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Adsorption of Cr (VI) and Cu (II) from Effluent of Metallurgical Industry by Activated Orange Peel

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Abstract: **The present study describes ability of activated orange peels powder to absorb heavy metals chromium and copper from waste water. Batch Adsorption studies were conducted to examine the effects of pH, contact time, adsorbent dosage and metal ion concentration on adsorption of Cr(VI), Cu(II) .The obtained results , shows that adsorption is dependent on these factors. The maximum removal efficiency were found 74% at pH=2. Equilibrium data were fitted to the Langmuir and Freundlich isotherm equation. The aim of this work is to develop less expensive and effective adsorbent orange peels powder as alternative to existing adsorbents.**

Keywords: Effluent, Adsorption , Cr(VI), Cu(II), Kinetics

INTRODUCTION

The presence of heavy metals such as copper, nickel, iron, chromium, lead, zinc and cadmium in industrial waste water is of concern as these are highly toxic, non biodegradable, carcinogen. These metal ions have high solubility in aquatic environment, their continuous deposition into various water sources within the vicinity causes bioaccumulation in the living organisms.

Various methods have been traditionally employed for heavy metal removal from industrial waste water such as chemical precipitation, chemical oxidation or reduction, filtration, electrochemical treatment, ion exchange, adsorption, membrane processing and electrolytic methods. The aim of present research work is to use a plant based renewable resource Orange peel as an adsorbent for removal of toxic heavy metal Cu(II) and Cr(VI)) .The adsorption capacity of this material was estimated by batch process at room temperature. Effects of various parameters like adsorption mass, pH, particle size, contact time and copper and chromium ion concentration have been studied.

Material and Methods

Preparing bio-sorbent: Orange peel was taken from a local market. The fruit was first peeled off and was washed with ordinary tap water to remove possible foreign materials present (dirt and sand). Washed sample was sun dried for 2-5 days and then crushed with a mortar and pestle to reduce the size. 250g of the small pieces was carbonized at 400°C for 15 minutes and then subsequently activated using 2.0 M $ZnCl_2$ at 400°C for two to three hours. The sample was then withdrawn from the furnace and cooled in a desicator. After cooling the sample was rinsed several times with distill water until obtaining flushing water whose pH range lies between 6-7**.**The wet sample was dried at 105°C during 24 hour.

Cu(II) and Cr(VI) solution: The stock solutions containing 1000 mgL^{-1}Cu(II) and Cr(VI) have been prepared in double distilled water separately. These solutions were diluted as required to obtain the standard solutions containing 50-250 mg L^{-1} of Cu(II) and Cr(VI) separately. The pH of the solutions were adjusted in the range of 2-5 by adding 0.1N HCl or 0.1N NaOH solution as per the requirement and were measured by a pH meter. All reagents were of analytical grade and were used without further purification.

Adsorption Experiment: Adsorption experiment were studied in batch mode as function of biomass dosages (3,5, 7, 9) g L^{-1}, pH (2-5), contact time (30, 50, 70, 90) minutes and metal ion concentration (100, 150, 200, 250) mg L^{-1} .The batch adsorption was carried out in 250mL borosil flask, required quantity of bio-sorbent was added to 55mL of metal ion solution and the mixture was agitated on rotor at 250 rpm.

The complete experiment was carried out at room temperature. After completion of every set of experiments the residual was separated by filtration using Whatmann filter paper no.42 and only 20 mL of each sample was stored residual for residual Cu(II) and Cr(VI) analysis separately. After completion of experiment, the concentration of residual Cu(II) and Cr(VI) was directly measured by atomic absorption spectroscopy.

Equation 1 is used to determine the percentage adsorption of metal (Ø, in %) by adsorbent.

...(1)

X
100

Ø= $\underline{C_0}$ Ce
C_e

where C_o is initial ion concentration and C_e is concentration of metal ion after adsorption.

Adsorption Isotherm: According to Langmuir theory, the saturated monolayer isotherm can be represented as-

$$qe = \frac{q\ maxbCe}{I + bCe} \quad ...(2)$$

The above eq. 2 can be arranged by following linear form-

$$\frac{C_e}{q_e} = \frac{1+}{bqmax} \quad \frac{C\ e}{qmax}$$

Freundlich found that if the concentration of solute in solvent at equilibrium C_e (mg L^{-1}) was raised to be the power of m, the amount of solute adsorbed being q_e then C_e^m/q_e was constant at a given temperature. This fairly satisfactory empirical isotherm can be used for non ideal sorption and is expressed by the following equation in the form of logarithm of both sides as shown in fig.2.

$$\log q_e = \log K_f + m \log C_e \quad ----(3)$$

An adsorption isotherm is characterized by certain constant, the value of which expresses the surface properties and affinities of the solvent and can also be used to compare bio-sorptive capacity of biomass for different metal ions. Out of several isotherm equations two have been applied for this study, the Freundlich and Langmuir isotherms. Freundlich isotherms of Cr(VI) and Cu(II) shown in fig 1 and fig 7 respectively and Langmuir isotherms of Cr(VI) and Cu(II) shown in fig 2 and fig 8 respectively.

Result and Discussion

Effect of adsorbent dosage on removal efficiency :

Different dosages of the adsorbents(3, 5, 7, 9) g $^{L-1}$ were added in different conical flasks containing 150 mg L^{-1} of sample solutions.They were analyzed for removal of metal ions as shown in fig 3 and fig 9 for Cr(VI) and Cu(II) respectively. Increase in adsorbent dosage also increased percentage removal of both Cu(II) and Cr(VI) respectively.

Effect of pH: The effect of pH on adsorption of metal ions were analyzed over the pH range from (2-5). In this study 100ml of sample solutions, corked and analyzed for removal of metal ions as shown in fig 4 and fig 10 for Cr(VI) and Cu(II) respectively. The figures show that with increase in pH, the removal decreases due to less hydrogen ion in less acidic medium.

Effect of contact time on removal efficiency: The effect of contact time on removal of metal ions was studied for a period of 30-90 minutes. First removal efficiency increases but at 90 minutes it becomes constant as shown by fig**.** 5 and fig 11 for Cr(VI) and Cu(II) respectively

Effect of metal ion concentration : The experiment was also carried out with the change in metal ion concentration from 100-250mgL^{-1} Increasing the concentration of metal ion , the adsorption percentage decreases as shown in fig 6 and fig 12 for Cr(VI) and Cu(II) respectively**.** This happens because the number of active sites are fixed in the adsorbent.

Effect of metal ion concentration : The experiment was carried out with the change in metal ion concentration from 50-250mgL^{-1}

With the increase in concentration of metal ion , the adsorption percentage decreases as shown in fig7 and 12 for Cr(VI) and Cu(II) respectively **.** This happens because the number of active sites are fixed in the adsorbent.

Conclusion

The present research concludes that orange peel is effective adsorbent in the removal of Cu(II) and Cr(VI). Experimental data indicate that the adsorption efficiency is dependent on operating variable such as adsorbent dosage, pH, contact time and metal ion concentration. The adsorption data fit well with Freundlich and Langmuir adsorption isotherm model.

Ion exchange and hydrogen bonding can be a suggested for mechanism in removal of Cu(II) and Cr(VI) ions.

Table 1

Experimental conditions for Cr(VI) and Cu(II)

Experimental conditions	M_s (g L^{-1})	*p*H	T (min)	C_0 (mg L^{-1})
Effect of adsorbent dosage M_s (g L^{-1})	3-9	3	70	150
Effect of *p*H	7	2-5	70	150
Effect of contact time T (min)	7	3	30-90	150
Effect of concentration of Cu (II) and Cr (VI) ion C_0 (mg L^{-1})	7	3	70	100-250

Table 2

Langmuir and Freundlich model parameters estimated from the fitting of experimental point of Cr(VI) adsorption

Langmuir Isotherm			Freundlich isotherm		
R^2	q_{max} (mg g^{-1})	**b** (L m g^{-1})	R^2	K_f (mg g^{-1})	m
0.991	8.051	6.98	0.997	3.073	0.833

Table 3

Langmuir and Freundlich model parameters estimated from the fitting of experimental point of Cu(II) adsorption

Langmuir Isotherm			Freundlich isotherm		
$_R2$	q_{max} (mg g^{-1})	**b** (L m g^{-1})	$_R2$	K_f (mg g^{-1})	m
0.984	7.541	7.589	0.999	3.042	0.818

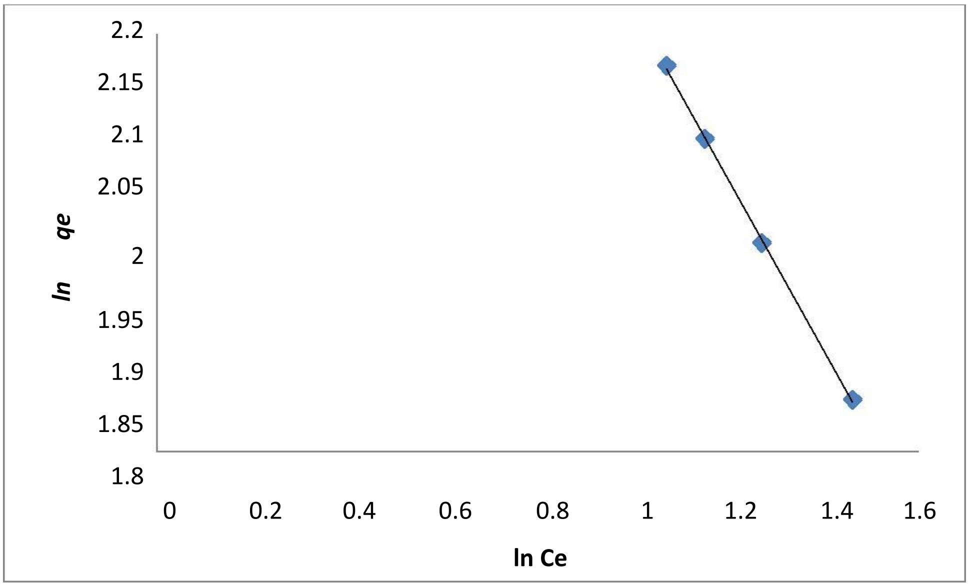

Fig: 1 Freundlich isotherm for Cr(VI)

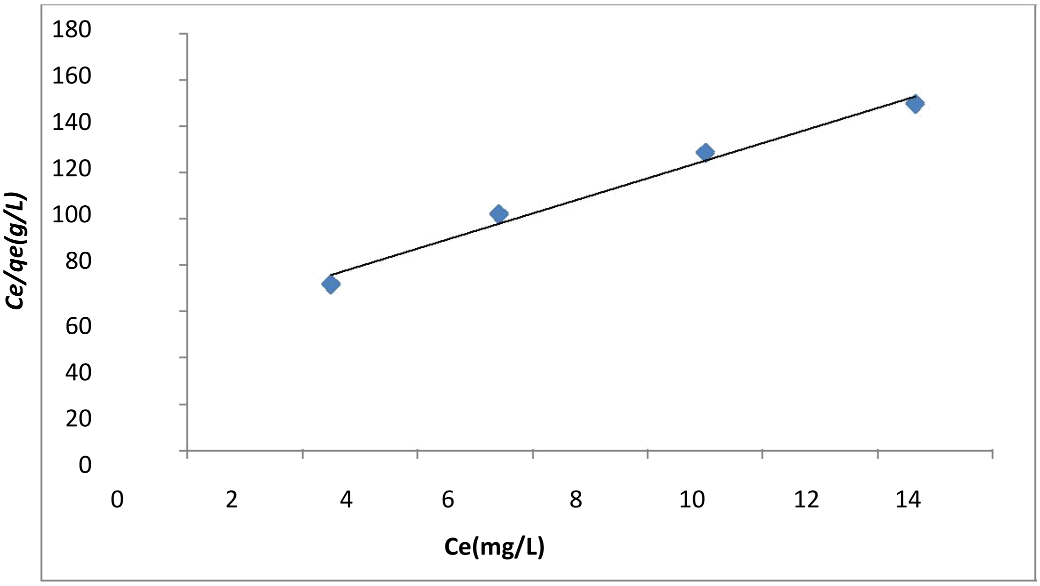

Fig: 2 Langmuir isotherm for Cr(VI)

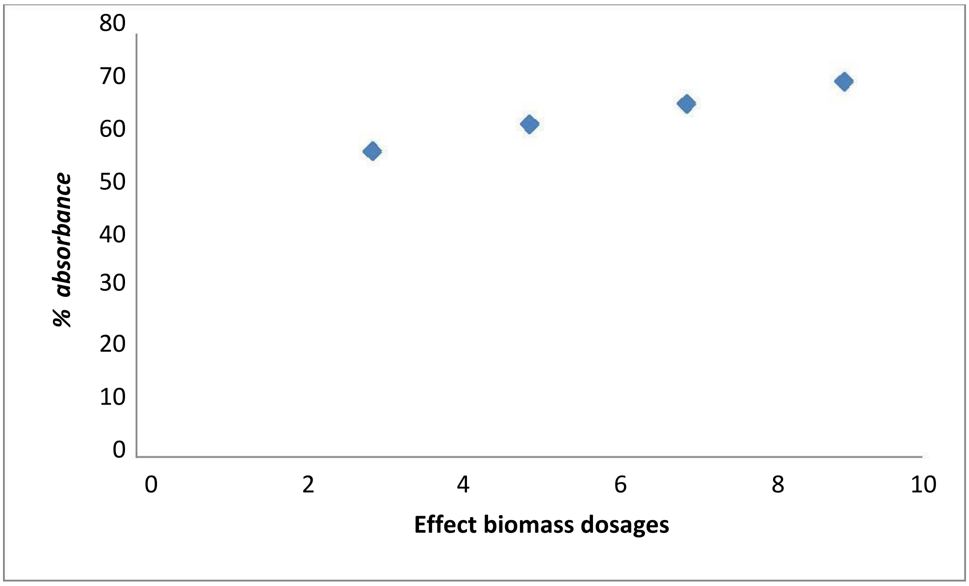

Fig: 3 Effect of biomass dosages

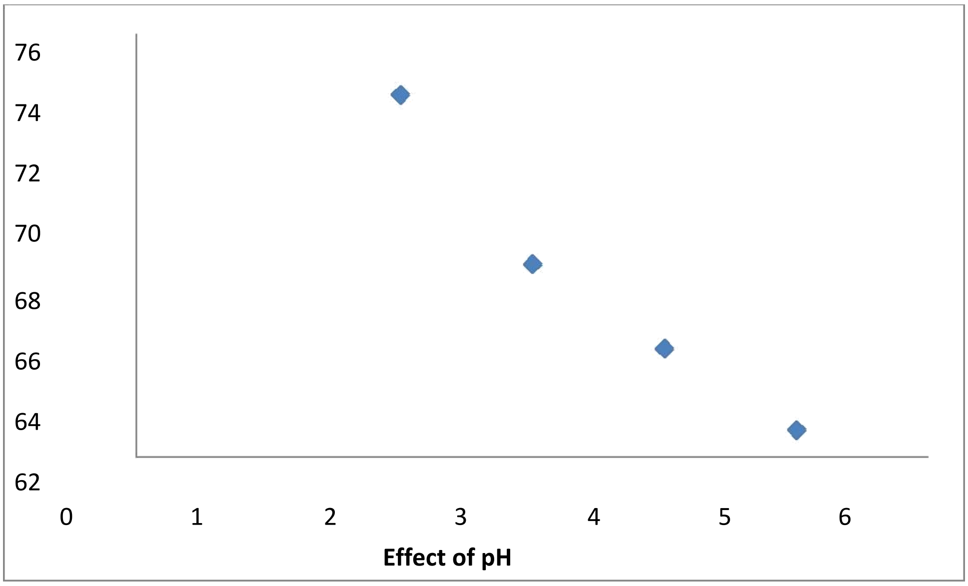

Fig: 4 Effect of pH

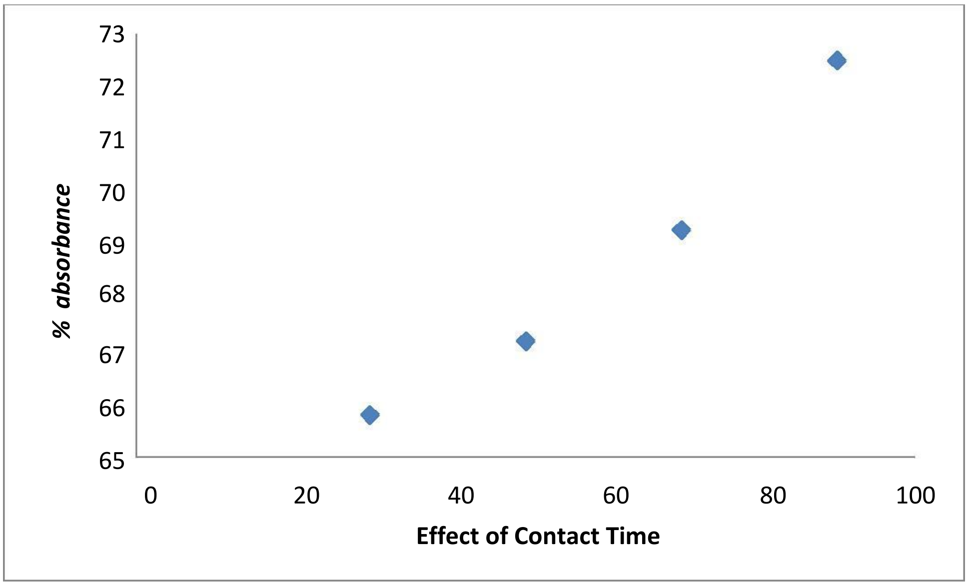

Fig: 5 Effect of contact time

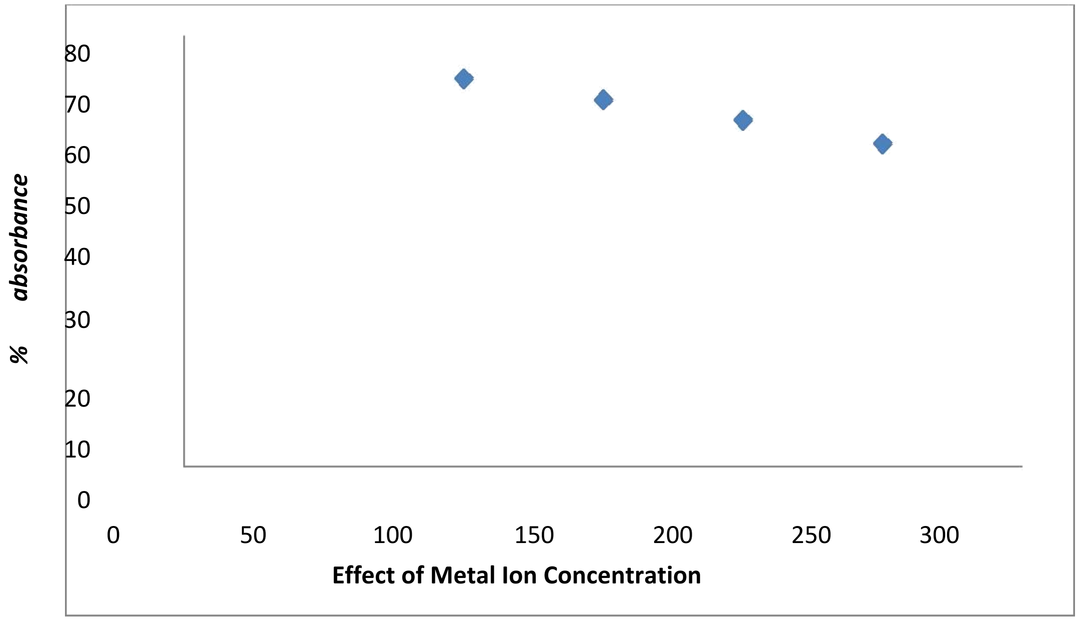

Fig: 6 Effect of Metal ion concentration

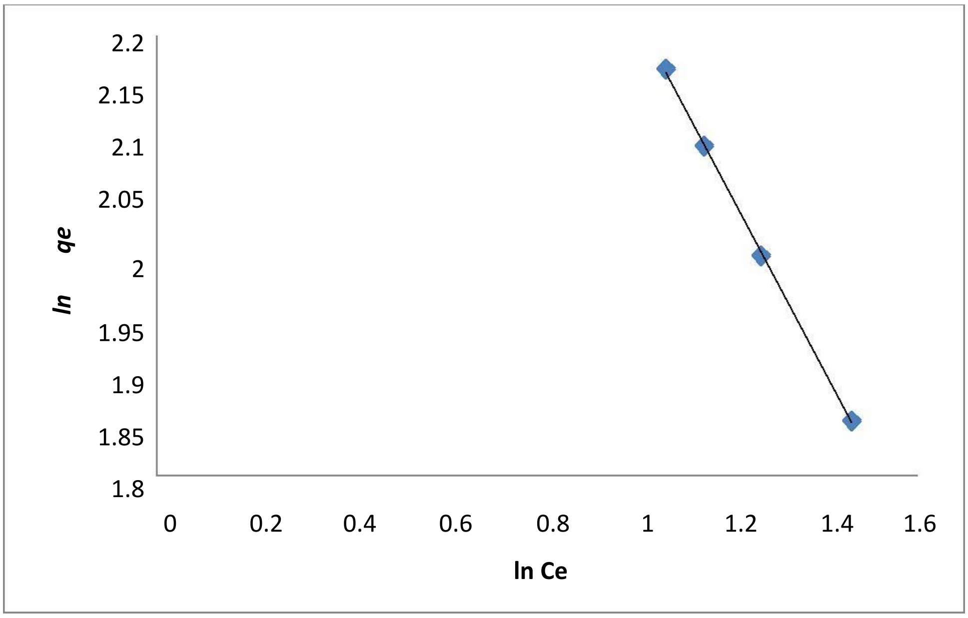

Fig: 7 Freundlich isotherm for Cu(II)

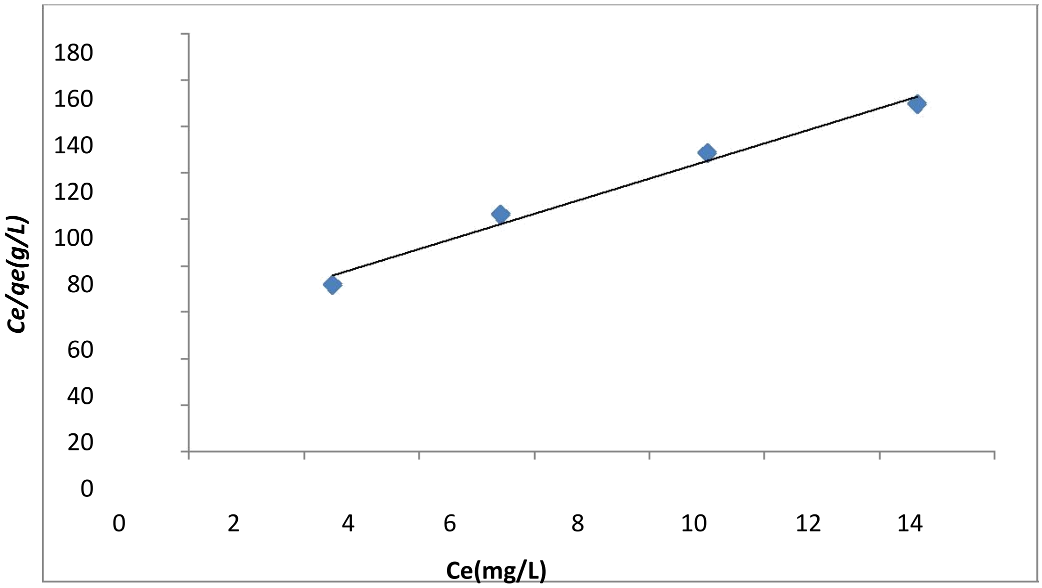

Fig: 8 Langmuir isotherm for Cu(II)

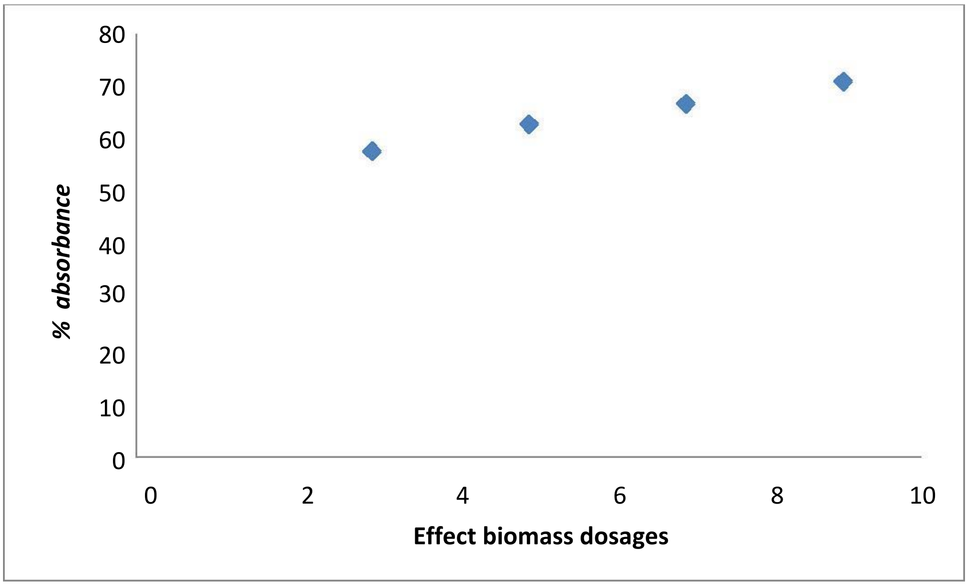

Fig: 9 Effect of biomass dosages

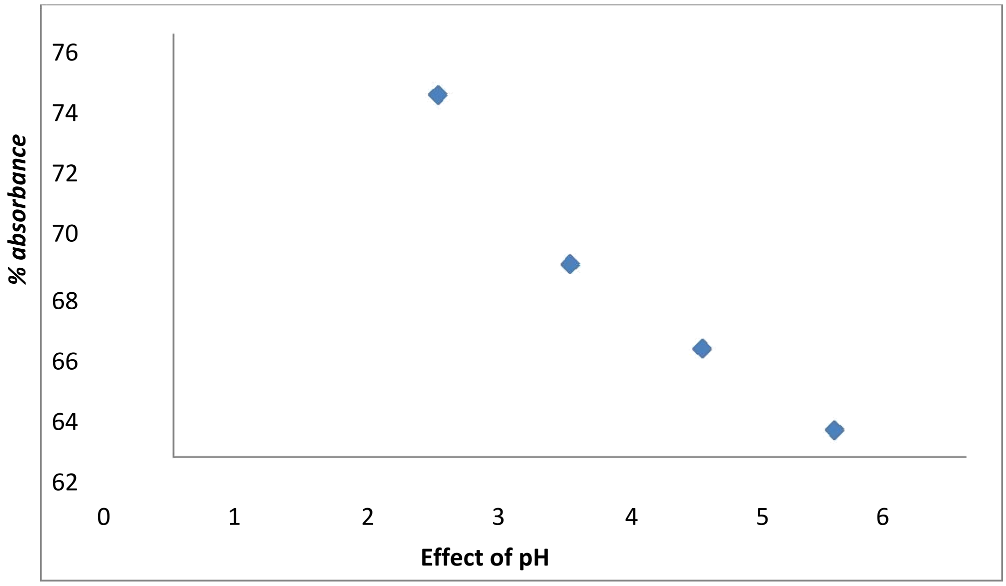

Fig: 10 Effect of pH

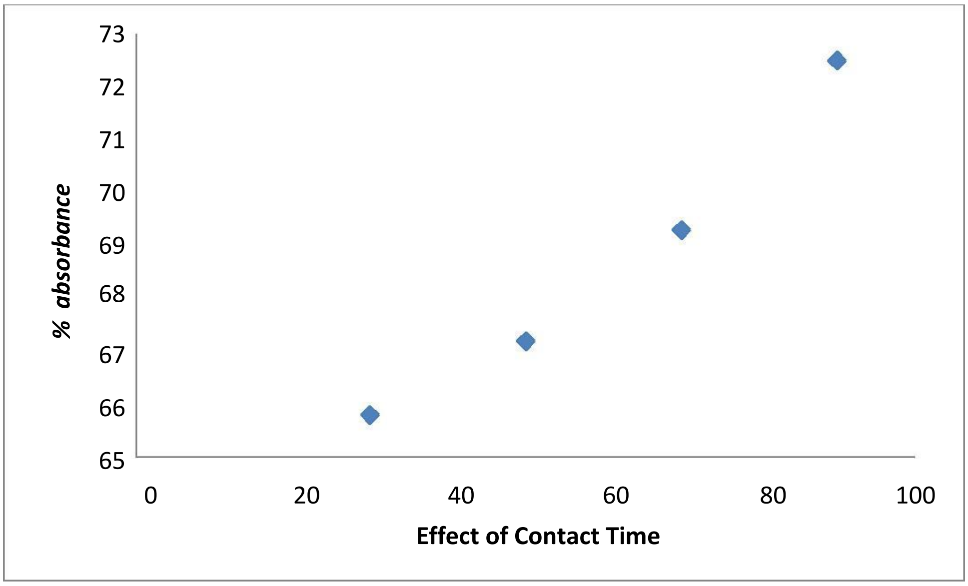

Fig: 11 Effect of contact time

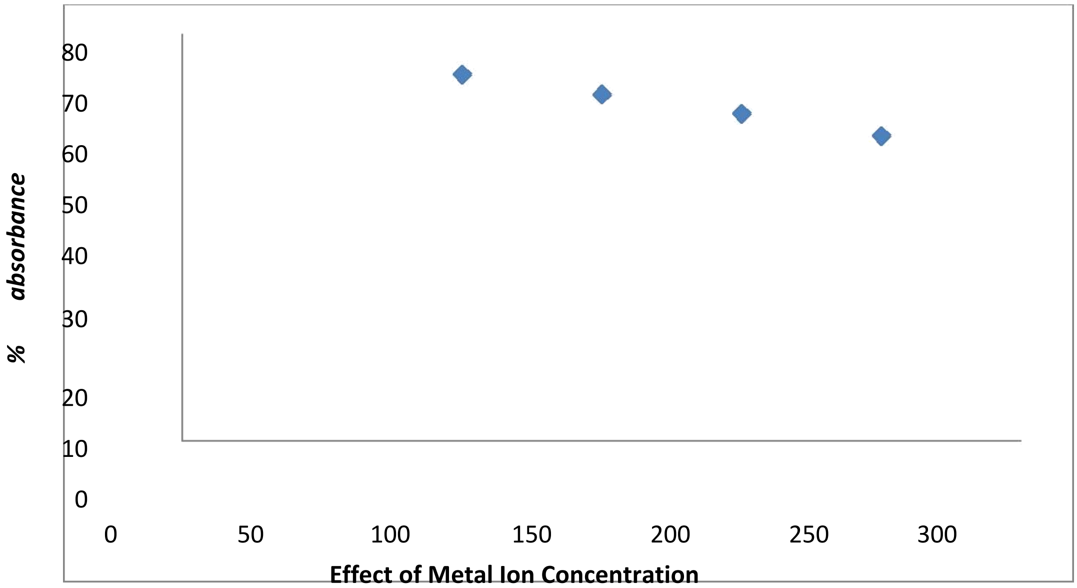

Fig: 12 Effect of Metal ion concentration

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