International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
IJCS 2017; 5(4): 1062-1066

Received: 20-05-2017
Accepted: 21-06-2017

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Adsorption study of Fe^{2+} ions in presence of co-metal ions from aqueous solution on *Cuscuta* powder

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Abstract
Heavy metals are one of the most important pollutants which pollute environment by several ways. The present work deals with the adsorption of Fe^{2+} metal ions from its aqueous solution in presence of co-metal ions (Cu^{2+}, Mn^{2+}, Ca^{2+} and Zn^{2+}) using cheap and biodegradable adsorbent prepared from *Cuscuta* biomass. The studies were carried out by batch method and metal ions concentrations were measured by atomic absorption spectrophotometer. The effect of pH and concentration of Fe^{2+} ions on percentage adsorption of Fe^{2+} ions on *Cuscuta* powder were studied. The results of this study found that metal ions affected the adsorption of Fe^{2+} ions onto *Cuscuta* powder in the following order: $Cu^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+}$.

Keywords: Adsorbent, Adsorption isotherms, *Cuscuta*, Heavy metals, Fe^{2+} ions

Introduction
Water pollution is a very serious problem of present time and it raises a great concern now-a-days since water constitutes a basic necessity of all living things. Various factors such as Sewage & Wastewater, Marine Dumping, Industrial Waste disposal, Radioactive Waste, Oil Pollution, Atmospheric Deposition, Global Warming, Eutrophication etc. are responsible for the water contamination. Industrial waste water is polluting our groundwater and introducing various contaminants such as heavy metals into soil & water resources. Presently heavy metal ions are one of the most important pollutants because of their toxicity, bioaccumulation tendency, threat to human life and the environment [1]. Due to rapid industrialization and urbanization the higher amounts 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 deposition in aquatic ecosystem they also create harmful effects in the organisms living in the water. The heavy metals also accumulate in the foods and feeds and then affect food chain and the health of human beings [3-5].
Heavy metals are elements of high density which generates 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). Fe (II) is required by the living organisms for proper transport and storage of oxygen by means of haemoglobin and myoglobin while its oxidized forms, methemoglobin and metmyoglobin, which contain Fe(III),does not bind oxygen [6]. The excess of iron leads to debilitating and life-threatening problems such as poor growth, heart failure and diabetes, haemochromatosis & siderosis disease. According to EPA, the acceptable value of iron in drinking water is 0.3 mg L^{-1} [7]. The presence of higher concentration of iron in drinking water causes toxic and carcinogenic effects in human beings. The extra amount of iron also causes serious health problems or premature death. The toxicity of iron damages the liver, heart and endocrine glands, leading to debilitating and life-threatening problems such as diabetes, heart failure and poor growth [8].
A lot of methods such as ion exchange, chemical precipitation, reverse osmosis, membrane filtration and adsorption biological treatment have developed and are used to remove heavy metals. The drawback of these methods are high operational cost, not suitable for small-scale industries and non-biodegradable waste generation. Now a days, adsorption process is a most common technique for the removal of heavy metals [9-11].

Therefore, more interests have recently arisen in the development and investigation of low-cost adsorbents with higher sorption capacity to remove heavy metal ions from wastewater.

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 compounds like phenols and flavonoids which exhibit anti-inflammatory and anticancer activities [12]. *Cuscuta* is a problematic weed spreading to the new areas and adversely affecting the agriculture production. In view of its problematic nature and its zero value, the present study was carried out develop an adsorbent from *Cuscuta* and to test it for the adsorption of Fe^{2+} metal ions in presence of co-metal ions from their aqueous solution by the batch method.

Materials and methods

Adsorbent and stock solution

The *Cuscuta (Cassytha filiformis)* plants material was collected from the campus area of Govind Ballabh Pant University of Agriculture and Technology, Pantnagar, District Udham Singh Nagar (Uttarakhand). The *Cuscuta* Plants were dried at room temperature (25 ºC) in shadow and then cut down to small pieces and finally dried in oven at 70 ºC for 3 days. The oven dried *Cuscuta* plants were grinded to fine powder of the size of 425 microns. The *Cuscuta* powder was then activated for 3 hrs by 0.1N NH_4Cl solution at 50 ºC. Activated *Cuscuta* powder was washed with distilled water and then it was again oven dried at 110 ºC for 3 hours and sieved. It was stored in a closed polycarbonate container for the experiments. The stock solution of Fe^{2+} ions, Zn^{2+} ions, Ca^{2+} ions, Cu^{2+} ions and Mn^{2+} ions were prepared of 100 ppm from Ferrous ammonium sulphate, Zinc Chloride, Calcium Chloride, Cupric Chloride and Manganese Chloride. All the chemicals used for solutions were of analytical grade and the solutions were prepared using double distilled water and stored at 20 °C.

Equipment and apparatus

The experiments were performed by batch method and metal ions concentrations were measured using Atomic Absorption Spectrophotometer under the following conditions Lamp Current- 7.0 mA. Flame Type- Air- Acetylene (oxidizing). Wavelength- 248.3nm. Slit Width- 0.2 nm.

Adsorption studies

The experiments were performed with 10 ml of Fe^{2+} 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 pre-dipped in distilled water before using for filtration. Now the filterate was taken in another test tube and its concentration was measured in ppm(µg/ml) using A.A.S under above mentioned parameters. The study was done under the parameters of adsorbate concentration and effect of pH. The adsorption of Fe^{2+} ions were studied in the presence of Cu^{2+}, Mn^{2+}, Ca^{2+} and Zn^{2+} ions separately at different concentrations of co- metal ions. The experimental parameters ; adsorption time 60 min, concentration of Fe^{2+} ions 10 ppm, temperature 30 ºC and dose of adsorbent 0.5 g were used. The pH of the solutions were maintained at 4.0 during each experiment

The removal percentage or percent adsorption of Fe^{2+} ions was calculated using the following expression:

$$\text{Percent Adsorption, \% R} = \frac{Ci - Ct}{\text{Ci}} \times 100$$

Where,

ci = Initial concentration (ppm) of the adsorbate solution before adsorption

ct = Final concentration (ppm) of the adsorbate solution after completion of adsorption

The adsorption capacity was calculated by using the expression;

$$\text{Q} = \frac{Co - Ce}{W} \times V$$

Where,

Q = adsorption capacity (µg/g)

Co = Initial concentration (ppm) of the adsorbate solution before adsorption

Ce = equilibrium concentration of the adsorbate (ppm)

w = mass of dry adsorbent used

V = volume of the solution

Results and Discussion

Effect of pH and concentration of Fe^{2+} ions

The effect of pH and different concentrations of Fe^{2+} ions in adsorbate solution on percentage adsorption of Fe^{2+} ions on *Cuscuta* powder was studied in the pH range from 2.5 to 8 and concentration 5-25 ppm which is presented in Figure 1. It was found that on increasing the pH and concentration of Fe^{2+} ions the percentage adsorption of Fe^{2+} ions on *Cuscuta* powder increases upto pH 4.0 and after that pH the percentage adsorption of Fe^{2+} ions was observed decreasing. The maximum percentage adsorption 91.8% of Fe^{2+} ions was achieved at pH 4.0. The increasing pH value results in the lesser adsorption of Fe^{2+} ions on *Cuscuta* powder which seems that maximum adsorption occurred at acidic pH. This may be due to OH group present in the *Cuscuta* powder which attract or dissociate protons depending on the pH solution. The adsorption of Fe^{2+} ions on *Cuscuta* powder was found to decrease with the increase in initial concentration of Fe^{2+} ions in the solution. Similarly, the adsorption of Fe^{2+} ions was found to be maximum 91.0 % at 10 ppm adsorbate concentration at pH 4.0. 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 [13-14]. The reason behind the decrease in percentage adsorption of Fe^{2+} 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^{2+} ions in solution.

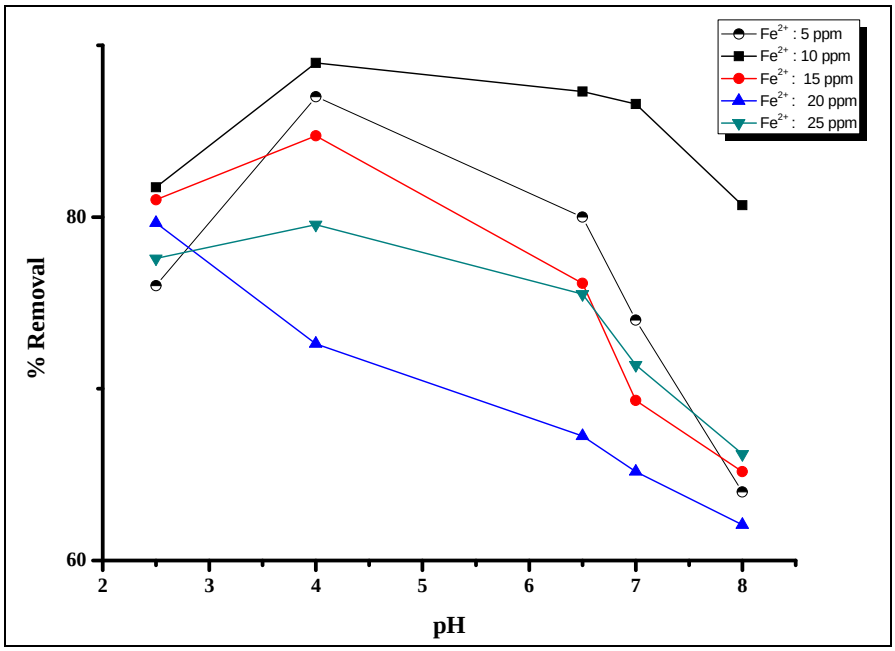

Fig 1: Effect of pH and concentration of Fe^{2+} ions in adsorbate solution on percentage adsorption of Fe^{2+} ions on *Cuscuta* powder

Effect of co-metal ions on percentage adsorption of Fe^{2+} ions on *Cuscuta* powder

Effect of concentration of Cu^{2+} ions on percentage adsorption of Fe^{2+} ions on *Cuscuta* powder from aqueous solution

The percentage adsorption of Fe^{2+} ions on *Cuscuta* powder without any co-metal ions was found 91.0% & adsorption capacity was 182.2µg/g. As depicted in Figure 2 it reveals that in presence of Cu^{2+} ions the percentage adsorption of Fe^{2+} ions decreases with the increase of the concentration of Cu^{2+} ions & adsorption capacity also decreased in the same manner. Percentage adsorption of Fe^{2+} ions decreased sharply upto 3 ppm Cu^{2+} ions concentration and after it there was an increase in percentage adsorption of Fe^{2+} ions at 5 ppm of Cu^{2+} ions concentration. After it percentage adsorption of Fe^{2+} ions slowly decreased to 78.7% at 10 ppm concentration of Cu^{2+} ions. Similar results were reported by Kabata – Pendias & Pendias (2001 [15]. The ionic radius of Cu^{2+} ions (73 nm) is less than the ionic radius of Fe^{2+} ions (78 nm), hence the adsorption of Cu^{2+} ions is more favourable than Fe^{2+} ions.

Effect of concentration of Mn^{2+} ions on percentage adsorption of Fe^{2+} ions

The results shown in Figure 3 that the percentage adsorption of Fe^{2+} ions on *Cuscuta* powder without any co-metal ions was found 91.0% & adsorption capacity was 182.2µg/g. Initially at 1 ppm of Mn^{2+} ions concentration the percentage adsorption was observed 87% and after this concentration, percentage adsorption was observed to slightly decrease at 3 ppm concentration of Mn^{2+} ions. Again it increases from 5 ppm to 7.5 ppm concentration of Mn^{2+} ions. After 7.5 ppm concentration of Mn^{2+} ions percentage adsorption was rapidly decreased. The ionic radius of Mn^{2+} ions (67 nm) is smaller than the ionic radius of Fe^{2+} ions (78 nm), hence it looks that the adsorption of Mn^{2+} ions is more favourable than Fe^{2+} ions. Another possible reason for this type of results may be electrostatic force of attraction between metal- metal ions and negatively charged sites of adsorbent. Initially Mn^{2+} ions suppress the adsorption of Fe^{2+} ions but later on it favours Fe^{2+} ions adsorption due to metal – metal interaction upto 7.5 ppm concentration of Mn^{2+} ions.'

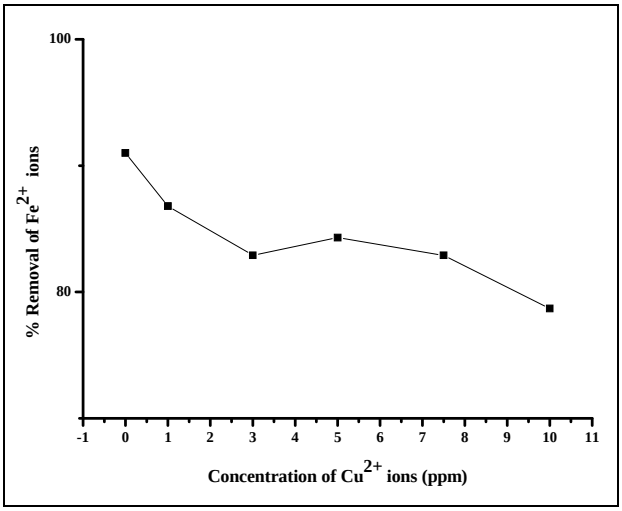

Fig 2: Effect of concentration of Cu^{2+} ions on percentage adsorption of Fe^{2+} ions on *Cuscuta* powder from aqueous solution

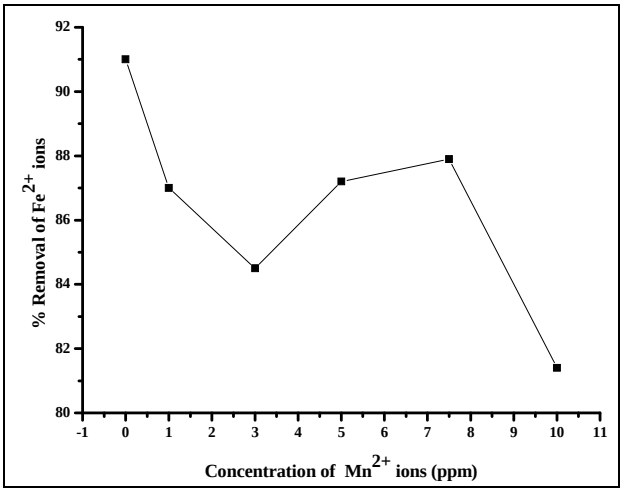

Fig 3: Effect of concentration of Mn^{2+} ions on percentage adsorption of Fe^{2+} ions on *Cuscuta* powder from aqueous solution

Effect of concentration of Ca^{2+} ions on percentage adsorption of Fe^{2+} ions on *Cuscuta* powder from aqueous solution

The results depicted in Figure 4 shows that initially, when no any co- metal ion is present the percentage adsorption of Fe^{2+} ions was observed 91.0% & adsorption capacity was 182.2µg/g. With 1 ppm concentration of Ca^{2+} ions in the adsorbate solution the percentage adsorption of Fe^{2+} ions was found 88.0% and adsorption capacity was 176µg/g. On further increasing the concentration of Ca^{2+} ions the percentage adsorption of Fe^{2+} ions also increases upto 5 ppm where percentage adsorption was found 89.6% and also the adsorption capacity was 179.2 µg/g. After 5 ppm concentration of Ca^{2+} ions the percentage adsorption goes on decreasing slowly and also the adsorption capacity slightly decreased. It may be explained on the basis of ionic radius of metal ions. The ionic radius of Fe^{2+} ions (78 nm) is smaller than the ionic radius of Ca^{2+} ions (100 nm) hence, Fe^{2+} ions get preferably adsorbed when Ca^{2+} ions concentration were lower. But as the concentration of Ca^{2+} ions increases in the solution Fe^{2+} ions interact with Ca^{2+} ions due to which percentage adsorption of Fe^{2+} ions was reduced upto 3 ppm concentration of Ca^{2+} ions. But as higher concentrations percentage adsorption of Fe^{2+} ions was observed an increase due to exchange of ions on adsorbent surface.

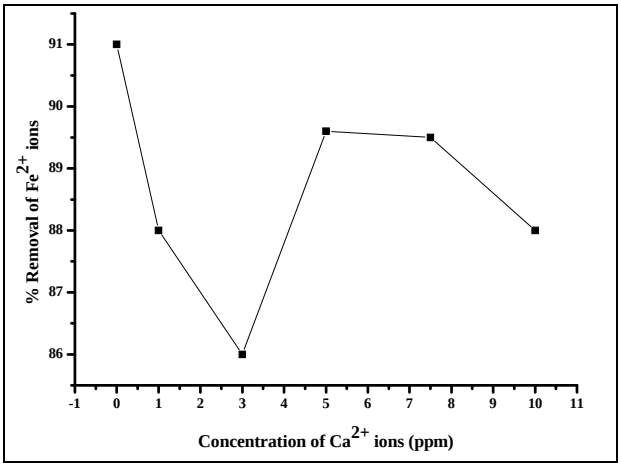

Fig 4: Effect of concentration of Ca^{2+} ions on percentage adsorption of Fe^{2+} ions on *Cuscuta* powder from aqueous solution

Effect of concentration of Zn^{2+} ions on percentage adsorption of Fe^{2+} ions on *Cuscuta* powder from aqueous solution

The experimental results given in Figure 5 indicated that in the absence of any co-metal ions the the percentage adsorption of Fe^{2+} ions on cuscuta powder was 91.0% & adsorption capacity was 182.2µg/g. The percentage adsorption of Fe^{2+} ions was found to be decreased from 91.0% to 83% with the increase of Zn^{2+} ions concentration in adsorbate solution. But with further increase in the concentration of Zn^{2+} ions percentage adsorption of Fe^{2+} ions was increased to 86.0%. From 5 to 10 ppm of Zn^{2+} ions concentration % adsorption of Fe^{2+} ions was decreased to 79.8%. The ionic radius of Zn^{2+} ions (74 nm) is smaller than the ionic radius of Fe^{2+} ions (78 nm) hence, the adsorption of Zn^{2+} ions onto *Cuscuta* powder looks more favourable than Fe^{2+} ions when Zn^{2+} ions are in competitive concentrations in the solution. The interaction between Fe^{2+} ions and Zn^{2+} ions also takes place as reported by Kabata – Pendias & Pendias (2001) [15].

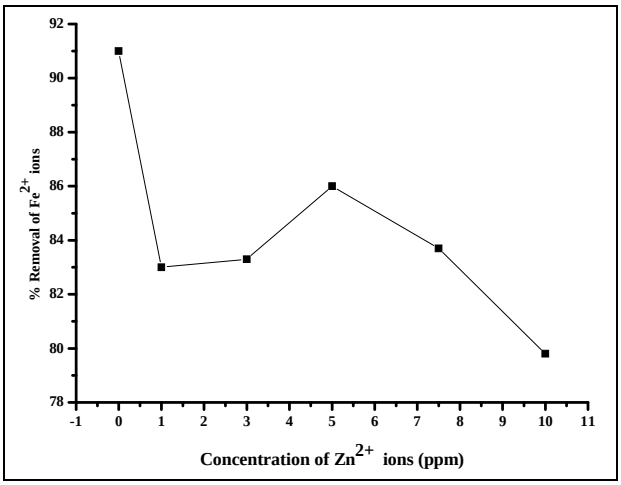

Fig 5: Effect of concentration of Zn^{2+} ions on percentage adsorption of Fe^{2+} ions on *Cuscuta* powder from aqueous solution

Adsorption isotherm

The adsorption isotherms are very important in describing the adsorption behaviour of solutes
on specific sorbents [16]. 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 in presence of co-metal ions. 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 which indicates that iron metal adsorption on *Cuscuta* powder in presence of co-metal ions Cu, Mn, Ca and Zn follows the Tempkin model with R^2 value of 0.986, 0.979, 0.994 and 0.981 for Fe-Cu, Fe-Mn, Fe-Ca and Fe-Zn respectively. Comparing all the data fitted to the isotherm models, the Tempkin isotherm model was found to have the best fit to the experimental data since this isotherm exhibited the highest value of R^2.

Table 1: Adsorption isotherm model constants for adsorption of Fe(II) ions in presence of co-metal ions on *Cuscuta* powder

Model	Parameter	Fe^{2+}-Cu^{2+}	Fe^{2+}-Mn^{2+}	Fe^{2+}-Ca^{2+}	Fe^{2+}-Zn^{2+}
Langmuir	qm(mg/g)	0.1467	0.1449	0.1574	0.1484
	b(ml/mg)	0.8006	0.8960	1.2658	0.8628
	R^2	0.913	0.908	0.973	0.915
Freundlich	Kf(mg/g)	2.1043	2.1043	2.1064	2.1043
	qe(mg/g)	5.9888	6.3694	7.8740	6.25
	R^2	0.980	0.973	0.993	0.974
Tempkin	A(J/mol)	6.6458	6.6458	6.5810	6.6458
	B(ml/mg)	88484.71	91761.92	112616.90	91761.92
	R^2	0.986	0.979	0.994	0.981

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^{2+} ions adsorption and their removal from wastewater. The adsorption of metal ions on agricultural by-products may involve metal interactions or coordination to functional groups present in natural proteins, lipids and carbohydrates positioned on cell walls [17-18]. Bhatti *et al*. and

Gilbert *et al*. stated clearly from their studies of natural plant materials that the biochemical characteristics of acidic functional groups are responsible for the metal ions uptake [19-20].

Conclusion

The adsorbent developed from *Cuscuta* plants was found as a promising and cheap adsorbent for the removal of iron metal ions from synthetic wastewater. The co-metal ions affected the adsorption of Fe^{2+} ions onto *Cuscuta* powder in the following order: $Cu^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+}$. The Tempkin isotherm model showed a better fit than the Freundlich and Langmuir models for adsorption data.

Acknowledgement

The author are thankful to the Dean C.B.S&H and Vice Chancellor of G.B. Pant University of Agriculture and Technology, Pantnagar (India) for providing the necessary facilities and. assistance required for completion.

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