Low Cost Cuscuta Based Adsorbent for Removal of Iron from its Aqueous Solution

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Present study deals with the adsorption of iron(II) from its aqueous solution on cuscuta powder. Several parameters like adsorbate concentration, adsorbent dose, pH, adsorption time and temperature were studied in batch experiments. Langmuir, Freundlich and Tempkin adsorption models were applied to describe the isotherms and isotherm constants. Equilibrium data fitted well in the Langmuir model. The pseudo-first-order and pseudo-second-order kinetic equations were used to model the adsorption kinetics. The second order kinetics found a better fit.

Keywords: Adsorption, Cuscuta powder, Heavy metals, Fe(II) ions, Atomic absorption spectroscopy.

INTRODUCTION

About 71 % of the Earth's surface covers with water and it is supreme for all known forms of life. All living beings such as humans, plants, animals, insects, *etc.* cannot survive without water. Water is an universal solvent and plays an important role in the world economy. Various factors such as sewage and wastewater, marine dumping, industrial waste, radioactive waste, oil pollution, atmospheric deposition, global warming, eutrophication, *etc*. are responsible for the water contamination. Industrial water creates a wastewater that has a potential risk for our environment by introducing various contaminants such as heavy metals into soil and water resources. Presently heavy metal ions are one of the most important pollutants, which are polluting surface and groundwater [1]. Due to industrialization and urbanization higher amount of heavy metals are released into the environment. It has created great problem worldwide. Currently, the removal of heavy metal contaminants from wastewater is one of the most important environmental issue being researched. Once metal ions enter the environment, their chemical form largely determines their potential toxicity [2]. Besides the existence in aquatic eco-system heavy metals may cause harmful effects on organisms living in water and heavy metals also accumulate throughout the food chain and affect the health of human beings [3-5].

Heavy metals are non-biodegradable and causing various diseases and disorders. Iron is the fourth most abundant element in the earth's crust, it is present in a variety of rocks and soil minerals both as Fe(II) and Fe(III). Iron(II) is required for proper transport and storage of oxygen by means of haemoglobin and myoglobin while its oxidized forms, methemoglobin and metmyoglobin, which contain Fe(III) not bind oxygen [6]. Iron plays an essential role in photo-synthesis and is the limiting growth nutrient for phytoplanktons in some parts of the ocean. Both Fe(II) and Fe(III) are important in the biosphere, serving as an active centre of a wide range of proteins and enzymes such as oxidases, reductases and dehydrases. Iron overload may lead to debilitating and life-threatening problems such as poor growth, heart failure and diabetes, haemochromatosis and siderosis disease. According to EPA, the acceptable value of iron in drinking water is 0.3 mg L^{-1} [7]. The presence of iron in drinking water causes toxic and carcinogenic effects on human beings. Heavier amount of iron can cause serious health problems or premature death. Toxicity of iron may damage the liver, heart and endocrine glands, leading to debilitating and life-threatening problems such as diabetes, heart failure and poor growth [8].

A number of methods are used to remove heavy metals due to new and effective separation technologies. The most widely used methods for removing heavy metals from waste-waters include ion exchange, chemical precipitation, reverse osmosis, membrane filtration and adsorption biological treat-ment. Most of these methods suffer from some disadvantages such as high operational cost and are not suitable for small-scale industries or do not lead to a satisfactory result. Among these technologies, adsorption is a most common technique

for the removal of heavy metals. This process seems to be more users friendly and effective if combined with appropriate bio-adsorbent and regeneration steps. Activated carbon has been widely applied for removing heavy metals from water and wastewater [9-11]. Recently, the number of researches focused on the use of activated carbon as adsorbents are reducing due to their high capital and operational costs. Therefore, more interests have recently arisen in the investigation of low-cost adsorbents with a good sorption capacity to remove heavy metal ions from wastewater. For the past few decades, more researchers have concentrated on the use of agricultural wastes as adsorbents. Agricultural wastes such as fly ash, natural zeolite, wheat bran, bark and sawdust, peanut shells and rice husk have been developed for heavy metals removal from aqueous solution [12-17].

Cuscuta (Family-Convolvulaceae) is an obligate angiosperm parasitic climber found commonly throughout India. *Cuscuta reflexa Roxb* has been used from ancient times, for various purposes *viz.*, as a purgative, in the treatment of liver disorders, cough and itching and for its carminative and anthelmintic actions. The cuscuta is known to contain several antibacterial, antiviral and antiproliferative substances. It is known to contain compound like phenolics and flavonoids and exhibit anti-inflammatory and anticancer activities [18]. In India, cuscuta possess a serious problem in cultivation of crops and also parasitizes numerous species of dicotyledonous weeds and wild plants. The infestation of cuscuta results in heavy loss in terms of quantity and quality of produce and it may cause complete failure of the crops. The highly efficient absorption system allows the parasite to divert resources of water, amino acids from the host and assimilates to itself [19,20], thus reducing host's vigour and crop production. The twining vines not only deprive the host plants of nutrients but also inhibit the growth and seed germination of host plants. Cuscuta also transmits the viral diseases in host plants [21,22]. The cuscuta is a problematic weed spreading to new areas and adversely affecting the agricultural production. In view of its problematic nature and zero value, the present study was done to develop an adsorbent from cuscuta and to test it for the adsorption of Fe(II) metal ions from their aqueous solution by batch method.

EXPERIMENTAL

Adsorbent and stock solution: The cuscuta plants material was collected from the campus area of Govind Ballabh Pant University of Agriculture and Technology, Pantnagar, District Udham Singh Nagar (India). The cuscuta plants were cut down to small pieces and then dried at room temperature (25 °C) in shadow and finally dried in an oven at 70 °C for 3 days. The oven dried cuscuta plant's mass was grinded to fine powder by the grinder to the size of 100-425 microns. Activated cuscuta powder was washed with distilled water and then it was oven dried at 110 °C for 3 h. The cuscuta powder was activated by 0.1 N NH_4Cl solution at 50 °C and oven dried. It was stored in a closed polycarbonate container for use. The stock solution of Fe(II) ions was prepared of 100 ppm from ferrous ammonium sulphate in triple distilled water.

All the adsorption experiments were performed by batch method and metal ions concentrations were measured using

atomic absorption spectrophotometer under following conditions, lamp current: 7.0 mA. Flame type, air: acetylene (oxidizing). Wavelength: 248.3 nm and slit width: 0.2 nm.

Adsorption studies: The experiments were performed with 10 mL of Fe(II) ions adsorbate solution. The solution was taken in each sample test tube and 0.5 g of adsorbent (cuscuta powder) was added in the solution and kept for the adsorption time completion with continuous shaking for uniform adsorption. After completion of adsorption time (60 min), the suspension was filtered with Whatman No. 2 filter paper. The filter paper was dipped in distilled water before using for filtration. Now the filtrate was taken in another test tube and its concentration was measured in ppm (μg/mL) using AAS under above mentioned parameters. The study was done under the parameters of adsorption time, adsorbate concentration, adsorbent doses, effect of pH, adsorption temperature.

The removal percentage or per cent adsorption of Fe(II) ions was calculated using the following expression:

$$Adsorption (\%) = \frac{C_i - C_t}{C_i} \times 100$$

where, C_i = initial concentration (ppm) of the solution before adsorption; C_t = final concentration (ppm) of the solution after adsorption completion

The adsorption capacity was calculated by using the expression:

$$q_e = \frac{C_i - C_t}{W} \times V$$

where, q_e = adsorption capacity (μg/g); C_i = initial concentration (ppm) of the solution before adsorption; C_t = equilibrium concentration of the adsorbate (ppm); W = mass of dry adsorbent used; V = volume of the solution.

RESULTS AND DISCUSSION

Effect of adsorption time: Fig. 1 shows the effect of contact time on percentage adsorption of Fe(II) on cuscuta powder. It was found that initially percentage adsorption of Fe(II) ions increases with increase of adsorption time rapidly upto 4 min, but after 4 min percentage adsorption was increasing slowly upto 60 min. The maximum adsorption 90.3 % was attained at 60 min of contact time. After it, percentage adsorption was found to slowly saturate with further increase of the time. The adsorbent was activated by 0.1 N NH_4Cl solution hence most of the sites were activated on the surface, which makes the adsorption process rapid. Similar results were reported by Zhang *et al*. [23].

Effect of adsorbate concentration: The percentage adsorption of Fe(II) ions from aqueous solutions on cuscuta
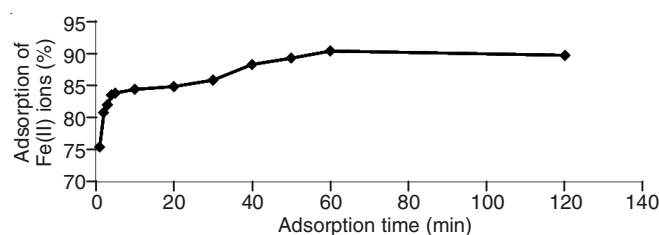

Fig. 1. Effect of adsorption time on percentage adsorption of Fe(II) ions on cuscuta powder from aqueous solution

powder was studied at different initial concentrations of Fe(II) ions from 10 to 30 ppm at 30 °C. The adsorption of Fe(II) ions on cuscuta powder was found to decrease with the increase in initial concentration of Fe(II) ions in the solution. In this study, the adsorption of Fe(II) ions was found to be maximum 91 % at 10 ppm adsorbate concentration (Fig. 2). The adsorption of ions is highly dependent on the initial concentration of metal ions. The adsorption of metal ions on cross linked starch was reported to decrease with increasing initial metal ion concentration [24,25]. The reason behind the decrease in percentage adsorption of Fe(II) ions may be due to precipitation of metal hydroxide on the surface or inside the pores of walls of the adsorbent at higher concentration of Fe(II) ions in solution. Similar results were found by Dahlan *et al*. [26].
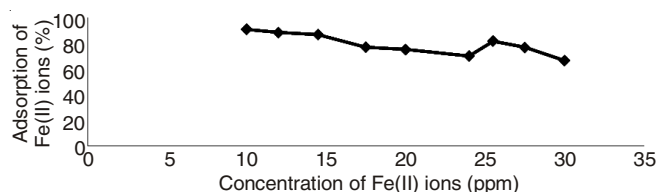

Fig. 2.   Effect of concentration of adsorbate solution on percentage adsorption of Fe(II) ions on cuscuta powder

Effect of adsorbent dose: The adsorption of iron(II) was studied at different doses from 0.1 g to 1.0 g/10 mL. Fig. 3 shows that the percentage adsorption of Fe(II) ions was initially found to increase with increase in adsorbent dose (cuscuta powder). At 0.4 g of adsorbent dose the percentage adsorption was maximum (95.5 %) and after it the percentage adsorption was found to slowly saturate with the further increase in adsorbent dose. The minimum percent adsorption was achieved 26 % at 0.1 g amount of adsorbent. The reason behind it may be that the percent adsorption at higher amount of adsorbent may be saturated as no more adsorption sites remain available on the surface of the cuscuta powder. Initially the adsorption capacity increases from 0.1 to 0.4 g of adsorbent dose where adsorption capacity was maximum191 µg/g. After it, the adsorption capacity was found to slowly saturate with further increase in adsorbent dose which coincided with those obtained by Rose and Rajam [27].
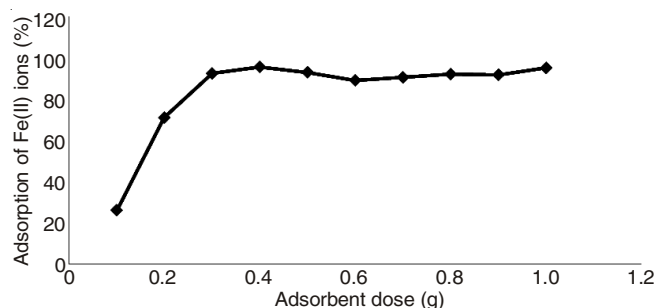

Fig. 3.   Effect of adsorbent dose on percentage adsorption of Fe(II) ions on cuscuta powder from aqueous solution

Effect of temperature: The percentage adsorption of Fe(II) ions onto cuscuta powder was investigated at different temperatures 293.15, 298.15, 303.15, 308.15 and 313.15 K. The results have shown that the percentage adsorption of Fe(II)

ions onto cuscuta powder increased from 69.8 % at 293.15 K to 88.7 % at 313.15 K and was found maximum (88.7 %) at 313.15 K. The adsorption capacity increased with increase in temperature and found to be maximum 177.4 µg/g at 313.15 K (Fig. 4). This shows that higher temperature is favourable for the adsorption as more thermal energy available for the adsorption. This observation was confirmed by Shiebani *et al*. [28] for removal of Fe(III) ions from aqueous solution by hazelnut hull as an adsorbent.
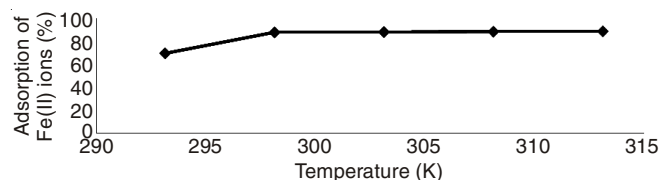

Fig. 4.   Effect of temperature on percentage adsorption of Fe(II) ions on cuscuta powder from aqueous solution

Effect of pH: The effect of pH on Fe(II) adsorption onto cuscuta powder was studied in the pH range from 2.5 to 8. The percentage adsorption of Fe(II) ions was found to be strongly dependent on pH. On increasing the pH, percentage adsorption of Fe(II) ions was observed decreasing. The maximum adsorption 91.8 % of Fe(II) ions was achieved at pH 4 (Fig. 5). The pH of solution was found to play a major role on the adsorption of metal ions from aqueous solutions onto solid adsorbents. It was observed that the increasing pH value results in the lesser adsorption of Fe(II) ions on cuscuta powder. The maximum percentage adsorption 91.8 % of Fe(II) ions was achieved at pH 4. The reason behind this might be the increase in H^+ ions concentration on adsorbent surface, which helped greater removal of metal ions from solution through exchange. As solution's pH was increased, the onset of metal hydrolysis and precipitation may occur above pH 4 for all metal ions. This indicated that the adsorption capacity of the adsorbent is clearly pH dependent. Generally, metal ions are more soluble at lower pH values and this enhances their adsorption as observed by Olayinka *et al*. [29].
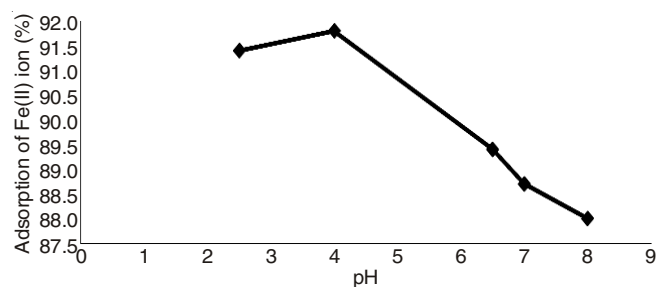

Fig. 5.   Effect of pH on percentage adsorption of Fe(II) ions on cuscuta powder from aqueous solution

Adsorption isotherm: The adsorption isotherms are very important in describing the adsorption behaviour of solutes on specific sorbents [30]. They are used to describe the equilibrium between the concentration of the dissolved adsorbate and the amount of adsorbate that accumulated on the sorbent. In the present work, the three models Langmuir, Freundlich, Temkin, eqns. 1-3 were used in the study of adsorption of Fe(II) ions.

$$q_e = \frac{bq_m c_e}{1 + bc_e} \quad \frac{1}{q_e} = \frac{1}{bq_m}\frac{1}{c_e} + \frac{1}{q_m} \tag{1}$$

$$q_e = k_f c_e^{\frac{1}{n}} \quad \ln q_e = \ln k_f + \frac{1}{n}\ln c_e \tag{2}$$

$$q_e = \frac{RT}{bt}\ln c_e + \frac{RT}{bt}\ln A \tag{3}$$

The applicability of the isotherm model was evaluated by the coefficient of correlation value (R^2). The calculated isotherm constants and the corresponding coefficient of correlation are summarized in Table-1. Fig. 6(a-c) shows the linear Langmuir, Freudlich and Tempkin isotherm plot which indicates that iron metal adsorption on cuscuta powder follows the Langmuir model with R^2 value of 0.874 while only 0.819 and 0.749 for Freudlich and Tempkin model. Comparing all data fitted to the isotherm models, the Langmuir isotherm model was found to have the best fit to the experimental data since this isotherm exhibited the highest value of R^2.

Adsorption kinetics: In batch experiments, kinetic study is very important to find out the contact time of the adsorbent with adsorbate and for evaluating reaction coefficients. In order to investigate the mechanism of iron adsorption onto the

TABLE-1
ADSORPTION ISOTHERM MODEL CONSTANTS FOR
ADSORPTION OF Fe(II) IONS ON CUSCUTA POWDER

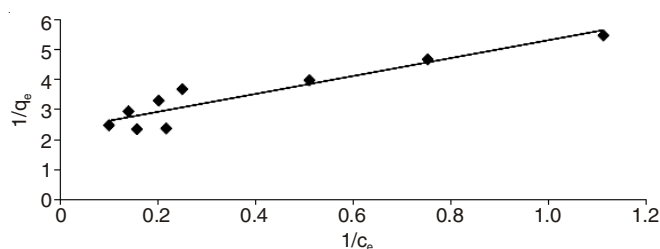| Model	Parameter	Cuscuta adsorbent
Langmuir	q_m (mg/g)	0.4233
	b (mL/mg)	0.3379
	R^2	0.874
Freundlich	K_f (mg/g)	5.1500
	q_e (mg/g)	2.9673
	R^2	0.819
Tempkin	A (J/mol)	7.2282
	B (mL/mg)	26079.7052
	R^2	0.749

Fig. 6a. Langmuir adsorption isotherm for the adsorption of Fe(II) ions on cuscuta powder
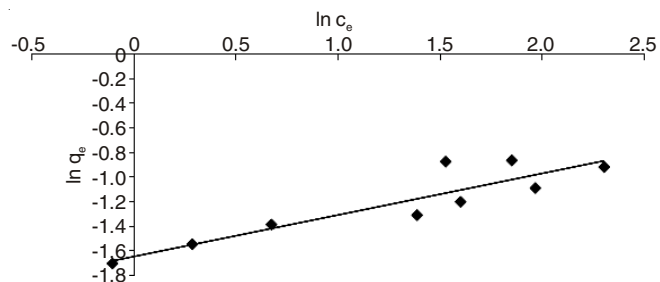

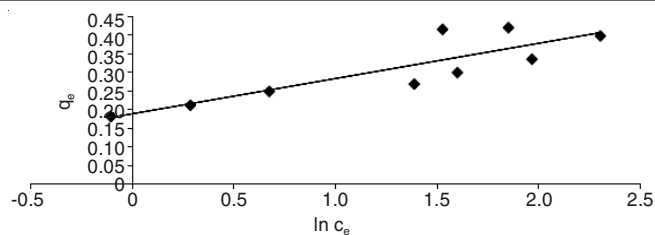Fig. 6b. Freundlich adsorption isotherm for the adsorption of Fe(II) ions on cuscuta powder

Fig. 6c. Tempkin adsorption isotherm for the adsorption of Fe(II) ions on cuscuta powder

cuscuta adsorbent, two kinetic models, *viz.*, pseudo-first-order equation and pseudo-second-order reaction model were analyzed and a comparison of the best fit sorption mechanism were made. The first order rate equation of Lagergren is represented as:

$$\ln(q_e - q_t) = \ln q_e - \frac{K_1}{2.303}t \tag{4}$$

where q_e and q_t are the amount of metal ion sorbed (mg/g) at equilibrium and at time t, respectively. K_1 is the Lagergren rate constant of the biosorbent (1/min). A plot of ln (q_e–q_t) *versus* t gives the result shown in the Fig. 7a. The value of K_1 and q_e, calculated from the slope and intercept are presented in Table-2. The linear form of pseudo-second-order equation can be written as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{5}$$

where q_e is the equilibrium biosorption capacity and K_2 (g/mg min) is the pseudo-second-order rate constant. A plot of t/q_t against t gives a linear relationship for the applicability of the second-order kinetic (Fig. 7b). Based on these results, it can be concluded that the pseudo-second order kinetic model provided a good correlation (R^2) 0.999 for the adsorption of Fe(II) than the pseudo-first-order kinetic model (R^2 = 0.832).

TABLE-2
KINETIC PARAMETERS FOR ADSORPTION
OF Fe(II) IONS ON CUSCUTA POWDER

Pseudo-first order	q_e (mg/g)	27.0314
	K_1 (min^{-1})	0.0552
	R^2	0.8320
Pseudo-second order	q_e (mg/g)	0.4051
	K_2 (g/mg min)	4.7779
	R^2	0.9990

Cuscuta plant contain phytochemical constituents like alkaloids, flavonoids, carbohydrates, glycosides, phytosterols, fixed oil and fats, proteins, phenolic compounds, tannins and saponins having different functional groups which might be responsible for its absorptive property. The results obtained here showed that the cuscuta powder is a very good adsorbent for Fe(II) ions adsorption and their removal from wastewater. The adsorption of metal ion on agricultural by-products may involve metal interactions or coordination to functional groups present in natural proteins, lipids and carbohydrates positioned on cell walls [31,32]. Bhatti *et al.* [33] and Gilbert *et al.* [34] stated clearly from their studies of natural plant materials that the biochemical characteristics of acidic functional groups are responsible for their metal ion uptake.
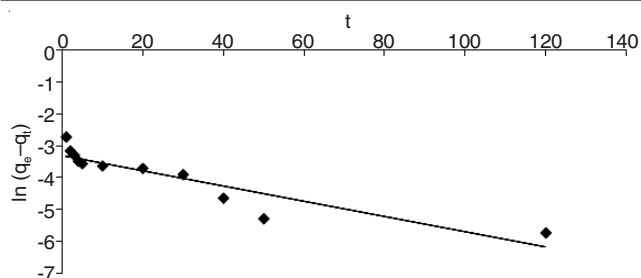
Fig. 7a. Pseudo-first-order kinetic plot for adsorption of Fe(II) ions on cuscuta powder
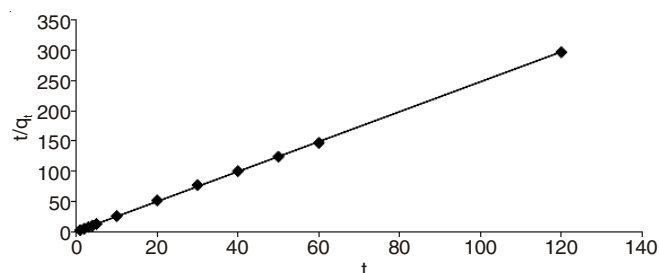

Fig. 7b. Pseudo-second-order kinetic plot for the adsorption of Fe(II) ions on cuscuta powder

Conclusions

• The adsorbent prepared from cuscuta plants was found as a promising and low-cost adsorbent for the removal of iron metal ions from wastewater.

• The equilibrium adsorption level has been determined as a function of solution pH, contact time, initial Fe(II) concentration, adsorbent dose and temperature.

• The kinetics of Fe(II) ions adsorption onto cuscuta powder followed the pseudo-second-order rate model.

• The Langmuir isotherm model showed a somewhat better fit than did the Freundlich and Tempkin models for adsorption. This study has showed the monolayer type adsorption of Fe(II) ions on cuscuta powder surface.

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