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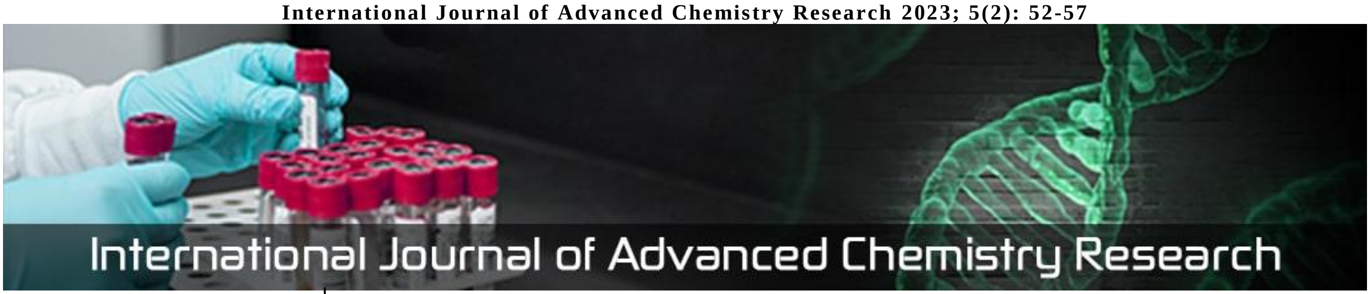

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Adsorption of Cd (II) and Hg (II) from aqueous phase by adsorbent prepared from *Cassia tora* fruit shell

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Abstract
The Cd (II) and Hg (II) are highly toxic when enters into the body of a living being. Present study describes the adsorption behaviour of these metal ions from aqueous phase using *Cassia tora* fruit shell substrate. The effect of various parameters like pH, contact time, initial metal ion concentration, doses of adsorbent and temperature on adsorption of metal ions was studied. Freundlich and Langmuir adsorption isotherm best fitted with experimental data. The adsorption capacity for Cd (II) and Hg (II) at pH 6 for optimum contact time of 75 minutes at 100 ppm concentrations was found to be 27.247 and 12.545 mg g^{-1}, respectively. An effective adsorption of about 85-92% of metal ions was observed in single batch. The temperature has inverse effect on extent of adsorption of metal ions and it increases with doses of substrate. The fruit shell substrate was found to be efficient medium for removal of Cd (II) and Hg (II) ions from aqueous solution.

Keywords: Adsorption, Cd (II) and Hg (II), batch studies, fruit shell, isotherm

Introduction
In this portion, the main problem, selected in the study should be discussed with the relevant earlier literature and the proposed method or solution. Proper references should be used in support to the content.

The heavy metals such as As, Cd, Cr, Hg, Pb etc. are non-biodegradable, persistent and considered as significant environmental pollutants [1] and are highly toxic to living organisms. They enter in natural water bodies and causes water pollution and at higher concentration threat living organisms and human beings [2]. The maximum permissible limits for discharge of toxic heavy metals in aquatic ecosystem has been set by different regulatory bodies, but still the concentration in water bodies are at much higher level than prescribed limits. This results in environmental pollution. So, it becomes very important to remove heavy metal ions from water before discharge to protect the public health.

Toxic heavy metals accumulated in natural water bodies by different natural and industrial sources. Various techniques are available for removals of toxic heavy metals are adsorption, coagulation, oxidation, membrane separation etc. Adsorption is the most effective and widely used method for metal removal [3].

The Cd (II) and its compounds are classified as carcinogenic by IARC [4]. The ingestion and inhalation of cadmium may cause kidney dysfunction and severe damage to lungs; and its chronic exposure may lead to death [5]. Hg (II) is another potential pollutant converts into methyl mercury – a major organic mercury in natural water causing high bioaccumulation in food chains. It leads to serious damage in the brain, heart, liver, kidneys as well as nervous and metabolic systems and may cause cancer [6]. Maximum permissible limit of Cd (II) prescribed by WHO in drinking water is 0.003 ppm and that of Hg (II) is 0.002 ppm [7].

In present work, we are trying to use an eco-friendly low coast adsorbent material for removal of Cd (II) and Hg (II) from water. A biotechnological approach involving fruit shell substrate of *Cassia tora* (Charota) plant for removal of Cd (II) and Hg (II) offers best solution.

Materials and Methods: The detailed experimental protocols, instruments and software etc. used in the study should be described here with their proper references. The details of the study area should also be provided.

a) Preparation of Adsorbent

Fruit shells of *Cassia tora* plant have been collected, sun dried, powdered in grinder and screened to get homogeneous powder. The powder was treated overnight with solution 25 ml formaldehyde in 100 ml 0.1 N nitric acid with occasionally shaking in electronic shaking machine. Then filtered and washed with distilled water to remove acid residue. Finally, sun dried and the adsorbent prepared was used for study.

b) Preparation of metal ion solution

All chemicals used in the study were of AR grade supplied by m/s Merk. Solutions were prepared by using metal salts of Cd (II) and Hg (II). The pH was adjusted by using dilute solution of nitric acid and/or sodium hydroxide, if necessary. Stalk solutions of 500 ppm of Cd (II) and Hg (II), were prepared respectively. Other dilutions prepared from respective stalk solutions.

c) Batch Study

Batch experiments were performed to know the effect of different parameters like pH, contact time, initial concentration of metal ions, doses of adsorbent, temperature etc. on adsorption of metal ions. 100 ml solution of metal ion agitated with different doses of fruit shell substrate ranging from 1-4 gm in 250 ml corked bottle on a shaking machine. Different concentrations of metal ion, different time duration and different temperature have been set for study. The amount of Cd (II) and Hg (II) adsorbed on treated biomaterial was recorded by using standard methods. Percentage removal of metal ions was calculated using equation-

$$\% \text{ Removal} = \frac{(C_0 - C_f)}{C_0} \times 100$$

Where, C_o is initial concentration and C_f is final concentration of metal ions in ppm.

Results

Effect of pH

The pH of solution affects adsorption of metal ions [8]. Removal of Cd (II) and Hg (II) changes with pH of solution ranging from 2-9. Variation of % Removal with pH is shown in Fig. 1. The maximum removal of Cd (II) and Hg (II) was observed at pH 6. At higher pH both metal ions precipitated due to the formation of hydroxides. At low pH higher concentration of hydrogen ions make metal binding sites unavailable metal ions. Negative charge density on adsorbent increases with pH due to deprotonating of metal binding sites, increasing adsorption of metal ions [9].

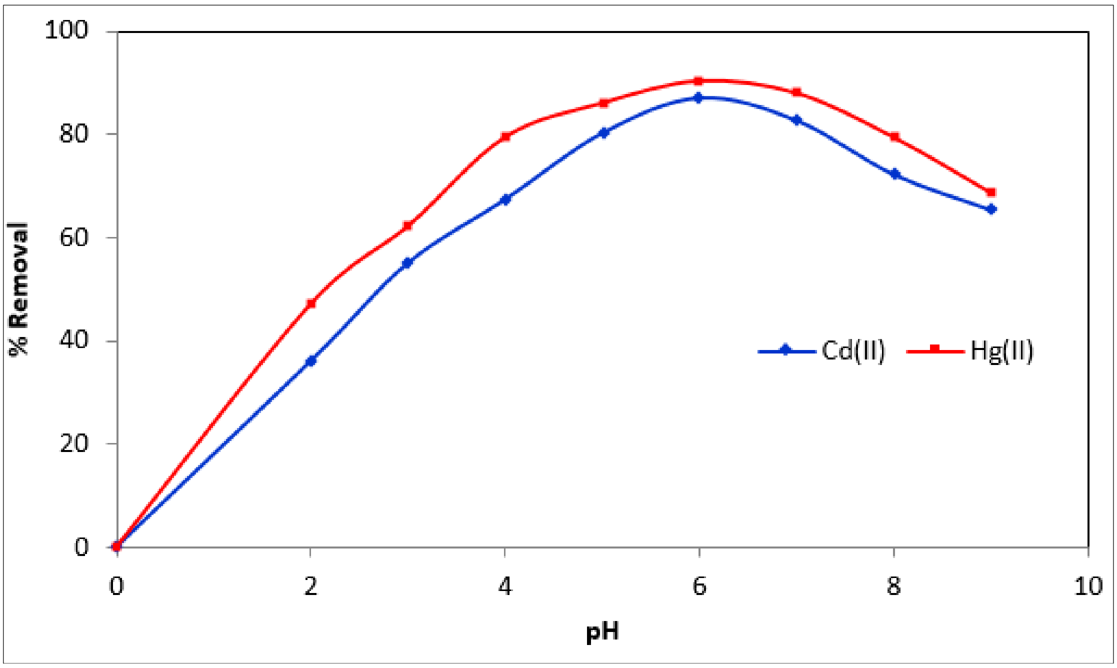

Fig 1: Effect of pH

Effect of contact time

The parameter is required to find out time required to establish equilibrium. 1 gm *Cassia tora* fruit shell substrate with 100 ml of metal ion solution at pH 6 was agitated for different time intervals of 15-120 minutes. The concentrations of solution were fixed to 100 ppm. The % removal of metal ions increases with time until equilibrium is reached after 75 minutes for each metal ion [10]. The results are shown in Fig. 2.

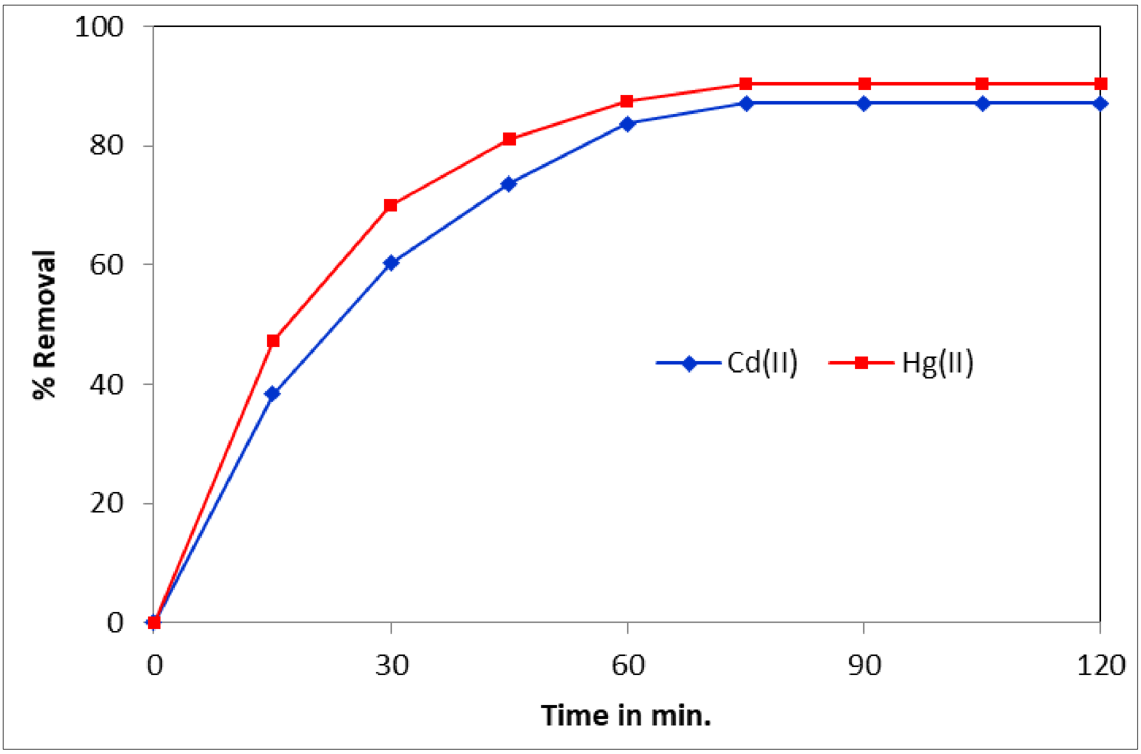

Fig 2: Effect of Contact time

Effect of initial concentration

Initial metal ion concentration affects efficiency of adsorbent. Concentration ranging from 50 to 200 ppm was fixed for comparative study. Results are shown in Fig. 3. At low concentration percent adsorption was high due to availability of more adsorption sites and at higher concentration most of adsorption sites are covered and adsorption capacities exhausted due to non-availability of active sites. Hence, % removal decreases at higher concentration [11].

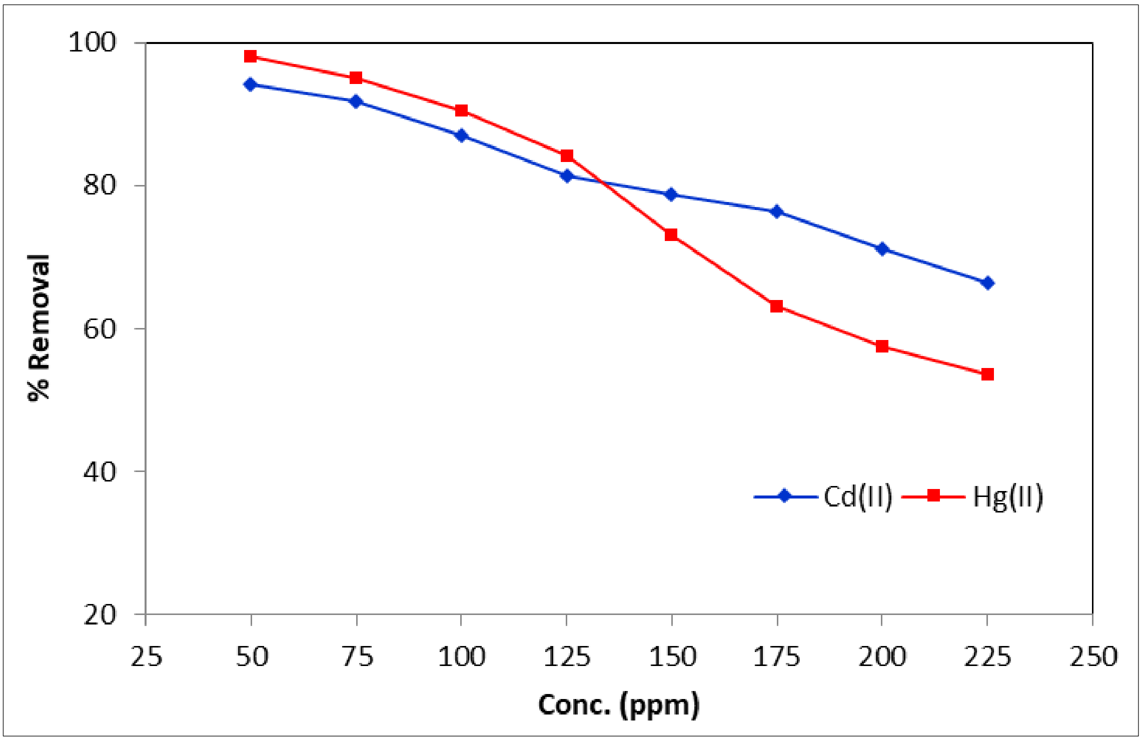

Fig 3: Effect of initial metal ion concentration

Effect of doses: Effect of adsorbent doses investigated by taking doses of adsorbent ranging from 0.1 to 1.0 g. Optimum condition was fixed as 100 ppm metal ion concentrations, pH 6 of solution, 75 min contact time, at room temperature. The results are given in Fig. 4. The % removal of both metal ions gradually increased with dosage from 0.1 to 1.0 g. The number of adsorbent sites increased with adsorbent doses [12]. Hence, 1 g dose of adsorbent was considered enough for the removal of Cd (II) and Hg (II) from 100 ml solution under given conditions [13].

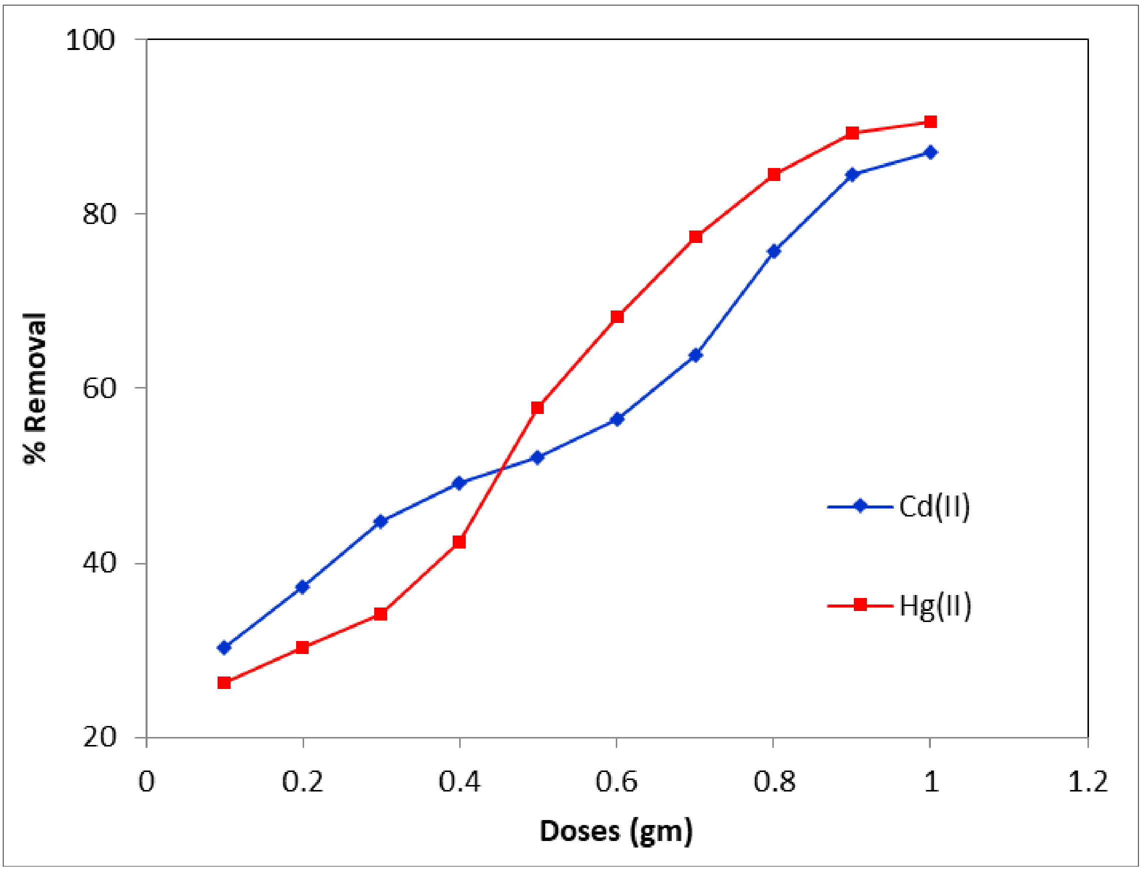

Fig 4: Effect of adsorbent doses

Effect of temperature

Temperature has marked effect on adsorption of metal ions [14]. 100 ml Cd (II) and Hg (II) solutions at fixed optimum conditions agitated with 1 gm of adsorbent at different temperatures from 30-90 °C. The results are shown in Fig. 5. Maximum % removal was observed at room temperature (30 °C). It decreases with increase of temperature, so, all further experiments were conducted at room temperature.

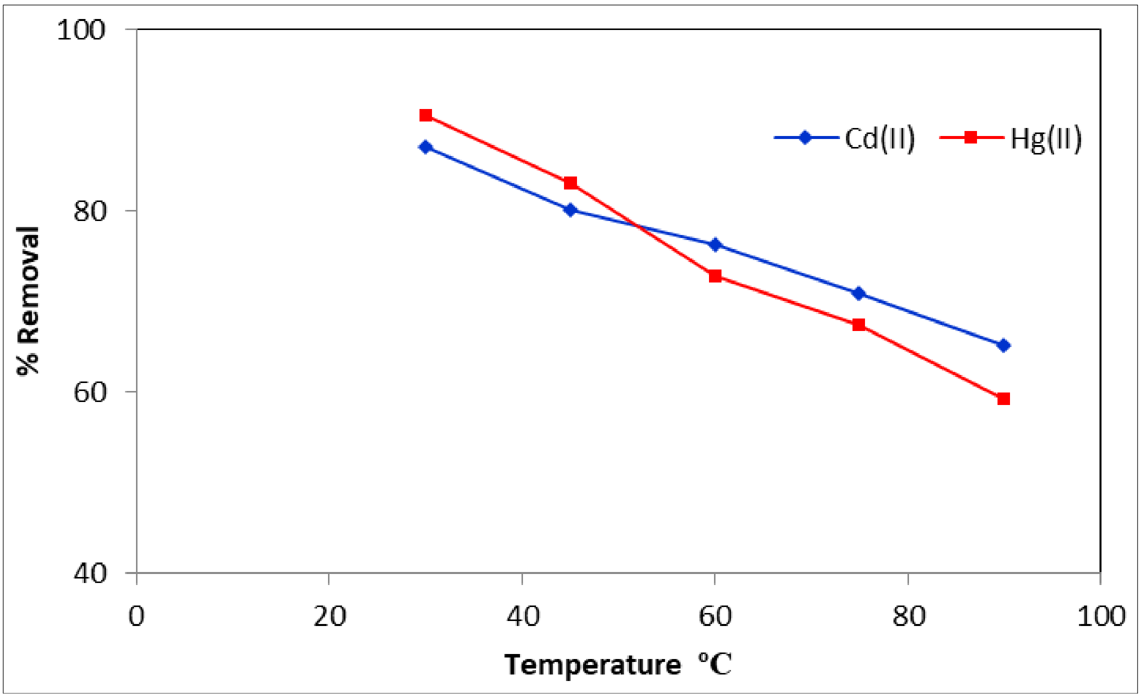

Fig 5: Effect of Temperature

Adsorption Isotherm: Freundlich and Langmuir adsorption isotherms were selected in the present study to understand mechanism of adsorption [15]. An empirical equation of Freundlich isotherm employed to describe adsorption on heterogeneous surface [16]. Given as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Where, K_f is Freundlich constant (mg g^{-1}); 1/n is absorption intensity (calculated from slope of the plot log q_e versus log C_e); q_e is amount of metal ion adsorbed per gram of adsorbent; C_e is equilibrium metal ion concentration. Freundlich isotherm for adsorption is given in Fig. 6.

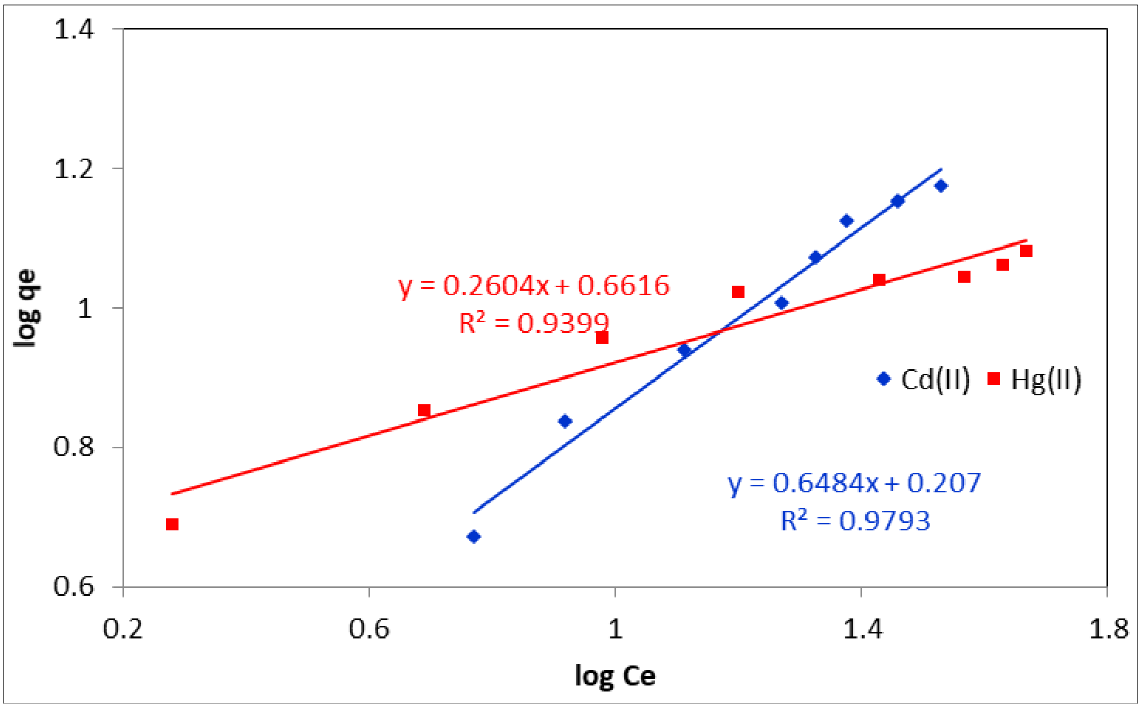

Fig 6: Freundlich adsorption isotherm

Langmuir isotherm is based on monolayer adsorption processes. Langmuir isotherm equation is represented as [17] follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m \mathrm{b}} + \frac{1}{q_m} C_e$$

Where, q_m is maximum metal ions uptake (mg g^{-1}); b is Langmuir constant (L mol^{-1}) A plot of C_e/q_e versus C_e gives a straight line of the slop $1/q_m$ and intercept $1/(q_m\ b)$. Langmuir isotherm is shown in Fig. 7.

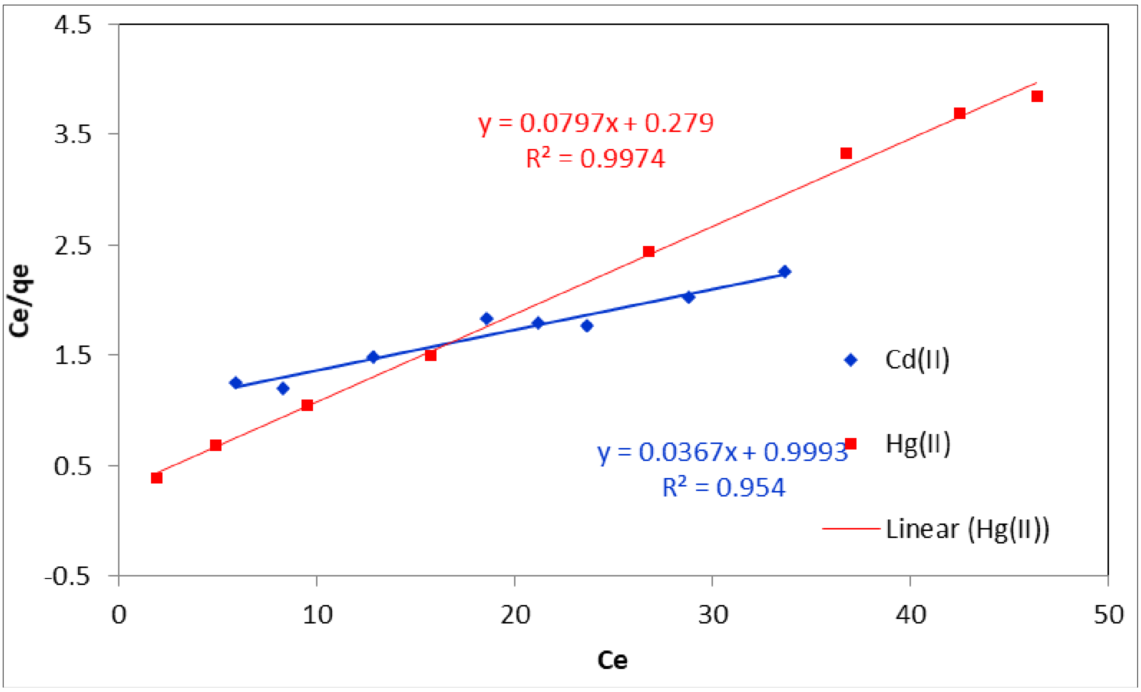

Fig 7: Langmuir adsorption isotherm

Discussion

Parameters of Freundlich and Langmuir isotherms for adsorption of Cd (II) and Hg (II) are given in Table 1. Langmuir isotherm model fits very well than Freundlich model for Hg(II) as R^2 of Langmuir plot >0.99 close to unity [18]. Freundlich constant *n* is the measure of deviation from linearity of adsorption. If *n* is below unity, adsorption process is governed by a chemical mechanism, but if *n* is above unity, adsorption is favourable a physical process. The values of *n* at equilibrium are >1, indicates physical mechanism refers to weak bonds.

Table 1: Parameters of Freundlich and Langmuir isotherms

Métal Ions	Freundlich			Langmuir		
	K_f (mg g^{-1})	N	R^2	q_m (mg g^{-1})	B	R^2
Cd(II)	1.610	1.542	0.9793	27.247	0.0367	0.9540
Hg(II)	4.577	3.840	0.9399	12.545	0.0797	0.9974

Conclusion

The study based on use of *Cassia tora* fruit shell substrate for removal of Cd (II) and Hg (II). It has been found that adsorption of metal ions was fast and equilibrium maintained in 75 minutes. The % removal of metal ions was increasing with pH and more than 8 pH leads to precipitation. With increasing adsorbent doses adsorption also increases and temperature has inverse effect on % removal. Freundlich and Langmuir equations have been used to describe the adsorption behaviour of Cd (II) and Hg (II). The values of correlation coefficients show Langmuir model provide better correspondence. The monolayer adsorption capacity of fruit shell substrate on the basis of Langmuir isotherm for Cd (II) and Hg (II) ions were found equal to be 27.247 and 12.545 mg g^{-1}, respectively. These values are quite satisfactory. Thus, the substrate was found better adsorbent for treatment of metal ions from aqueous phase.

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