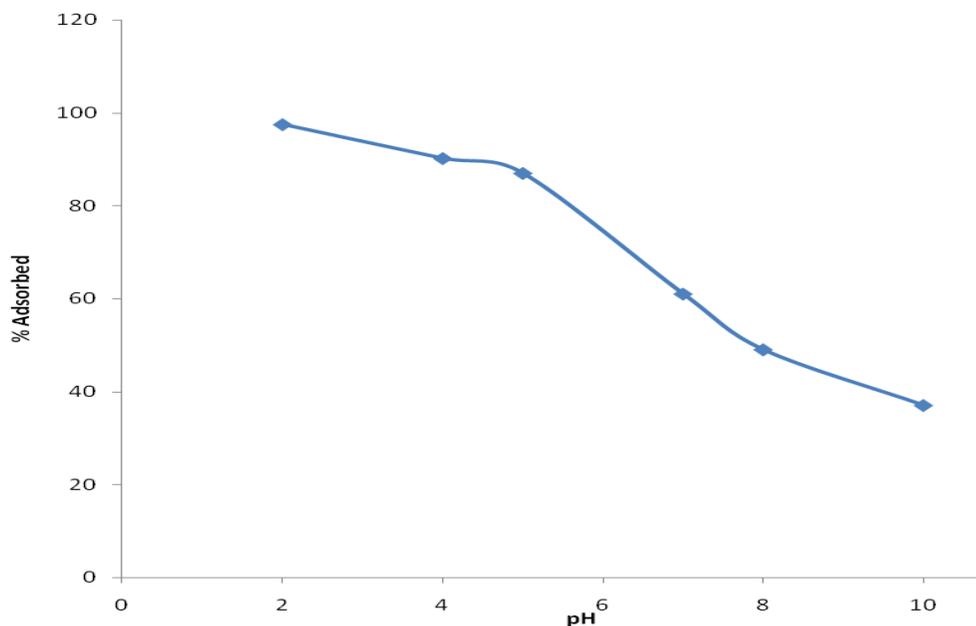


Fig 7: Effect of pH on metal ions

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