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Removal of Cd(II) from Aqueous Solution by Using *Arachis hypogea* as Low Cost Biosorbent

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Present study reports the removal of cadmium(II) removal from aqueous solutions by using *Arachis hypogea* as abundantly available biomaterial. Kinetic and equilibrium studies have been reported. Effects of various parameters such as pH, stirring speed, initial metal ion concentration, contact time, adsorbent dose have been found in batch experiments in their significant ranges. Freundlich and Langmuir isotherms have been applied to find adsorption behaviour.

Keywords: Cadmium(II), Biosorption, Wastewater, Heavy metals, *Arachis hypogea*.

INTRODUCTION

The rapid industrialization during last few decades without any concern for its impact on the environment has put survival of living beings at stake. Organic and inorganic compounds either deliberate through industrial emissions or accidental through chemical or oil spills, *etc*. released into the environment [1]. The heavy metals are introduced into water streams from various industries *viz*. refining of ores, incinerators, electroplating, paints, mining, alloys, batteries, pesticides, paper industry, leather tanning, sludge disposal, organo-chemicals, petrochemicals, fertilizer industries, automobiles, metal processing, *etc*. The presence of heavy metals into wastewater streams has turned to the serious concern to our ecosystem.

Cadmium(II) is one of the important metals widely used but highly toxic. The major sources of pollution due to Cd(II) are plastic manufacturing, electroplating, Cd/Ni batteries, metallurgical processes, pigments, fertilizers and pesticides, *etc*. [2]. Health impacts of Cd(II) in relatively low dosages have been observed as destruction of red blood cells, high blood pressure, kidney damage, bone fraction and renal disorder [2]. Itai-Itai desease is a classical example of the hazard caused by Cd(II) contamination in Jintsu river basin in Japan in 1912 [3].

The prime need of such industries releasing heavy metals is to have relatively simple but effective inexpensive technologies for wastewater treatment. In developing countries like India, there have been fewer and less rapid technological advances and industries rely much on unskilled labour and less on automation. Over the years, various technologies for taking up the heavy metals from wastewater have been explored. Conventional technologies for this purpose include flotation [4], chemical precipitation [5], adsorption on minerals, chelating resin [6-8], membrane separation, electrolytic recovery and reverse osmosis [9]. These conventional techniques have many limi-tations and disadvantages such as cost, sludge formation, availa-bility and reusability. Adsorption is found to be a better technique to overcome the limitations stated above. Adsorption on activated carbon [10-12] and activated carbon obtained from agricultural waste material [13] are widely used. However, the use of agricu-ltural waste materials/biomaterials as adsorbents has been studied during last few decades which reduces the cost to further extent providing an almost comparable efficiency. Biosorption using low cost biosorbents has been found considerably effective for removal and recovery of heavy metals from aqueous streams [14,15]. Many of cellulosic materials found in nature have been used for the purpose. Some of these are plant/agricultural wastes such as tea waste [16], coffee beans [17], coffee husks [18], mungbean husk [19], tree leaves [20], sugar beet pulp [21], potato peels and fruit shell [22], bamboo charcoal [23], papaya wood [24], peels of lemon, orange, grapefruit, apple, apple kernel, grape [25], sesame [26], cork biomass [27], pine-apple waste [28], *etc*.

In the present study, *Arachis hypogea* have been tried to observe its potential capacity for removal of Cd(II) from water stream. Kinetic and equilibrium studies have been made for Cd(II) sorption on this biomaterial. Through the batch experiments, effects of various parameters affecting the adsorption of cadmium on biomaterial have been investigated [29-34].

EXPERIMENTAL

Synthetic solutions of cadmium(II) ions have been used for performing the experiments. Analytical grade chemicals were used for all experimental purpose. For preparation of a stock solution of cadmium(II) concentration as 1000 mg/L, cadmium(II) nitrate (Merck) in double distilled water was used. To obtain solutions of desired Cd(II) ion concentrations by diluting stock solution, double distilled water was used. 0.01M HCl and 0.01M NaOH were prepared for adjustment of pH of the solutions. The pH and Cd(II) ion concentrations were measured by using pH/ISE meter (ThermoScientific Orion, model: DUAL STAR).

Arachis hypogea were collected from the local market at Longowal, India, and dried in sun for about 10 h and then at 110 ºC in hot air oven for 10-12 h. After grinding, the biomaterial was washed with double distilled water. The material was again dried at 110 ºC for 24 h and then sieved to get 250-300 micron size particles and packed in sealed polyethylene bags for further use.

Characterization of biomaterial: The biosorbent material was characterized by proximate analysis to find the moisture content, ash content and the loss of weight at various temperatures upto 500 ºC. The functional groups available over the biosorbent were analyzed by using FTIR.

Batch experiments: Batch experiments were performed to study the adsorption of cadmium from aqueous solutions at various pH (2-8), initial metal ion conc. (10-200 mg/L), stirring speed (50-300 rpm), adsorbent dose (400-2000mg) for 30 min contact time in the Erlenmeyer bottles on the orbital shaker.

Through the preliminary experiments, the suitable ranges of each parameter were found and the final experiments were performed for studying effect of various parameters mentioned above keeping other parameters constants. After fixing pH of the solution (100 mL) with known initial conc. of metal ion, desired dose of biosorbent was added and solution was kept on stirring on orbital shaker at specific speed for desired time. At the end, the solution was decanted off and filtered. Residual concentration of Cd(II) in the solution was analyzed by using pH/ISE meter. All experiments were replicated thrice.

Equilibrium studies: The relationship between equilibrium concentration of the metal ion in solution (Ce, mg/L) and the amount of metal adsorbed per unit mass of biosorbent (x/m, mg/g) is represented by Freundlich adsorption isotherm

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e$$

where n and K_f are Freundlich parameters representing extent of adsorption and the adsorption capacity of biosorbent towards the metal, respectively.

Langmuir isotherm expresses the monolayer adsorption over a surface with finite number of identical sites resulting in uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. It is given as:

$$\frac{C_e}{\left({}^{x}\!/_{m}\right)} = \frac{1}{Q_o b} + \frac{C_e}{Q_o}$$

where b and Q_o are Langmuir constants corresponding to energy of adsorption and adsorption capacity, respectively.

RESULTS AND DISCUSSION

Proximate analysis: A known quantity of the biomaterial sample was heated to different temperatures to carry out proximate analysis and the loss in weight was recorded upto 500 ºC. At 100 ºC, the moisture content was 1.38 % and dry matter was 98.62 %. The weight loss at 400 and 500 ºC was 74.5 and 90.5 %, respectively and the ash content at 500 ºC has been found to be 9.5 %.

FTIR analysis: Infrared spectrum of the biomaterial showed bands at 3370.9 cm^{-1} resulting in presence of surface hydroxyl groups, band at 2925.6 cm^{-1} attributing symmetric / asymmetric C-H. The stretching vibration of C-O bonds peaks observed at 1738.9 and 1637.3 cm^{-1} showed the presence of non-ionic carboxyl group. Hence, the present groups are responsible for the adsorption of Cd(II) on chosen biomaterial.

Effect of pH: The effect of pH has been examined in the range from 2 to 8 for Cd(II) removal by *Arachis hypogea* at all other parameters as constant (initial concentration of Cd(II) 50 mg/L; stirring speed 200 rpm; contact time 30 min, adsorbent dose 1500 mg/L, temperature 25 ºC). Percent adsorption increased on increase in pH from 2 to 5.5 and then decrease was observed after pH 5.5 upto 7. At pH 8, precipitation of cadmium occurred. As shown in Fig.1, the percent adsorption is found to be maximum at pH 5.5.

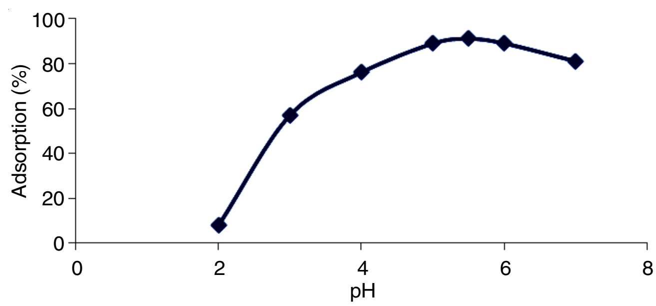

Fig. 1. Effect of pH on adsorption of Cd(II) from aqueous solution by using *Arachis hypogea* [initial Cd(II) conc. 50 mg/L, stirring speed 200 rpm, sorbent dose 1500 mg/100 mL sample solution, contact time 30 min]

Effect of contact time: Studies were conducted at varied contact time for removal of cadmium(II) by *Arachis hypogea* from 5-120 min at fixed stirring speed (200 rpm), initial cadmium concentration (50 mg/L), adsorbent dose (1500 mg per 100 mL sample solution), pH (5.5) and temperature (25 ºC). The percent removal increased with time and the maximum cadmium was adsorbed within 30 min (Fig. 2) upto the level of 91.22 % and became constant thereafter.

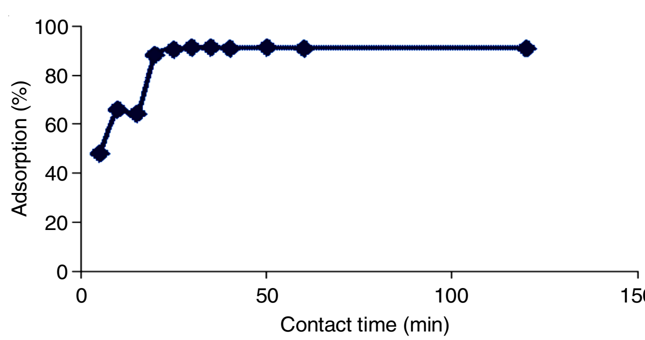

Fig. 2. Effect of contact time on % removal of Cd(II) by *Arachis hypogea* [pH 5.5, stirring speed 200 rpm, adsorbent dose 1500 mg per 100 mL sample solution, initital Cd(II) conc. 50 mg/L]

Effect of adsorbent dose: The efficiency adsorption of Cd(II) ion on *Arachis hypogea* was studied at different adsorbent doses (400, 800, 1200, 1400, 1500, 1600, 1800 and 2000 mg/100 mL) keeping other parameters constant at cadmium concentration (50 mg/L), stirring speed (200 rpm), pH (5.5), temperature (25 ºC) and contact time (30 min). Results showed that with increase in the adsorbent dose from 400 to 1500 mg/L, percentage adsorption of Cd(II) has increased from 35.54 to 91.20 % and further, it remained almost constant (Fig. 3).

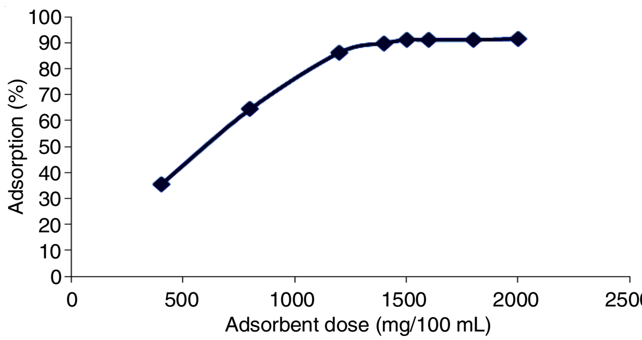

Fig. 3. Effect of adsorbent dose on removal of Cd(II) by *Arachis hypogea* [pH 5.5, stirring speed 200 rpm, initial Cd(II) ion conc. 50 mg/L, contact time 30 min]

Effect of stirring speed: The batch experiments had been performed at varied stirring speed from 50 to 300 rpm at Cd(II) conc. 50 mg/L, pH 5.5, temperature 25 ºC, contact time 30 min and adsorbent dose 1500 mg/100 mL of solution. Fig. 4 shows that the adsorption increases on increase in stirring speed from 50 to 200 rpm and thereafter it practically remains constant. It may be due to the maximum dispersion of the particles of adsorbent at 200 rpm giving the maximum surface area available and thereafter no significant surface area increased.

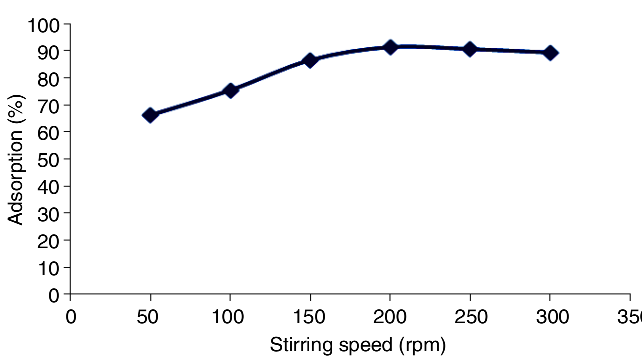

Fig. 4. Effect of stirring speed on removal of Cd(II) by *Arachis hypogea* [pH 5.5, adsorbent dose 1500 mg/100 mL of sample solution, initial Cd(II) ion conc. 50 mg/L]

Effect of initial concentration of Cd(II) ion: Effect of initial concentration of Cd(II) ion on its adsorption on *Arachis hypogea* was studied at its varied concentrations in solutions at 10, 20, 30, 50, 70, 90, 100, 150 and 200 mg/L at constant stirring speed 200 rpm, pH 5.5, contact time 30 min and adsorbent dose 1500 mg/100 ml of solution. The plot between adsorption *versus* initial conc. of Cd(II) ion (Fig. 5) shows that the adsorption of Cd(II) decreases as the initial concentration of Cd(II) increases.

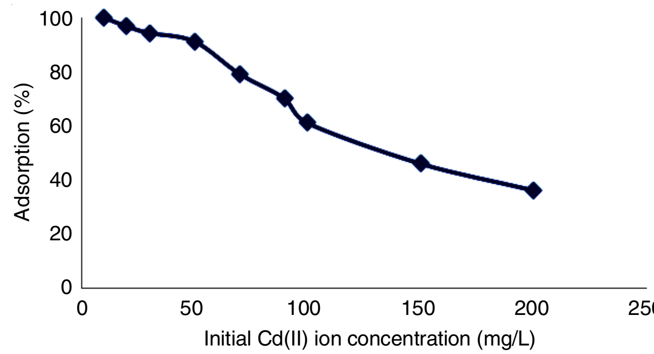

Fig. 5. Effect of initial Cd(II) ion conc. on removal of Cd(II) by *Arachis hypogea* [pH 5.5, stirring speed 200 rpm, adsorbent dose 1500 mg/100 mL of sample solution, contact time 30 min]

Equilibrium studies: Experimental results obtained for the adsorption of cadmium on *Arachis hypogea* at specified conditions of pH, adsorbent dose and stirring speed as 5.5, 1500 mg/100 mL of solution and 200 rpm, respectively were applied to fit the Freundlich and Langmuir adsorption isotherms (Table-1).

Freundlich isotherm *i.e.* the linear plot of log(x/m) *versus* log C_e for various initial concentrations (Fig. 6) indicates the applicability of Freundlich isotherm to adsorption of Cd(II) on said adsorbent. The value of correlation coefficient (R^2) was found to be 0.8382 (Table-1), which indicates that the data fitted fairly well to Freundlich model. From the isotherm (Fig. 6), Freundlich constants K_f and n are calculated as 1.129 L g^{-1} and 0.643, respectively.

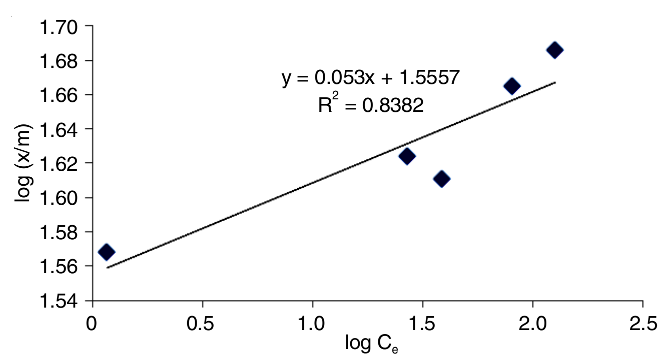

Fig. 6. Freundlich isotherm (pH 5.5, adsorbent dose 1500 mg/100 mL of sample solution, stirring speed 200 rpm, contact time 30 min, temperature 25 ± 1°C)

TABLE-1
FREUNDLICH AND LANGMUIR ISOTHERMS DATA (pH 5.5, ADSORBENT DOSE 1500 mg/100 mL OF SAMPLE SOLUTION, STIRRING SPEED 200 rpm, CONTACT TIME 30 min, TEMP. 25 ± 1 °C)

Adsorption	Freundlich isotherm			Langmuir isotherm		
	R^2	n	K_f	R^2	b	Q_o
Cd(II) on *Arachis hypogea*	0.8382	0.643	1.129	0.9985	6.782	7.485

Applicability of Langmuir adsorption isotherm is found through the linear plot of $C_e/(x/m)$ *versus* C_e (Fig. 7). Correlation coefficient (R^2) was found as 0.9985 (Table-1), which indicates that the Langmuir isotherm fits quite well to the data drawn in the present studies. Slope of the isotherm has been found to be less than unity describes the significant adsorption at low concentration of Cd(II) ion. Langmuir parameters Q_o and b are computed as 7.485 and 6.782, respectively.

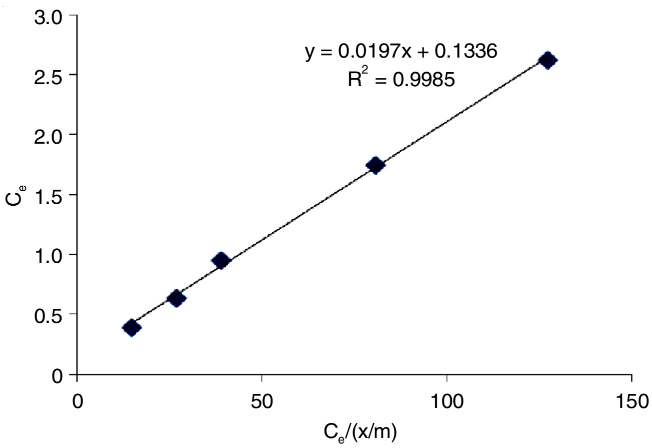

Fig. 7. Langmuir isotherm (pH 5.5, adsorbent dose 1500 mg/100 mL of sample solution, stirring speed 200 rpm, contact time 30 min, temperature 25 ± 1 °C

While comparing the two models for better fit to the equilibrium data, the values of R^2 show that Langmuir adsorption model fitted better as compared to Freundlich model.

Comparison of efficiency of *Arachis hypogea* with other biosorbents: Several biomaterials reported by various authors have shown good efficiency towards sequestering heavy metals and specifically cadmium(II) from aqueous streams. The percent removal of Cd(II) by most of the cellulosic biosorbents have been reported in the range 80-90 %. The adsorption capacities (mg/g) have been reported in Table-2 for some of the adsorbents. In the present work, the percent removal of Cd(II) by *Arachis hypogea* have been found to be of the order of 91 % and maximum adsorption capacity of the biomaterial as 7.485 mg/g, which are quite comparable or even better than several biosorbents as shown in Table-2. The biomaterial '*Arachis hypogea*' in its natural form has been found to be effective for sequestering Cd(II) from aqueous streams. The availability of functional groups (hydroxyl and carboxylic) responsible for uptaking Cd(II) from aqueous solutions make the adsorbent suitable for treatment of cadmium carrying industrial wastewater.

TABLE-2
ADSORBENT CAPACITIES OF SOME BIOMATERIALS

Adsorbent	Capacity (mg/g)	Ref.
Tea waste	8.32	[16]
Coffee beans	6.698	[17]
Coffee husks	8.012	[18]
Mungbean husk	35.41	[19]
Tree leaves	6.653	[20]
Sugar beet pulp	46.1	[21]
Potato peels and fruit shell	6.01 & 5.32	[22]
Bamboo charcoal	12.08	[23]
Papaya wood	17.32	[24]
Orange peels	0.67	[25]
Grapefruit peels	0.49	[25]
Peels of lemon	0.93	[25]
P. ruscipolia wood	7.40	[29]
A. donax L.	5.70	[29]
S cane bagasse	10.7	[29]
Peels of banana	5.71	[30]
Nauclea diderichii seed biomass	6.30	[32]
Granular activated carbon	3.70	[35]
Castor seed hull	6.98	[35]
Fung. tenuiculus	11.4	[36]
Coconut copra meal	2.59	[37]

Conclusion

The present studies showed that *Arachis hypogea* have high potentiality to sequester Cd(II) from aqueous solutions which can be a good alternative of other available adsorbents for low concentrations of metal ions and high volumes of wastewater. Parameters like pH, contact time, stirring speed, adsorbent dose and initial metal ion concentration affect the adsorption of Cd(II) on the studied biomaterial. The adsorption is found to be maximum at pH 5.5, adsorbent dose as 1500 mg/100mL of sample solution, stirring speed 200 rpm and contact time 30 min. Langmuir isotherm fits quite well to explain the behaviour of adsorption of Cd(II) on *Arachis hypogea*.

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