Kinetic and equilibrium studies on adsorption of cadmium from aqueous solution using *Aesculus Indica* seed shell

Anuja Bhardwaj[2], Piar Chand[2], Yogesh B Pakade*[2], Robin Joshi[2] & Mohit Sharma[2]

[1]CSIR-National Environmental Engineering Research Institute, Nagpur 440 020, India
[2]CSIR-Institute of Himalayan Bioresource Technology, Palampur 176 061, India
Email: yogesh_pakade@yahoo.com

Present study has been carried out to evaluate feasibility of *Aesculus indica* seed shell (AISS) for the removal of Cd (II) ions from water. The prepared adsorbent has been characterized by Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS) and Fourier Transform Infrared Spectroscopy (FTIR). The adsorption influencing parameters such as dose (0.06 g), *p*H (6.0) and time (40 min) are optimized. Maximum adsorption capacity (q_{max}) is found to be 34.36 mg/g for Cd (II) ions adsorption onto AISS using Langmuir adsorption isotherm. The experimental data followed pseudo-second order kinetics for adsorption of Cd(II) onto AISS. Negative value of ΔH° indicates exothermic nature of reaction and adsorption decreases as temperature increases from 303 to 333 K. The negative value of ΔS° show that there was no affinity of AISS and indicates decrease in randomness during adsorption process. The recovery and reuse processes for AISS can be continued up to 2 cycles. Thus, *Aesculus indica* seed shell can be used as an effective and low-cost adsorbent for removal of Cd (II) ions from aqueous solution.

Keywords: Adsorption, *Aesculus indica*, Cadmium, Kinetics, Langmuir

Cadmium (Cd) has been released to the environment through metal production, application of phosphate fertilizers, electroplating, manufacturing of batteries and pigments[1]. Cadmium (II) has been classified as a human carcinogen and teratogen impacting lungs, kidneys, liver and reproductive organs[2]. The permissible limit of Cd(II) in water is 0.003/0.005 mg/L according to World Health Organization/Environmental Protection Agency[3,4]. Moreover metals can't be degraded to harmless products and hence persist in the environment indefinitely. Therefore removal of Cd(II) is challenging upto permissible limits from drinking water and industrial wastewater.

Several methods are available such as electrochemical treatment, ion exchange, precipitation, reverse osmosis, evaporation, coagulation, chemical oxidation and membrane technology for removal of heavy metals[5]. However, these methods are economically expensive and having disadvantages like chemical requirements, low efficiency and large amount of sludge production. Therefore it is need to develop novel, cost effective and high efficacy technology to remove Cd ions from water.

Biosorption is attractive treatment option as it is eco-friendly, inexpensive, fast, easy to operate, recycling of adsorbent for removal of metal ions.

Various biosorbent like groundnut husk[6], olive stone[7], coconut shell[8], rice husk[9], pine cone[10], were reported to be efficient for cadmium removal from water.

Keeping in view, the present study was done to evaluate the efficiency of seed shell of *Aesculus indica* after extraction of *aescin* for the removal of cadmium (Cd) ion from water. *Aesculus indica* (Hippocastanaceae) is a large tree known as Himalayan chest nut or Indian horse chestnut, distributed in the Himalayas from Kashmir to Nepal. It is one of the common plants seen in the Himalayan forest, lying at elevations between 2000 and 3000 meters[11]. The plant seed is reported to contain a mixture of saponins, one of which is described as aescin. It also contains flavonoids, glycosides, tannins and phenolic substances[11]. As it contains more hydroxyl groups which is responsible for metal adsorption. The different parameters were optimized *viz.* dose, *p*H, time, temperature, concentration for adsorption of Cd (II) ions on *Aesculus indica* seed shell (AISS). To check the feasibility of AISS as a biosorbent for the removal of Cd (II) ion from water, experimental data were applied to Langmuir and Freundlich isotherms. Regeneration and desorption study was conducted to check the economical feasibility of the biosorbent.

Experimental Section

Reagents and chemicals

Chemicals used in experiment were of analytical reagent (AR) grade. Stock solution of Cd (II) was prepared from the salt of cadmium nitrate [Cd $(NO_3)_2.4H_2O$] by dissolving 1000 mg/L. Desired concentration of metal ion was prepared from stock solution by appropriate dilutions.

Sample collection

Aesculus indica seed shell (AISS) was collected from aesin extraction pilot plant in our institute. Initially dried at room temperature and finally crushed in an electric mixer to get smaller particle size (250 micron) and powder was used for adsorption studies.

AISS characterization

The external morphology and the metal ions adsorbed on the surface of AISS was characterized by Scanning Electron Microscope (SEM), HITACHI made in Japan, Tokyo and Electron Dispersive Spectroscopy (EDS), Thermo Scientific, Noron-7, Made in USA. To detect the major functional groups responsible for the binding of Cd (II) ions on the surface of AISS, FTIR Spectral analysis was done using the (FTIR) Thermo Scientific, Nicolet 6700, Madison, USA. *p*H of the solution was measured by Cyberscan PC 510, Eutech, Singapore. The concentration of Cd(II) ions in the solution was analyzed by Atomic Absorption Spectrophotometer (Shimadzu model AA 6300, Tokyo, Japan).

Batch adsorption study

Various parameters viz. adsorbent dose, *p*H, time, concentration were optimized by varying one parameter at a time and rest kept constant. All parameters were studied by taking 50 mg/L as a standard concentration of aqueous solution containing Cd (II) ions. Dose and *p*H range was varied from 0.01 to 0.1 g and 2 to 8. The time and concentration varied from 10 to 100 min and 10-200 mg/L respectively. Once the equilibrium was reached, filtered the mixture and estimated the residual concentration of metal ions.

Kinetics study

The rate of metal adsorption on adsorbent is an important factor for successful practical application. The adsorption of cadmium ions on AISS was analyzed as a function of time (5-40 min). Pseudo-second order of kinetics model was used to evaluate the experimental adsorption data[12].

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{t}{q_e} \qquad \text{... (1)}$$

where, K is rate constant, q_e and q_t are the amounts of metals adsorbed at equilibrium and at time t, respectively. A graph between t/q_t and t was plotted to find the values of K and q_e from intercept and slope respectively.

Adsorption isotherm

Langmuir and Freundlich adsorption isotherms were applied to the obtained experimental data for determination of the adsorption capacity (q_{max})[13]. Langmuir equation as follows:

$$\frac{1}{q_e} = \frac{1}{C_e q_{max} b} + \frac{1}{q_{max}} \qquad \text{… (2)}$$

where, q_e is the metal ions adsorbed (mg/g), C_e is the residual metal concentration, q_{max} is the maximum adsorption capacity (mg/g) and b is the Langmuir constant (L/g).
Freundlich equation as follows:

$$\log q_e = \log K + \frac{1}{n}\log c_e \qquad \text{… (3)}$$

where, q_e is the amount of metal ions adsorbed (mg/g), c_e is the concentration at equilibrium and K and n are the Freundlich constants which represent the adsorption capacity (mg/g) and adsorption intensity.

Thermodynamics study

Effect of temperature was analyzed from 20 °C to 60 °C. Agitation time for incubator shaker is 150 rpm. The distribution coefficient (K_d) was determined by using the following equation.

$$K_d = \frac{q_e}{c_e} \qquad \text{… (4)}$$

where q_e is the amount of metal ions adsorbed and c_e is the concentration of the metal ions in solution at equilibrium. The change in Gibbs free energy was calculated by using the equation[14,15].

$$\Delta G° = -RT\ln K_d \qquad \text{… (5)}$$

where, R = universal constant (8.314 J/mol/K) and T = temperature in K. The thermodynamic parameters like $\Delta H°$ and $\Delta S°$ were calculated by using Van't Hoff equation by plotting a graph of *log K_d* vs *1/T,* where slope gave the value of $\Delta H°$ and intercept represented $\Delta S°$.

$$\log k_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad \cdots (6)$$

Desorption and regeneration studies

Desorption and regeneration of biosorbent is very important factor in adsorption technique to be considered economical and eco-friendly. Desorption and regeneration experiment was conducted with 0.1N HNO$_3$ solution on AISS. After adsorption of Cd (II) ions onto AISS was dried in oven at room temperature and desorbed with 0.1N HNO$_3$ and concentration of Cd (II) ions was determined in filtrate. Biosorbent was thoroughly washed with double distilled water to remove excess acid and used for next cycle.

Results and Discussion

FTIR characterization

Functional groups responsible for metal binding onto *A. Indica* surface were characterized by FTIR and shown in Fig. 1. FTIR spectra of AISS showed characteristics bands attributed to functional groups of polyphenols (-OH) and amide (-NHCO) at 3298.28 cm^{-1} [16], -C=O at 1598.99 cm^{-1}, -C-N str. at1521.84 cm^{-1}, -NH bonding in secondary amines at 1442.75 cm^{-1}, -C-O-C at 1359.8 cm^{-1} and –CO str. at 1282.66 cm^{-1}, respectively[17]. FTIR bands at 1145.72, 1099.43, 1010.7 and 937.4 cm^{-1} attributed to functional groups of –C-O-C str. of polysaccharides, -CO str. in -COOH groups, -COO str. and –CH str. in vinyl groups, respectively[18]. Others FTIR band at 692.44 and 569 cm^{-1} attributed to -NH$_2$ and –C-C str., respectively. Results showed that major functional groups onto adsorbent surface were oxygen and nitrogen containing compounds which might be responsible for metal binding[19]

SEM and EDS characterization

SEM micrograph of AISS before and after adsorption of metal ions was shown in Fig. 2(a) and Fig. 2(b). The surface of AISS before adsorption was uneven, heterogeneous and porous in nature. After Cd (II) adsorption on AISS, surfaces become smooth and homogeneous. Cd(II) loaded with AISS was further characterized by EDS (Fig. 2(c)), helps to investigate the elemental composition of the AISS. EDS spectra of AISS showed the characteristics peak of Cd(II) was which demonstrated the successful adsorption of metal ions on AISS surface.

Effect of dose

Effect of dose on adsorption of Cd(II) onto AISS was studied in the range of 0.01-0.1 g per 50 mL of Cd (II) synthetic solution for AISS. The adsorption of Cd (II) was increased as the dose of adsorbent increases. With increasing dose, more surface area and binding sites were available for adsorption.
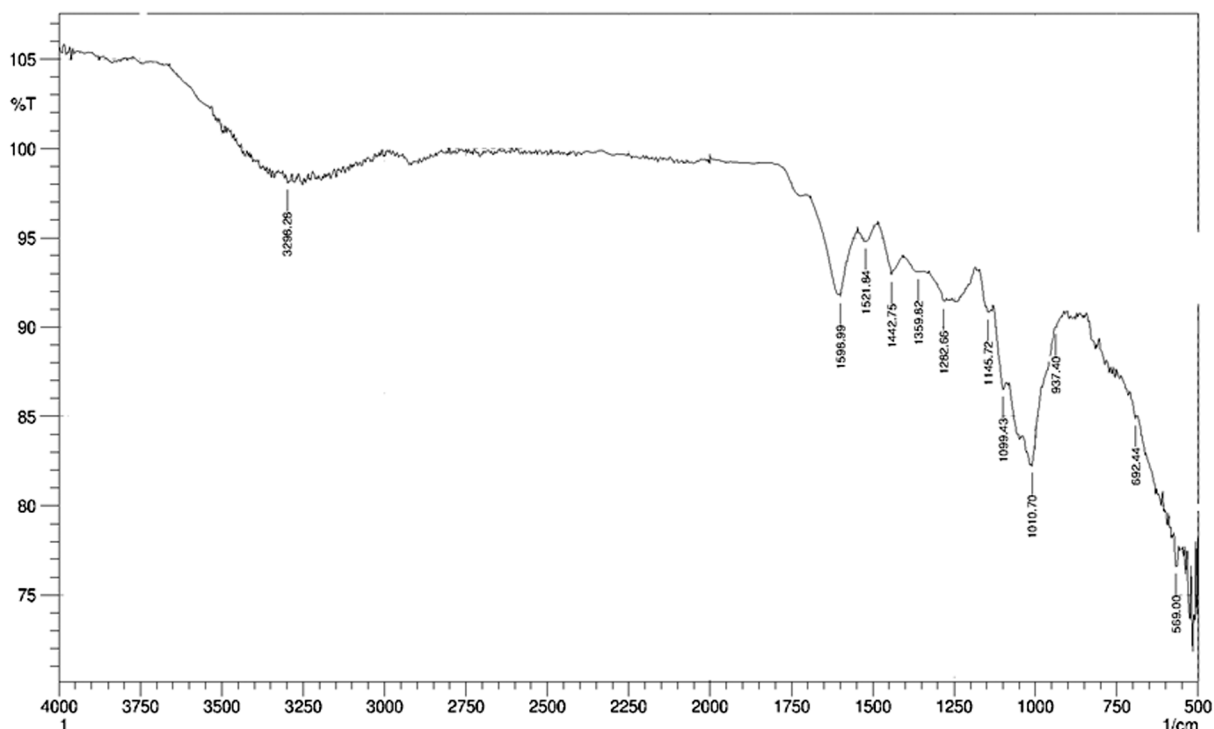

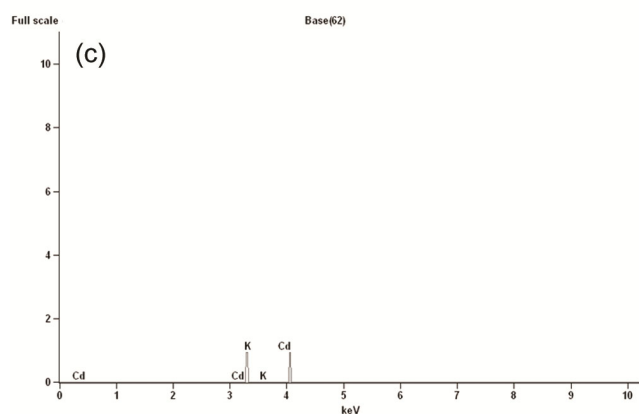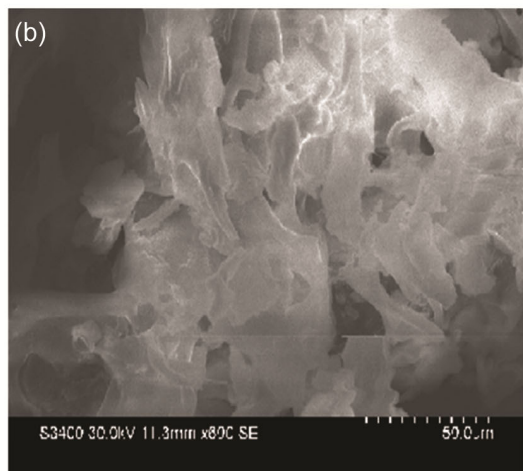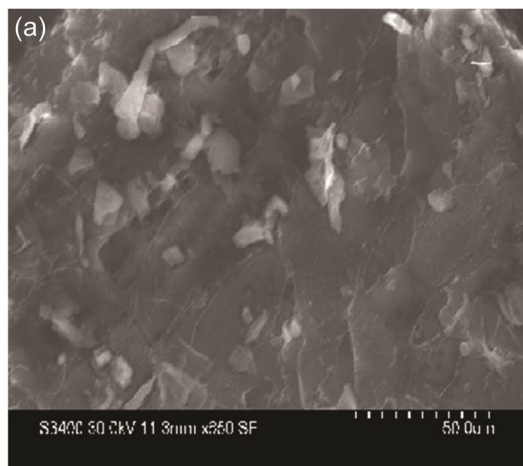Fig. 1— FTIR spectra of AISS for functional group characterization

Fig. 3— Effect of dose on Cd(II) adsorption using AISS

Fig. 4— Effect of *p*H on biosorption of Cd(II) ions using AISS

Effect of *p*H

The *p*H usually plays an important role in the biosorption of metals[20]. *p*H range from 2.0 to 7.0 was selected for adsorption of Cd (II) onto AISS (Fig. 4). As *p*H increases, adsorption percentage of Cd(II) ion was increased sharply up to *p*H 6.0. Further there was no significant increase in adsorption observed on increasing *p*H. This can be related to the insoluble metal hydroxide precipitation from the solution at higher *p*H values[21]. Thus *p*H 6.0 showed maximum adsorption of 81.6% of Cd(II) ions. At *p*H 6.0 was selected for further adsorption studies.

Sorption time and kinetics study

Time of contact should be sufficient to allow biosorbent to adsorb maximum amount of metal. The time interval ranged from 10 to 100 min was evaluated

Fig. 2— SEM characterization of *Aesculus indica* seed shell (AISS) before (a) and after (b) Cd (II) adsorption and EDS (c) spectrum

Maximum removal of Cd(II) was found to be 78.8% at 0.1g dose of AISS, while 77.5% removal was obtained at 0.06 g of AISS. As the bisorbent should be cost effective, 0.06 g of AISS was selected as optimized dose for further adsorption studies (Fig. 3).
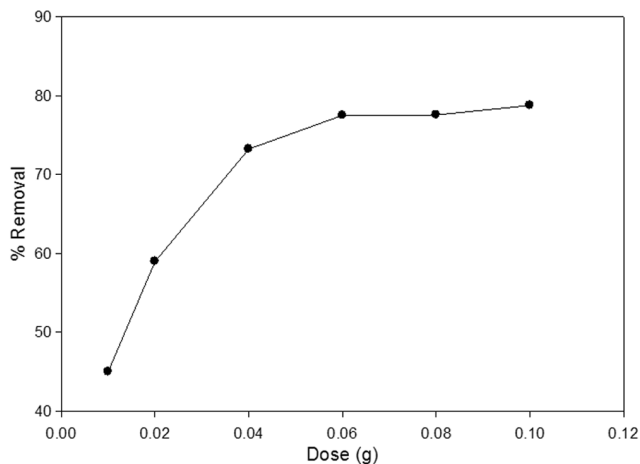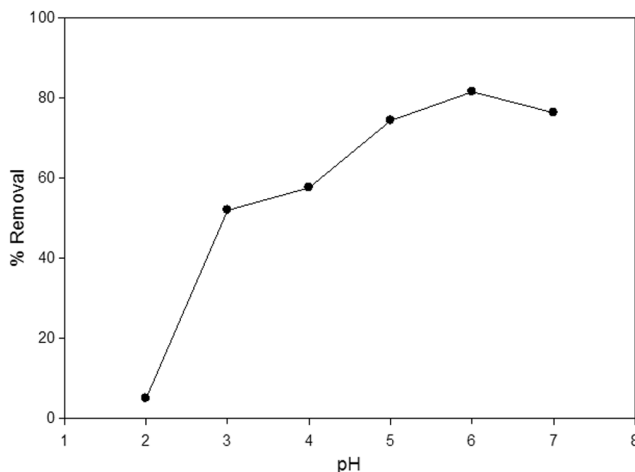
for maximum adsorption of Cd(II) ions (Fig. 5). The result revealed that maximum adsorption rate was observed at 40 min (71.07%). Hence 40 min was considered as optimized time for rest of the studies.

Kinetic study indicates the rate of the reaction and time requirement to attain equilibrium during adsorption process. The adsorption efficiency was determined in the range of 5-40 min. Pseudo-second order kinetics model was used to evaluate experimental kinetics data for AISS. The correlation coefficient (r^2) of AISS was in the range of 0.945 to 0.97 which showed the reaction rate followed pseudo-second order kinetics (Fig. 6). Sorption kinetic in divalent metal ions using several different biosorbent materials were well described in literature[22].

Adsorption isotherm

The Langmuir and Freundlich adsorption isotherm were applied to the experimental data for determination of the adsorption capacity (q_{max})[13] (Fig. 7). The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites[23]. The experimental adsorption data was followed Langmuir isotherm with correlation coefficient $r^2 = 0.98$. The maximum adsorption capacity of AISS for Cd (II) ions was found to be 34.36 mg/g (Table 1). Suitability of the Langmuir adsorption isotherm demonstrates the homogenous and monolayer type of adsorption onto surface. The adsorption capacity (q_{max}) of AISS was compared with reported biosorbent (Table 2). The
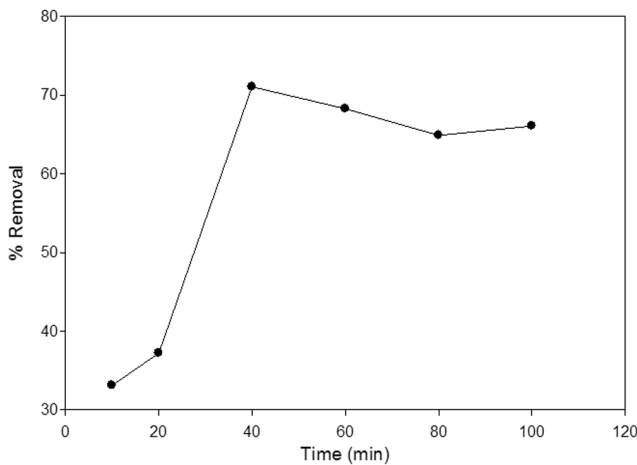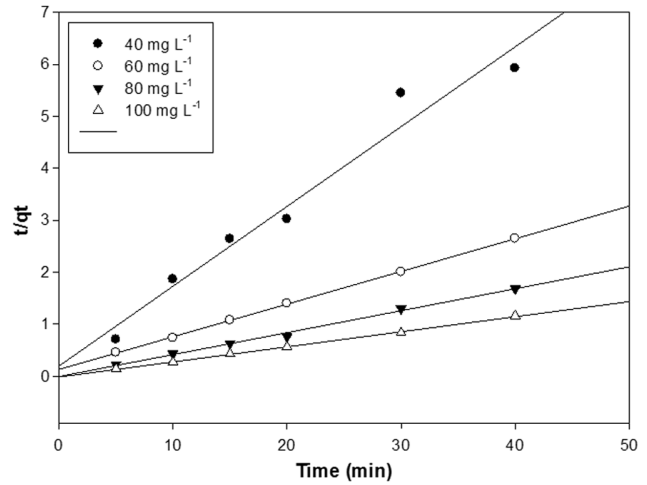

Fig. 6— Pseudo second order kinetics study for Cd(II) adsorption on AISS
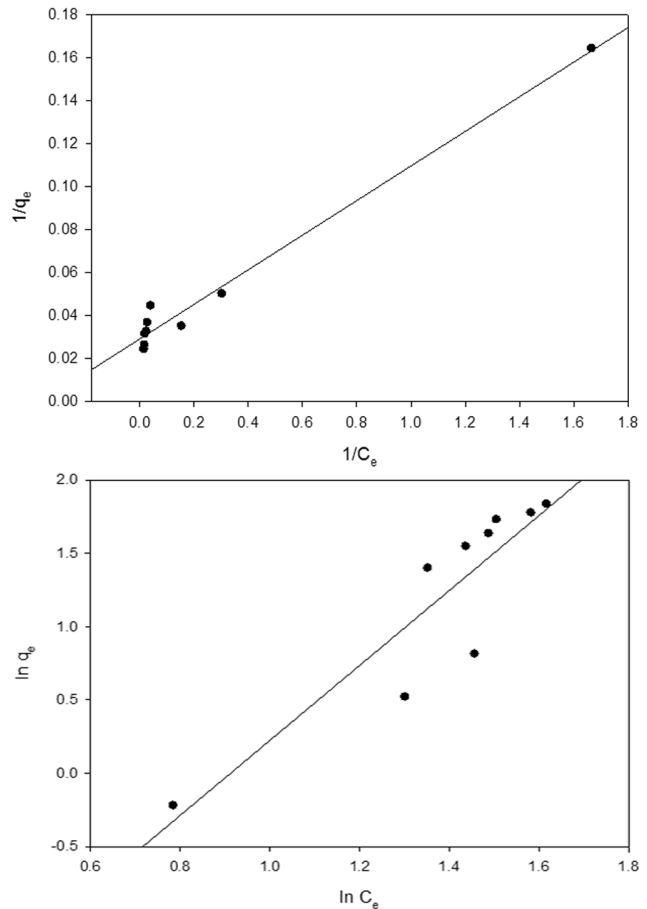
Fig. 7— Langmuir and Frendulich adsorption isotherm for Cd(II) adsorption on AISS

Fig. 5— Effect of sorption time on biosorption of Cd(II) ions using AISS

Table 1— Langmuir and Freundlich isotherm for the adsorption of Cd (II) onto AISS

Metal	Langmuir				Freundlich			
	Equation	q_{max} (mg/g)	r^2	B (L/g)	Equation	r^2	K (mg/g)	n
Cd(II)	y = 0.0806x + 0.0291	34.36	0.98	0.36	y = 0.3162x + 1.0038	0.80	10.23	3.2

Table 2 — Comparison of various biosorbent available for removal of Cd (II) with present study

Biosorbent	q_{max} (mg/g)	References
Groundnut husk	42.71	[8]
Olive stone	6.97	[9]
Green coconut shell	285.7	[10]
Rice husks	8.58	[11]
Untreated coffee grounds	15.65	[28]
Pomelo peel	21.83	[29]
AISS	34.36	Present study

Table 3 —Thermodynamics parameters for Cd (II) ions adsorption onto AISS

Biosorbent	T (^{o}C)	T (K)	ΔG^{o} (J/ mol)	r^2	ΔH^{o} (KJ/ mol)	ΔS^{o} (J/ mol)
	20	293	-962.72	0.99	-12.27	-34.5
	30	303	-619.1			
AISS	40	313	-375.69			
	50	323	-465.07			
	60	333	-375.69			

Langmuir constant (l/g) for Cd(II) ions was found to be 0.36 L/g predicts that AISS have better adsorption affinity because the Langmuir constant is directly proportional to binding energy.

Similar adsorption experimental data were applied to Freundlich adsorption isotherm. Freundlich isotherm signifies heterogeneous surface nature of adsorbent and correlation coefficient (r^2) was not found satisfactory for adsorption data of Cd(II) ions. The correlation coefficient (r^2) for Freundlich model was found to be 0.80, which indicated that adsorption follows Langmuir isotherm than the Freundlich isotherm.

Thermodynamics study

Different thermodynamics parameters such as ΔG^{o}, ΔH^{o} and ΔS^{o} were given in the Table 3. Negative value of ΔG^{o} indicated the feasibility and spontaneity of the reaction for Cd(II) ions adsorption on AISS. The values of ΔG^{o} were found to increase as temperature increased, indicating more driving force and hence resulting in higher biosorption capacity[1]. Value of ΔH^{o} was found to be negative (-12.27 KJ mol^{-1}) which indicated an exothermic reaction and adsorption decreased as temperature increased from 293 to 333 K. The negative value of ΔS^{o} showed there was no affinity of biosorbent and indicated towards decrease in randomness during adsorption process.

Desorption and regeneration study

For commercial purpose, desorption and regeneration study is very important factor, which should be fulfilled for practical application of biosorbent. Desorption of metals or regeneration of adsorbents from used-adsorbents are crucial to repeat the use of adsorbents, recover of precious metals and reduce the cost of operation in any water treatment system[24]. The result indicated that AISS showed decreased per cent removal after first cycle. The recovery and reuse processes for AISS can be continued up to two cycles. AISS showed maximum removal of 98.7% initially and decreased up to 25.06% after three cycles. Similar trend was made by Sankararamakrishan (2007)[25] and Chauhan (2008)[26] who reported the adsorption decreased as the number of cycles increased.

Conclusion

In this study, the potential of AISS was evaluated for the adsorption of Cd(II) ions from water. At low dose (0.06 g), maximum adsorption was obtained. Adsorption followed Langmuir isotherm models with maximum adsorption capacity of 34.36 mg/g. The rate of adsorption followed pseudo second order kinetics with correlation coefficient in the range of 0.945 to 0.97. Regeneration of AISS upto two cycles make AISS become an eco-friendly and cost effective biosorbent for the removal of Cd(II) from water. Thus, the use of bioresource as an adsorbent can be viewed as a part of waste treatment technology.

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