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Kinetics and thermodynamics study of biosorption of Hg^{2+} by sulphonated biomass of *Cicer arientinum*- batch studies

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ABSTRACT

Present work deals with fundamental investigation on the removal of heavy metal from aqueous solutions by chemically treated biomass of Cicer arientinum is conducted in batch conditions. Adsorption kinetics and isotherm data are determined, and effect of different parameters such as contact time, sorbent dose, pH and temperature has been studied. Modeling of kinetics results shows that sorption process is best explained by pseudo – second order model with determination coefficients 0.997 for S-III under all experimental conditions. Weber and Morris intraparticle diffusion model is used to determine the mechanism. Thermodynamic parameter via KD, ΔG has also been calculated to determine the spontaneity of the process.

Key Words S-III (Sulphonated biomass of Cicer arietinum), E.D.T.A., Adsorption, biosorption

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INTRODUCTION

The processes adsorption is found to be highly effective, cheap and easy method. Heavy metals in waste water as well as industrial effluents have emerged as the focus of environmental remediation effort because of their toxicity to human being. Active carbon in most cases has been used as adsorbent for reclamation of municipal and industrial waste water for almost last few decades but the high cost carbon has inspired investigation to search for low cost agriculture waste as adsorbents. The ground water is mainly contaminated by heavy metals released from industrial and their persistence in food chain has been of major concern as it is seriously poisoning aquatic culture including fisheries. The heavy metal Hg^{2+} present in high concentration in the waste of industries like pharmaceutical, paint, pigment, insecticide, cosmetics and polymer etc. causes serious problems to environment. The Hg^{2+} reported by WHO is highly toxic to human life, and other heavy metals are reported to be bio-accumulated into flora and fauna creating ecological problems. The toxicity of hexavalent chromium from the discharge of various industrial wastes is well studied by D.K. Singh[1]. The use of various adsorbent such as activated carbon rice husk carbon saw dust, and fly ash, ash- woolastonite have also been documented for the Biosorption of Chromium (VI) from aqueous solutions by the husk of Bengal gram[2] (Cicer arientinum)**.,** was reported by N. Ahalya., R.D. Kanamadi. K.S. Subramanian have reported lead[3] contamination of drinking water and utilization of fly ash and waste tea leaves as decolorizing agent for dye effluents. Periasamy and Namasivaym used the agricultural waste activated carbons reported that the carbon prepared from the waste is successfully employed for the removal of Ni (II) from waste water [4]. Marshall and Johns evaluated the sorption properties of deflated rice bran, soya bean and cotton seed hulls and their resistance to mechanical abreation[5] Othman and Amin have used the rhizopus oligosporus biomass for the biosorption of Cu^{2+}, Mn^{4+}, Zn^{2+} at the maximum adsorption rate[6] . Li Q., Wu, S. worked on comparison between biosorption of Pb^{2+} ions and Cd^{2+} by the biomass of P. Chrysosporium [7]. Ricardo. C., Tarley and Arruda characterized the rice milling by-products [8]**,** used for removing Cd (II) and Pb (II) ions from effluents. Biosorption of nickel (II) and Copper (II) ions from aqueous solution by dried Streptomyceous colicolor Al (II) [9] was studied by Ozturk. as a function of concentration, pH and temperature. Mirtezky. studied the mechanism of simultaneous metal removal Cd (II) Ni(II), Cu(II), Zn(II) and Pb(II) by three macrophyte biomass[10] Partially converted crab shell waste which contains chitosan was used by Pradhan to remove nickel from water[11] . Alternative. Padmavathy worked on the biosorption of nickel (II) ions by deactivated protonated yeast [12]. Akar. Carried out a study on Pb^{2+} accumulatation on the surface of Botrytis cinerea [13]. The biosorption of cadmium and lead ion from artificial aqueous solution using waste baker's yeast biomass [14] was investigated by Goksungur. Choy and McKay studied the rate of adsorption of cadmium[15] **,** copper and zinc ions onto bone char in three single component systems using an agitated batch adsorbent Rice straw soybean hull, sugar baggase. Adsorption behavior of Cd^{2+}, $Pb^{2+,}$ NI^{2+} Cd^{+2} and Zn^{2+} from aqueous solutions by mangifera indica[16] seed shell was reported by Mohammad Ajmal . , Tsunetaka Sasaki has been worked on adsorption of dyes, chromate and metallic ions by polyethleneimine [17]**,** Removal of fe^{2+}, $Zn^{2+}$and Mg^{2+} from polluted water using thioglycolic modified oil-palm fibre [18] was done by J.O.Akaniwor**.** Mazahar Farooqui reported that the use leaves of Cauliflower [19] for removal of iron from waster water**.** Bad S. Girgis has been worked on activated carbon from cotton stalks [20] by impregnation with phosphoric acid. A Sorption study of Al^{3+},Co^{2+} and Ag^{+} in aqueous solutions by Fluted Pumkin [21] waste biomass was carried out by Michael Horsfull Jnr and Ayebaemi I. Spiff. The uptake capacity of Chromium (VI) by nitrated and sulphonated Coconut Shell carbon[22] was studied by V. Selvi and G.P. Jeyanthi , A batch study was carried out by Mohamed Chaker Ncibi on biosorption of textile dyes[23] from aqueous solutions using Posidonia oceanica leaf sheath fibers. Srivastava et al have studied adsorption of heavy metal ions on carbonaceous material [24] developed from waste slurry of fertilizer plants.

MATERIALS AND METHODS

2. Experimental

2.1 Preparation of biosorbent:

The sieved biomass of *Cicer arientinum* was taken in a beaker and soaked in AR conc. Sulphuric acid for 2 hours. It was then washed thoroughly with distilled water till the black mass was acid free. The black mass was then dried at 110 ^{0}C in the oven for 3 hours. The material sieved though 63 mm mesh to get particles of uniform size. S-III. The present work deals with the study of adsorption of heavy metals Hg^{2+} ions on chemically treated biomass of *Cicer arientinum S-III* Adsorption experiments were carried out for adsorption of mercury using sorbents S-III. For the adsorption experiments stock solution of $HgCl_2$ was prepared of strength 1.96 $x10^{-3}$ $gm/Hg^{2+}/ml$. (solution A). 50 ml of solution A and 50 ml of distilled water were taken in a conical flask maintained at constant temperature in a thermostat. To this 500 mg of the appropriate S-III was added, it was stirred for 2.5 minutes and then filtered The same procedure was followed for time intervals 5.0,7.5,10,15,30,90,120, and 180 minutes. Similar experiments were repeated using different material doses 1.0 gm. 2.0 gm, 5.0 gm. Amount of lead in the filtrate was determined by titrating against standard E.D.T.A. solution. The effect of contact time, temperature, pH of solution, and material dose on removal of the Hg^{2+} ion was studied.

RESULTS AND DISCUSSION

3.1 Effect of time:

The percentage of Hg^{2+} adsorbed by the sorbent was found to increase with time, equilibrium being attained into 2 hours on the S-III. Initially the adsorption was very fast and at equilibrium % removal was 80 to 81% **(Fig-.1).** Initially the adsorption was very fast and at equilibrium % removal was 74 to 76 %.

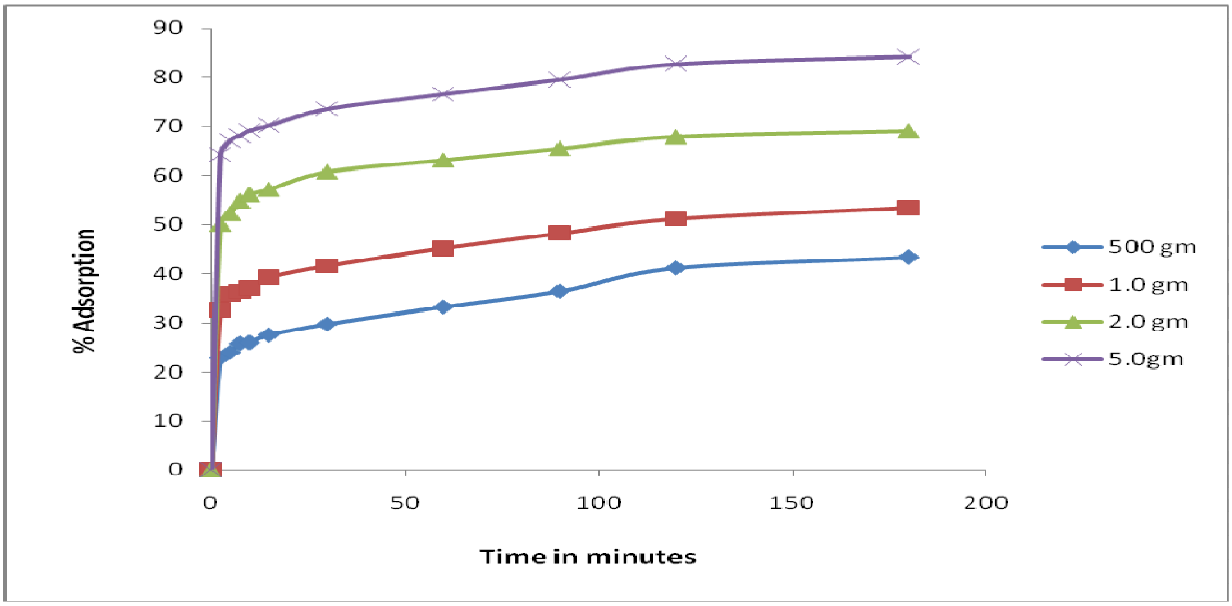


Fig. 1

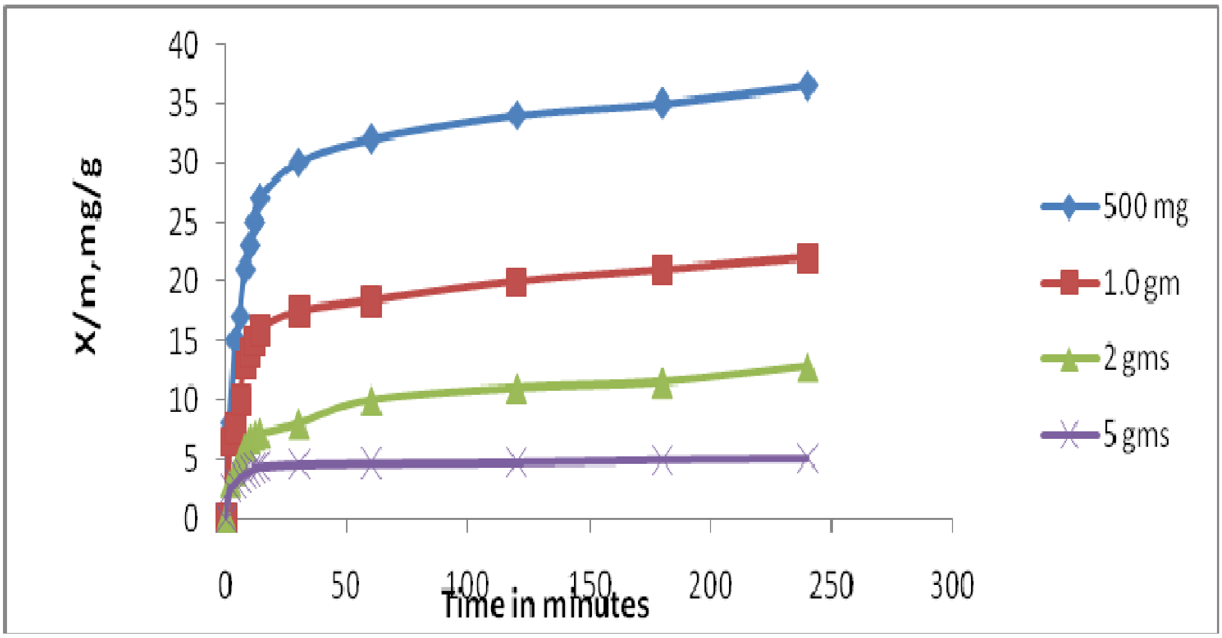


Fig. 2

3.2 Effect of sorbent dose:

The adsorption of Hg^{2+} ions on S-III was studied using the doses - 500 mg /100ml, 1g/100ml, 2.0 g/100ml and 5 g/ 100 ml. For S-III with increase in sorbent dose **(Fig-2).** , percentage of metal ions adsorbed increased from 36.01 % to 75.45 %. The x/m values in mg/g showed a decrease with increasing sorbent dose. This can be attributed to the increased surface area and availability of more sorption sites.

3.3 Effect of pH:

The initial pH of the solution influences the kinetics of the sorption. This was because with increase pH, the metal ion has a greater chance to react with the active sites on the surface. The increase in pH also leads to deprotonation of the functional groups present on the surface. Present study indicates that at pH 4 the % adsorption was 52.5 % and it increased to 54.7 % at pH 5. A substantial increase was observed when the pH was raised to 6. The % adsorption at this pH was 67.6 % on S-III **(Fig-.3).** indicating the best compatibility of surface sites and chemical species of Hg^{2+} present for the adsorption to occur. The increase in pH probably leads to increase in the concentration of $Hg(OH)_2$ and to a lesser extent $Hg(OH)^+$. At a higher pH precipitation or solubilization of hydroxide may be causing a reduction in the % adsorption.

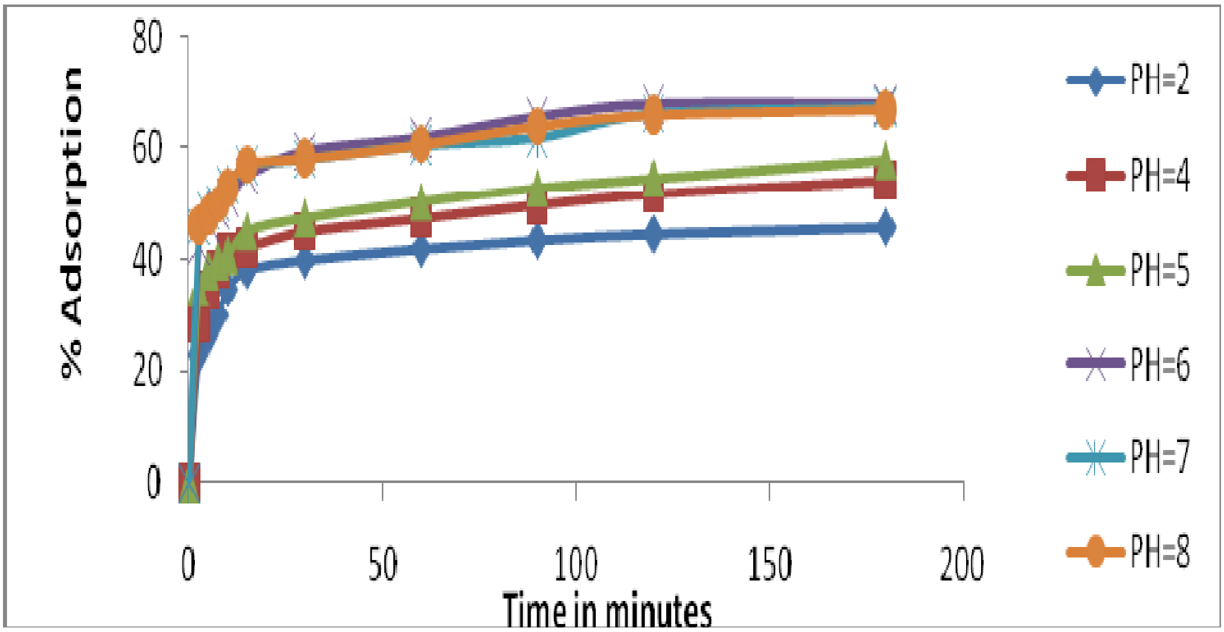


Fig. 3

3.4 Effect of temperature:

Adsorption appears to be an energy activated process in all cases where the rise in temperature results in the enhancement of adsorption. Results show that the process of adsorption of Hg^{2+} on S-III is highly temperature dependent. The adsorption is found to increase from 38.4 % at 15°C to 79 % at 45°C for S- III **(Fig-4).** .

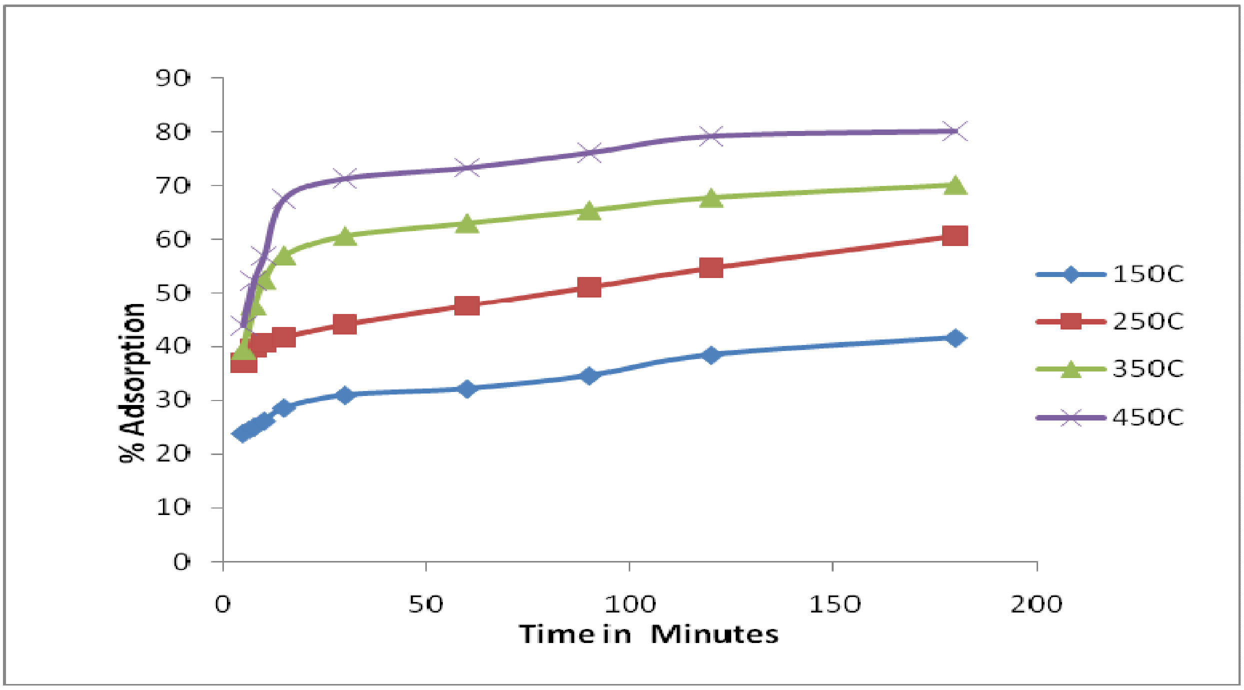


Fig. 4

3.5 Thermodynamic study of Hg^{2+} on S-III

The adsorption of Hg^{2+} on S-III gives KD values ranging from 0.7130 to 4.99 **(Table-1).** Sorbent III shows spontaneity in adsorption from room temperature onwards, as indicated by negative values of ΔG, The ΔG values are much better for S-III and Esoteric heat of adsorption ΔH of Hg^{2+} on S-III **(Fig-.5).** is found to be 7.6949 KJ/Mole.

Table-1: Thermodynamic study of Hg^{2+} on S-III

Temperature in K	KD	ΔG J/mole
288	0.7130	+806.35
298	1.544	-1071.79
308	2.359	-2188.7
318	4.99	-4232.44

3.6 Adsorption isotherm:

The plot of Ce/qe Vs time gave straight plots but the values of Langmuir constants were negative and with low coefficient of determination, indicating the no applicability of the isotherm to this system. The plots of log qe *vs.* log Ce gave straight line with intercept and slope having values 1.055 and 0.094 respectively. The value of Kf and n were found to be 11.36 and 10.0 respectively. Values of n between1-10 indicate favorable adsorption. Smaller value of 1/n indicate stronger bonds between sorbate and sorbent. The values of Kf 11.36 indicate a fair rate of adsorption. The R^2 value is found to 0.8061. From these observations it can be concluded that although the bond between sorbent and sorbate is strong the removal of Hg^{2+} by S-III and adsorption is not the only mechanism of removal but involves a combination of other mechanisms such as ion exchange, electrostatic attraction etc.

3.7 Kinetics of the adsorption of Hg^{2+} on S-III

The adsorption kinetics on S-III can be assessed by applying various mathematical models proposed. The data was therefore fitted in the Lagergrens first order model. The plots of log (qe –qt) vs. qt **(Fig-.6).** gave lines with low regression coefficients indicating the non applicability of the model. The lines obtained from the plots of t/qt vs. t gave straight lines with linear regression coefficients very close to unity (0.9971). For sorbent S-III values of Intercept and slope were found to be 0.2573 and 0.0525 respectively **(Table-2)** From these results it can be concluded that adsorption of Hg^{2+} on treated *Cicer arientinum* follows pseudo second order mechanism [25]

Fig-5 Plot of log qe-qt vs. Time for adsorption of $Hg^{2+}$by S- III

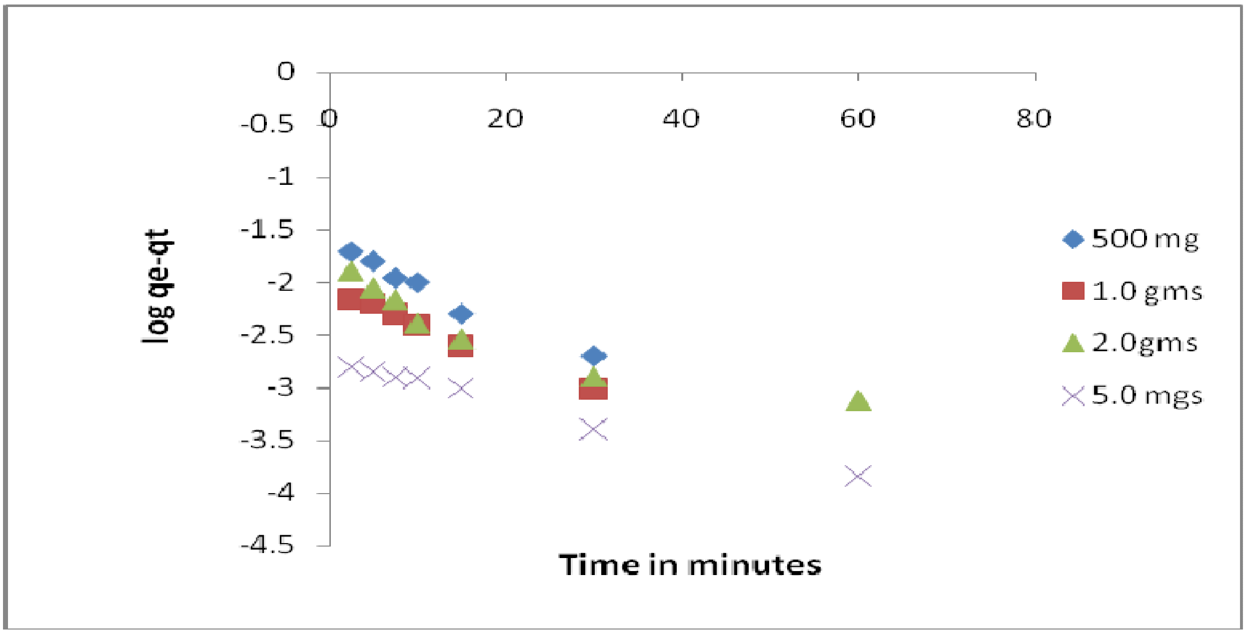
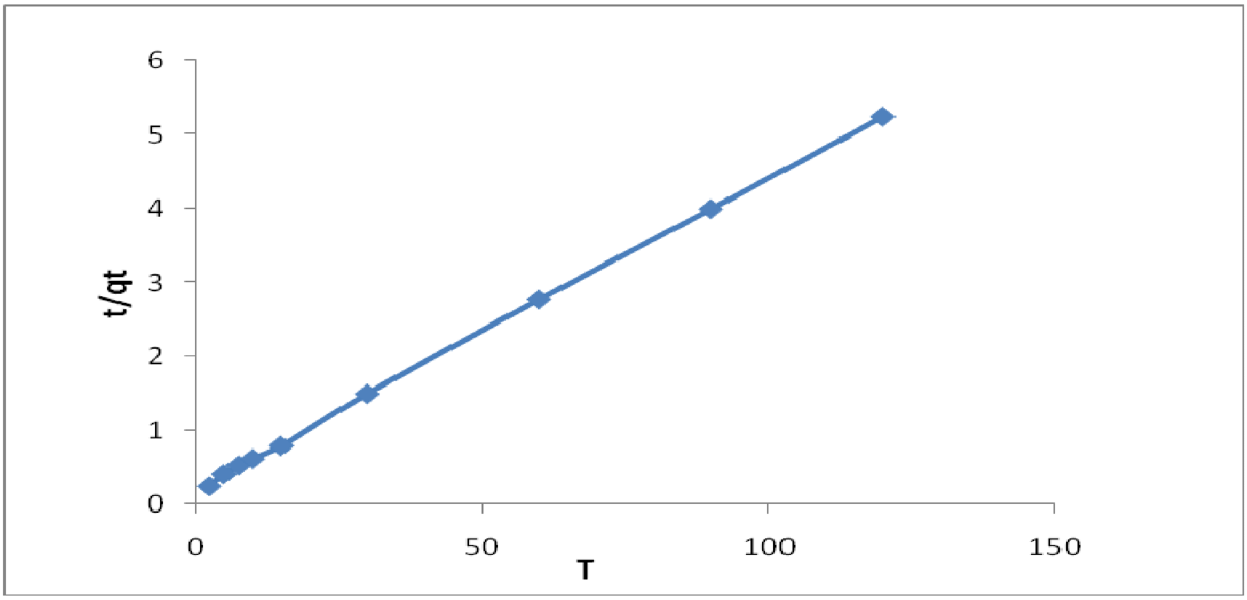


Fig. 6 Plot t/qt vs. T for S- III , Hg^{2+}



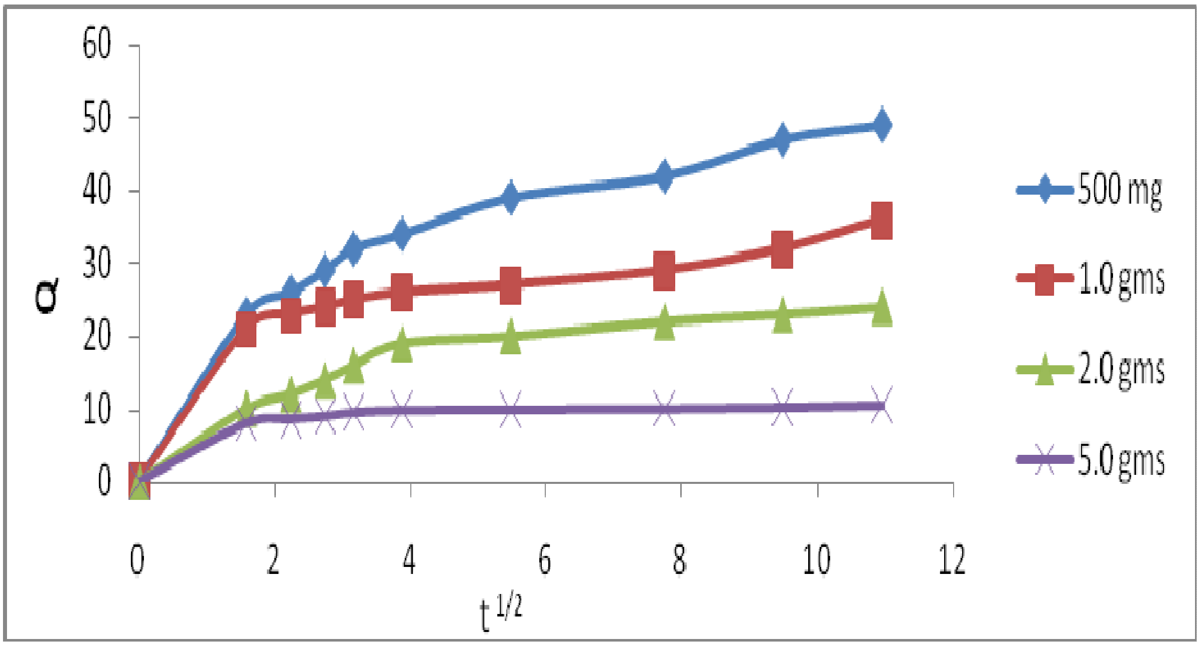
3.8 Webber –Morris intraparticle diffusion model:

The plots of Q vs. t ^{½} show different portions. The initial portion of the curve is attributable to rapid external diffusion or boundary layer diffusion, linear portion representing the intraparticle diffusion and the third plateau region where intraparticle diffusion starts to decrease due to the lower concentration [26]. A careful observation of the plots of Q vs. t $^{1/2}$ with varying material doses **(Fig-7).** reveal that **at** low material dose both external diffusion and intraparticle diffusion mechanisms [27] are functional, when the material dose is increased to 5.0 g/100 ml after the initial rapid external diffusion the plot shows the plateau indicating that the concentration of the Hg^{2+} in the solution is much low, and effect of intraparticle diffusion is almost negligible and the boundary layer is much insignificant compared to lower material doses cases. Values of intercept with different sorbent doses also show a substantial decrease which reflects the decreasing boundary layer effect with increase in sorbent dose. The deviation of lines from the origin clearly indicates that intraparticle diffusion is not the rate limiting step. At higher doses the macropore diffusion is predominant while at lower doses the effect of intraparticle diffusion is seen.

Table-2

Dose /100 ml	Intercept	K id (mg/g)
500 mg	27.04	2.02
2 g	17.34	0.571
5 g	9.0	0.491

Fig. -7 Plot of Q vs. $t^{1/2}$ for S- III



CONCLUSION

- Equilibrium is attained within two hours. But initial adsorption is very fast
- Maximum adsorption on S-III is 80%.
- The percentage adsorption increases in the order 500 mg < 1 g < 2g < 5 gm.
- On S-III maximum adsorption takes place at pH 6
- KD values show an increase from 15° C to 45° C.
- ΔG values for S-III are 7.6949 KJ/moles.
- Freundlich isotherm is applicable with Kf values to be 11.36 and 10.0 for S-III.
- Linear plots of t/qt vs. t with R^2 values close to unity are obtained indicating that adsorption of Hg^{2+} follows pseudo-second order mechanism.
- Plots of Q vs. t ½ for data obtained on S-I show three distinct regions at high sorbent dose so it has been concluded that both external diffusion, intraparticle diffusion mechanism are

functional at higher material dose. boundary layer effect becomes insignificant. S-III and micro pore diffusion is predominant as indicated by Kid values.

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