



COLUMN STUDIES INTO ADSORPTION OF Fe(II) AND Mn(II) FROM AQUEOUS SOLUTIONS USING MODIFIED *ALBIZIAPROCERA* LEGUMES SUBSTRATE

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Abstract

The uncontrolled growth of industrialization in the world is responsible for change in the chemical and biological properties of both surface and ground water which constitute a health hazard. The heavy metals render the water unsuitable for drinking and are also highly toxic to human beings. Removal of these materials is therefore essential. The studies pertaining to the use of inexpensive agro-based adsorbents, such as tree bark, saw dust, corncob, straw, and fly ash etc. for heavy metal ion removal are gaining a lot of importance. In the present study removal of Fe(II) and Mn(II) ions has been investigated using *albiziaprocera* legume substrate through packed adsorption column and results obtained are quite encouraging. Batch adsorption studies have shown that removal of metal ions is dependent upon process parameters like contact time, temperature, metal ion concentration, doses and pH. The maximum removal of Fe(II) and Mn(II) to the extent of 82 % has been achieved at pH 4.5 in 30 min in the concentration range 30 to 90 mg/L. The use of packed adsorption column has been investigated at the optimized conditions, to study the feasibility of the process for application in small scale industries. The adsorption data obtained from batch studies at optimized conditions have been subjected to Freundlich isotherm studies. The data fits well to the Freundlich isotherm models indicating favorable and monolayer adsorption. Freundlich constants have been calculated.

Keywords: adsorption; *albiziaprocera* legumes; batch studies; column studies; Freundlich isotherm model; Iron (II); manganese (II).

1.Introduction

Toxic heavy metals are released into the environment from a number of industries such as mining, plating, dyeing, automobile manufacturing and metal processing. The presence of heavy metals in the environment has led to a number of environmental problems. In order to meet the water quality standards for most of countries, the concentration of heavy metals in wastewater must be controlled[1].The heavy metal ions are stable and persistent environmental contaminants since they cannot be degraded and destroyed. These metal ions are harmful to aquatic life and water contaminated by toxic metal ions remains a serious health problem[2], so their concentration must be reduced to acceptable levels before discharging into environment, otherwise these can pose a threat to public health. The metals of most immediate concern are zinc, chromium, iron, nickel, mercury, cadmium and lead[3].

Conventional physico-chemical treatment methods for removing heavy metals include precipitation, ultra-filtration, oxidation-reduction, ion exchange, reverse osmosis, electrochemical dispersion, ion exchange and membrane separation are generally ineffective or expensive when the heavy metals are present at low concentration [4-9].

The adsorption process plays an important role in removing heavy metals, such as lead, from wastewater. There has been much research into the development of low-cost alternatives to activated carbon; these materials include fly ash, metal oxides, zeolites, peats, chitosans, and activated sludge [10-15].For low concentrations of metal ions in wastewater, the adsorption process is highly recommended for their effective removal. The process of adsorption implies the presence of an “adsorbent” solid that binds molecules by physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is available in large quantities, easily re-generable and cheap [16].



As a result, recent research has been focused on development of cost effective alternatives. Adsorption is one of the physico-chemical treatment process found to be effective in removing heavy metals from aqueous solution using low cost adsorption [17]. Most commonly used adsorbents are untreated plants wastes such as teak leaf powder[18], rubber leaf powder [19], papaya wood [20], newspaper pulp [21], baggage fly ash [22], banana and orange peels[23], carrot residue[24], tea waste [25], etc.

The objective of the present study is to investigate the adsorption through packed column in order to study the feasibility of the process for application in small scale industries. Batch adsorption studies have been carried out to study the effect of pH, contact time, metal ion concentrations, binding capacity as well as temperature.

2. Experimental

2.1. Preparation of metal ions aqueous solution

All the chemicals, ferrous ammonium sulfate, o-phenanthroline, hydroxyl amine hydrochloride, and potassium periodate used were of analytical grade purchased commercially and were used without further purification. The metal ion solutions of required concentration of Fe (II) and Mn (II) were prepared from ferrous ammonium sulfate and potassium permanganate respectively in double distilled water. The glasswares used were leached with conc. HNO₃ and dried in an oven at 50 °C. The pH of ferrous ammonium sulfate and potassium permanganate solutions was adjusted to 4.5 using buffer solution to prevent hydrolysis.

2.2. Adsorbent Material Development

The *albiziaproceralegumes* were collected from Sirpur village of Chandrapur district (M.S.) India. It was dried at room temperature in

the air, grinded with grinder and sieved through a 500 μm . Required quantity of the *albiziaprocera legumes* substrate was mixed with 0.25 N sulfuric acid and 39% v/v formaldehyde. The mixture was continuously agitated for 6 hrs using commercial shaking machine. The mixture was then filtered and washed, several times with de-ionized water until the pH of filtrate was attained to 5. The residue was dried in an oven at 50 $^{\circ}\text{C}$ for 24 hrs. The modified *albiziaproceralegumes* substrate was used for final adsorption experiments of the waste water treatment.

2.3 Batch adsorption studies

Batch experiments were carried out by agitating a known weight of *albiziaproceralegumes* substrate placed in contact with 100 ml of metal ion solutions of different concentrations. The suspension was continuously stirred in a shaker, the effect of pH and initial metal ion concentration have been studied for pH range 2.5-9.5 and for initial metal ion concentrations ranging from 30-90 mg/L of iron and manganese. The pH of the solution was adjusted by the addition acidic buffer. The contact time was varied from 5 min to 240 min, The concentration of Fe(II) and Mn(II) was determined by spectrophotometrically [26].

3. Result and discussions

3.1 Effect of pH

Effect of pH on the adsorption characteristics of *Albiziaproceralegumes* substrate was determined in the pH range 2.5 -9.5. Studies indicate that the system is strongly pH dependent. The rate of adsorption is maximum at pH 4.5, as is apparent from figure 1.

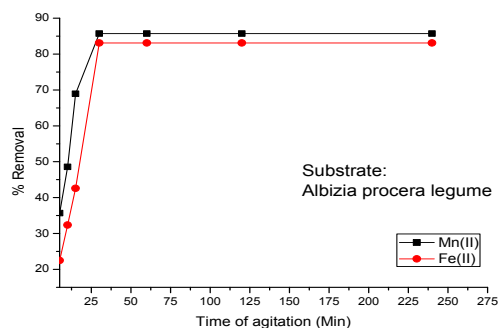
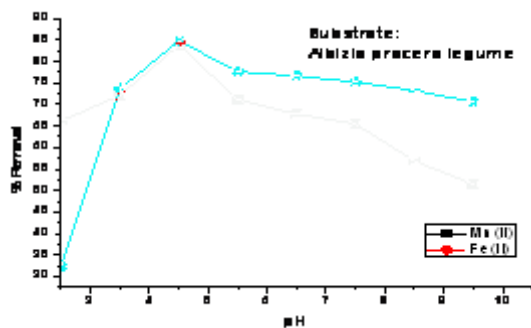


Fig 1: Effect of pH on adsorption of Fe(II) and Mn(II) Fig 2: Effect of agitation time on adsorption of Fe(II) and Mn(II) at pH 4.5 and at 30°C

In each case 1 g of the substrate at the desired pH was agitated for 30 min. The percentage removal was found to increase upto certain extent and then decreased. This decrease in adsorption may be due to precipitation of metal hydroxide. The data showed that adsorption of Fe(II) and Mn(II) is optimum at 4.5 pH. The physicochemical characteristics of the adsorbent may also play an important role. It was reported that free metal ions are adsorbed better than hydroxides of metal ions[27]. Hence, pH 4.5 was selected for all studies.

3.2 Effect of contact time

Contact time is also an important factor affecting removal, most of adsorption occurs in the initial half hour and increases very slowly later similar results have been reported[28]for adsorption of cobalt on rice husk. A further increase in contact time tends to decrease adsorption (Figure 2),probably due to desorption. Variation of time of contact from 5 min to 240 min shows that maximum removal occurs at 30 min.

3.3 Effect of metal concentration

The concentrations of Fe(II) and Mn(II) ranging from 70-110 mg/L were used in the experiment. The amount of metal ion adsorbed increases with concentration, however, percentage removal increases with decrease in

the concentration of Fe(II) and Mn(II) ions (figure 3). The increase in percentage adsorption with dilution is explained on the basis of availability of larger number of active surface sites of the adsorbent.

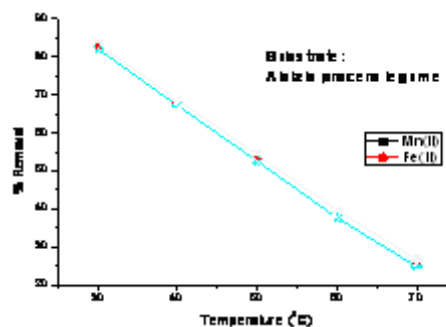
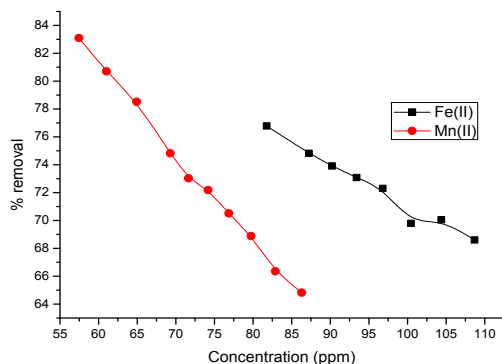


Fig.3: Effect of concentration of adsorption of Fe(II) and Mn(II) at 4.5 pH and at 30 °C Fig4: Effect of temperature on adsorption of Fe(II) and Mn(II) at 4.5 pH and at 30°C

3.4 Effect of temperature

The temperature dependence of adsorption studies of Fe(II) and Mn(II) by *albiziaproceralegumes* substrate was studied over the range of 30°C to 70°C (303K - 343K). Increase of temperature from 303K to 343K decreases the adsorption, indicating the process is exothermic (figure 4).

3.5 Adsorption isotherm studies

The data for the uptake of Fe(II) and Mn(II) by *albiziaproceralegumes* substrate has been analyzed in the light of Freundlich model of adsorption and adsorption of Fe(II) and Mn(II) on *albiziaproceralegumes* substrate was also found to confirm to Freundlich adsorption isotherm at 30 °C. The linearized form of the Freundlich equation can be given as

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

where C_e is the equilibrium concentration (mg/L) and q_e is the amount adsorbed (mg/g). The values of n and K_f at 30 °C were determined from

slope and intercept of the linear plots of $\log q_e$ vs. $\log C_e$ (Figure 5). The values of n are 4.39 for iron and 7.33 and those for K_f are 32.8473 and 35.2776 at 30°C respectively. Since the value of $1/n$ is less than 1, it indicates favorable adsorption. A smaller value of $1/n$ indicates better adsorption mechanism (table 1) and formation of relatively stronger bond between adsorbate and adsorbent [29]. The higher numerical values of K_f confirm the significant affinity of Fe (II) and Mn(II) ions for *albiziaproceralegume* substrate.

Table 1. Freundlich Isotherm parameters for Fe(II) and Mn(II) adsorption by *albiziaprocera* legume substrate and activated charcoal

Species	Metal ion	$1/n$	K_f
<i>Albiziaprocera</i>	Fe(II)	0.227 6	32.847 3
	Mn(II)	0.136 4	35.277 6
<i>Activated charcoal</i> ^[30]	Fe(II)	0.459 7	2.3955
	Mn(II)	0.746 6	1.1413

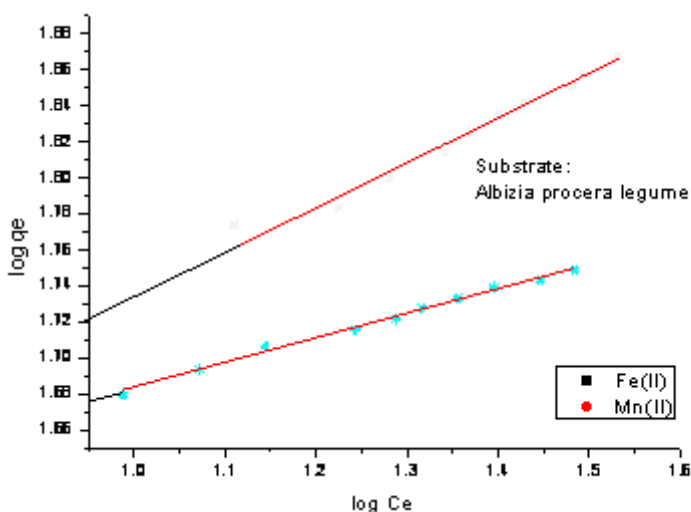


Figure 5: Freundlich adsorption isotherm for adsorption of Fe(II) and Mn(II) on *Albiziaprocera* legumes substrate at 30 °C and at pH 4.5.

3.6 Column studies

Column adsorption studies

Column studies were carried out in a column made of Borosilglass of 1.5 cm internal diameter and 15 cm length. The two columns were filled with 1 g of dried modified *albiziaprocera* legume substrate by tapping so that maximum amount of adsorbent was packed without gaps for adsorption of Fe(II) and Mn(II) respectively. The influent aqueous solution of Fe(II) and Mn(II) containing known concentration were filled in the two different reservoir of large cross sectional area. The height of the liquid level was adjusted so as to maintain constant flow rate of effluent. The influent solution was allowed to pass through the packed column at constant flow rate of 2 mL/min. All the experiments were carried out at room temperature. The effluent solution was collected at every 5 minutes intervals and the concentration of the Fe(II) and Mn(II) solution was determined by Beer's law [26] using spectrophotometer.

Column adsorption studies of Fe(II) and Mn(II) on *albiziaprocera* legume substrate at room temperature are investigated using aqueous solution of 70 mg/L influent concentrations at the optimal 4.5 pH value. Faster and effective adsorption of Fe(II) and Mn(II) occurs during the initial phase. Adsorption reaches to the optimum value at 45 min and upto the 100 mL effluent. Subsequent adsorption decreases as a consequence of the progressive saturation of the binding sites. It was observed that the column gets saturated after passing 160 mL of iron and manganese solutions (Figure 6). Optimum adsorption of Fe(II) and Mn(II) observed between 40 - 45 min in a packed column of *albiziaprocera* legume substrate.

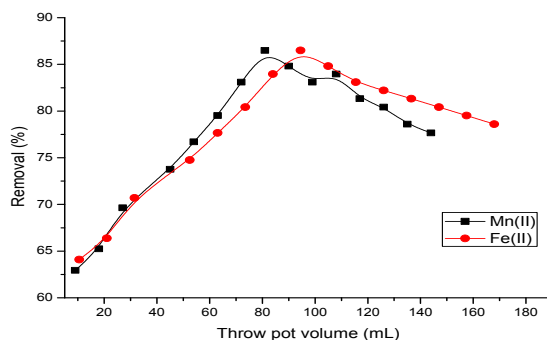


Fig 6: Optimum adsorption of Fe(II) and Mn(II) observed at 100 mL of throw pot volume.

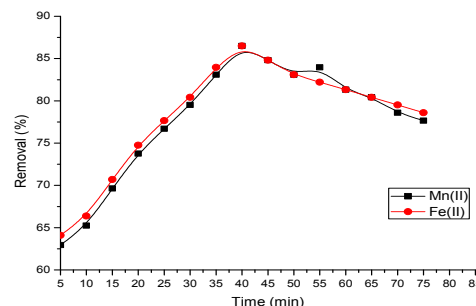


Fig7: Optimum adsorption of Fe(II) and Mn(II) observed between 40 - 45 min in a packed column

4. Conclusions

Present study demonstrates that a modified *albiziaprocera* legume substrate could be used successfully for the removal of iron (II) and manganese (II) from aqueous solution. The maximum adsorption capacity of formaldehyde modified *albiziaprocera* legume substrate achieved upto 86% at 45 min. Numerical value of Freundlich isotherm parameter for *albiziaprocera* legume substrate indicated that *albiziaprocera* legume substrate has more binding capacity compare to activated charcoal. The substrate materials are inexpensive and easily available, needs simple processing for effective removal of metal ions without use of any sophisticated equipment or expert attention. It could be effective alternative to conventional adsorbents like activated charcoal or alumina and expensive ion exchange resins. Thus the method could be utilized for removal of heavy metal ions from industrial effluents after prior separation of a particular metal from other impurities present.



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