Research Article

Removal of Fe (II) from Aqueous Solution and Waste Water by Prosopis Juliflora Leaf Powder by Adsorption

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Abstract

Prosopis Juliflora Leaf Powder (PJLP) was treated with nitric acid and used as a low cost, easily available adsorbent for the removal of Fe (II) from aqueous solution and industrial waste water. Batch experiments were conducted to determine the effects of contact time, pH, initial concentration of adsorbate, temperature and adsorbent dose. The adsorption of Fe (II) was found maximum (86.27 %) at 50 min contact time, (93.99 %) at 7 pH. (92.28 %) at 1 ppm metal ion concentration, (89.06 %) at 313 K and (86.26 %) at 1 g dose. Equilibrium data were well represented by the Freundlich isotherm model for all tested adsorption systems. The thermodynamic study has showed that the Fe (II) adsorption onto PJLP was favorable and spontaneous. The kinetics study showed that Fe (II) adsorption follows the second order kinetics.

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Keywords: Adsorption, Low cost material, Prosopis Juliflora, Freundlich and Langmuir isotherms.

Introduction

Water is the principal need of life on earth, and is an essential component for all forms of lives, from micro-organism to man. The unplanned urbanization and industrialization [1] has resulted in over use of environment particularly of water resource [2]. A kind of crises situation has made getting clean water a serious problem. It is a known fact that when pure water is polluted its normal functioning and properties are affected [3]. International World Water Day is held annually on 22nd March as a means of focusing attention on the importance of freshwater and advocating for the sustainable management of freshwater resources.

High industrialization causes the high discharge of effluents into water bodies. Heavy metals like iron, mercury, cobalt, chromium, copper, nickel, lead etc. are present in it. Due to their non-degradable nature they cause disposal and environmental problems. These heavy metals such as Nickel (II), Copper, Cadmium, Lead, Zinc and iron have harmful effects on human physiology and other biological systems when they exceed the tolerance level [4, 5].

In water the iron occurs mainly in the divalent and trivalent state. The main source of iron in industrial wastewater is iron, steel, hardening, metal processing and fabrication industries. Iron is an essential element in human nutrition. It is contained in a number of biologically significant proteins, but ingestion in large quantities results hemochromatosis where in tissue damage results from iron accumulation.

The removal of toxic heavy metal contaminates from aqueous waste streams is currently one of the most important environmental issue being investigated [6]. As pollutants, heavy metals were intensively studied due to their significance from the point of view of persistence and toxicity. These toxic metals can cause accumulative poisoning, cancer and brain damage when found above the tolerance levels [7]. The agencies for the environmental monitoring have set permissible limits for heavy metals levels in drinking water because of their harmful effects. The removal and rapid decontamination of heavy metals (Cd, Pb, Cu, and Hg) become very important for the environmental remediation. Many processes have been used for the removal of heavy metals from waste water, such as chemical precipitation, coagulation, solvent extraction, membrane separation, ion exchange and adsorption [8].

For dilute metal concentrations ion exchange, reverse osmosis and adsorption can be applied [9]. However, the common use of ion exchange and reverse osmosis is restricted by the high operating cost. As an alternative to chemical precipitation, membrane filtration, or ion exchange, adsorption processes with wide variety of adsorbents have been tested. Adsorption processes for removal of metals has been found cheaper and more effective than the several technologies [10].

The adsorbents used should have some specific properties, such as a high ability to reduce the

concentration of heavy metals below the acceptable limits, high adsorption capacity and long lifetime [11]. Thus, it is a continuing need to identify and develop low-cost and efficient adsorbents for facile and efficient removal process. Heavy metal adsorption was studied on various adsorbents such as activated carbon [12], fly ash [13], and bioadsorbents (adsorbents from plant and animal-origin materials, for example bark/tannin-rich materials, humus, peat moss, modified cotton and wool, chitin, chitosan, seaweed, and biopolymers) [14-16]. Activated carbon is the most widely used adsorbent but commercially available activated carbons are very expensive [17]. Many low cost adsorbents have been used for the removal of heavy metals e.g. brick kiln ash, fly ash, bidi leaves, teak leaves, amla dust , wallastonite, peanut hull and neem leaves [18]. Other such adsorbents are pine cone [19], peels of banana, grape bagasse [20], which were used for removal of particular metals from water.

Literature survey indicates that the use of PJLP as a low cost adsorbent for removal of heavy metals from aqueous solutions and industrial waste water has not been reported. Thus in the present study the systematic work was carried to investigate the adsorption properties of PJLP for the removal of Fe (II).

Materials and Methods

Preparation of Adsorbent

The adsorbent selected for the present study was Prosopis Juliflora which is locally available plant and was collected in Ahmednagar District of Maharashtra. The sample leaves were dried in shadow, avoiding direct sunlight on them. The dried leaves were grinded into powder and washed with distilled water and filtered. The residue left was treated with very dilute solution of nitric acid (0.1 N). It was then stirred for half an hour vigorously using mechanical stirrer at room temperature. Then it was filtered and washed with distilled water repeatedly to remove free acid. After chemical treatment the residue was dried first in air and finally in oven at $90\text{-}100^0C$ for 8-10 hours and powdered using electric grinder. The homogeneous powder was passed through mesh for desired particle size. The adsorbent once prepared was used throughout the experimental work. The particle size of adsorbent selected for these experiments was on the basis of their settlement at the bottom of the system, so that the portion of the solution could be taken out conveniently from the supernant liquid.

Preparation of Fe (II) Metal Ion Solution

Fe (II) prepared by dissolving ferrous ammonium sulphate in double distilled water. The chemicals used were of analytical grade and used without further purifications. The solutions were prepared in doubly distilled water. A distilled water prepared by using first metal distillation unit and then all quick fit glass assembly in permanganatic condition, wherever

necessary the prepared solutions were standardized as per literature[21]. Industrial waste water samples were collected from MIDC area of Ahmednagar.

Adsorption Experiments

Each batch adsorption study was carried out by using nitric acid treated PJLP with iron ion solution under different conditions at maximum time 50 minutes. Iron was determined using spectrophotometer (SL-159 ELICO UV-VISIBLE SPECTROPHOTOMETER).

Iron from Industrial waste water was determined using AAS (LABINDIA AA 7000, Atomic Absorption Spectrophotometer) before adsorption experiments and using spectrophotometer (SL-159 ELICO UV-VISIBLE SPECTROPHOTOMETER) after the adsorption experiments.

After batch experiments percentage adsorption of Fe (II) from aqueous solution and industrial waste water were computed [22],

$$\% \text{ Adsorption} = (C_I\text{-}C_F) / C_I \times 100 \qquad (1)$$

Where, C_I and C_F are the initial and final Fe (II) concentrations respectively.

Results and Discussion

The experimental data obtained from the different batch type experiments, in the present investigation was analyzed and interpreted based on the adsorption of Fe (II) on PJLP.
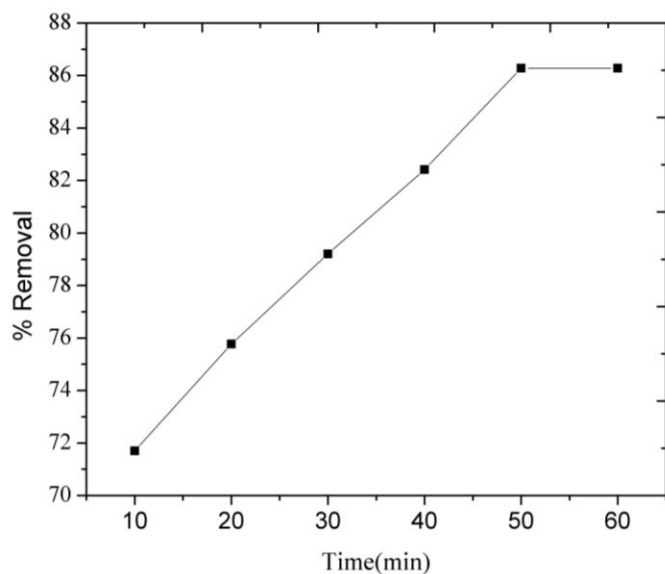
Effect of Contact Time

The effect of contact time was studied by keeping adsorbent dose 1 g, initial concentration of adsorbate 4 ppm, pH 2 and room temperature (303 K) and varying time. It was found that the adsorption percentage increases with increase in time from 10 minutes to 50 minutes and after 50 minutes the % adsorption remains constant (**Fig. 1**). Time taken for the completion of adsorption was 50 minutes. It was in good agreement with the reported work of Jute and Sunnhemp as adsorbent [23]. The equilibrium contact time was 50 minutes. Ions diffuse to surface and in to the pores of PJLP which have very large number of surface area. When the time increased more than 50 minute remaining ions adsorbed or diffused into the pore could be saturated, the affinity of metals adsorbed will decrease. Thus, the affinity of metal adsorbed is depending upon appropriate time. Therefore the contact time 50 minutes was selected in all experiments.
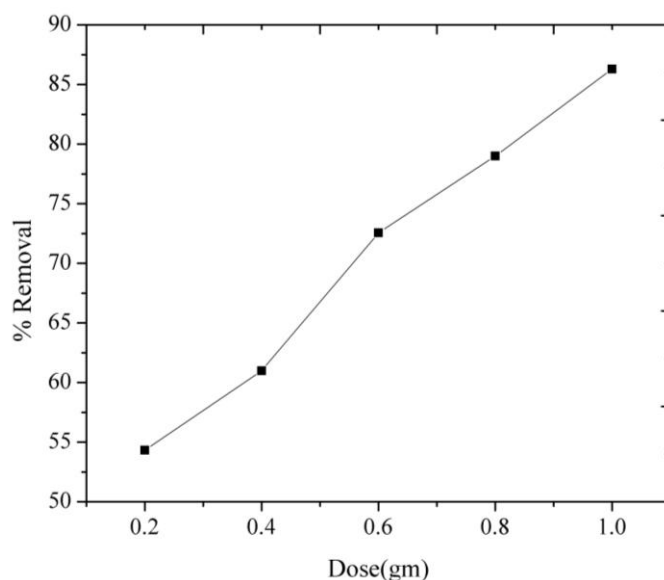
The experimental data was tested by first and second order equations.

In pseudo –first order kinetic model a simple kinetics of adsorption given by Lagergren rate equations [24] were as,
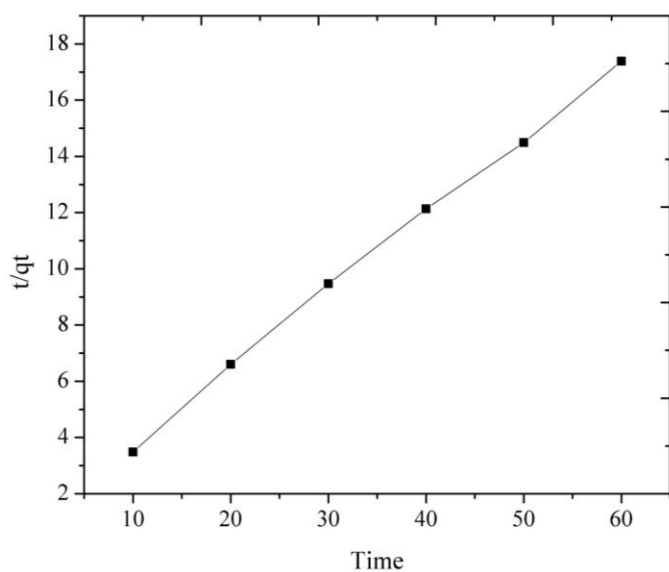
$$q_e /dt=k_1 (q_e\text{-}q_t) \qquad (2)$$

Figure 1 Effect of contact time
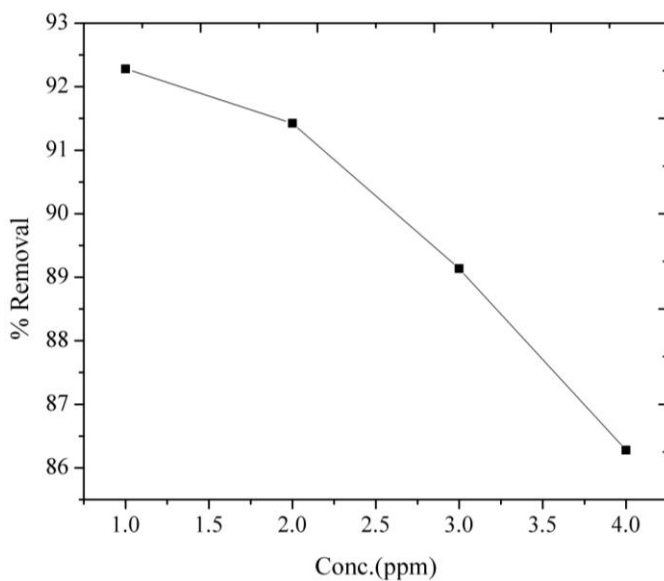

Figure 3 Effect of adsorbent dose

Figure 2 Second order kinetics for effect of contact time

Figure 4 Effect of initial concentration of absorbate

The integrated form is,

$$\log (q_e - q_t) = \log q_e - k_1/2.303 \times t \qquad (3)$$

Where q_e and q_t represent the amount of Fe adsorbed (mg/g) at equilibrium time and at time t(min) respectively, k_1 represents the first order rate constant (min^{-1}). If plot of log $(q_e - q_t)$ versus t was linear then the adsorption process was followed pseudo-first order kinetics but it was not followed the pseudo-first order kinetics. In second order adsorption kinetics, the plot of t/qt versus t was found to be linear with $R^2 = 0.989$ (**Fig. 2**). The present studies reveal that adsorption of Fe (II)

onto the surface of PJLP followed second order kinetic model.

Effect of Adsorbent Dose

Amount of adsorbent plays an important role in standardizing the adsorption process with quantification of adsorbate solution and the adsorbent. In our present study with increase in the amount of PJLP as adsorbent the Fe (II) removal efficiency increased rapidly (**Fig. 3**) which may be due to the greater availability of the exchangeable sites or surface areas at higher concentration of the adsorbent. Our findings are in good support with the reported work by Srinivas et al [25].
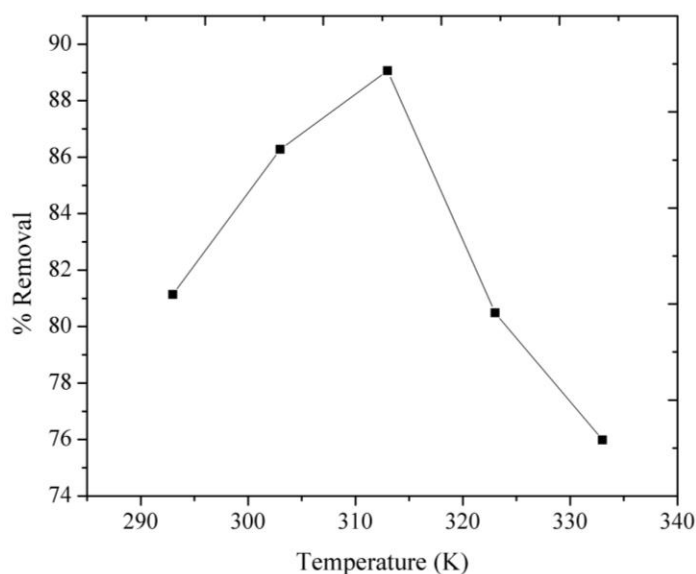
Figure 5 Effect of temperature

Figure 6 Effect of pH

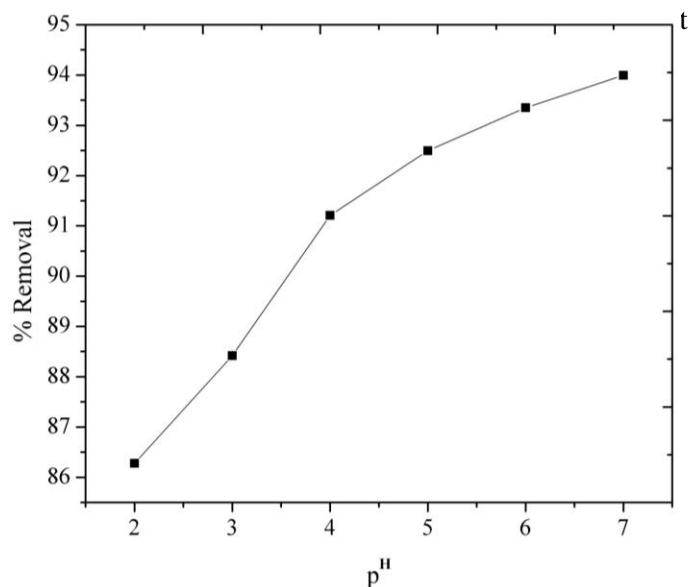**Effect of Initial Concentration of Adsorbate**

The adsorption of Fe (II) onto the surface of PJLP was rapid initially, slows down later on and finally reached towards equilibrium indicating saturated adsorption [26]. The increased in adsorption may be attributed to increase in surface activity and due to micelle formation or the aggregation of iron ions in the concentration range studied [26]. In our present investigation the percentage removal of iron decreased with the increased in the initial concentration of adsorbate (**Fig. 4**). Our findings are supported by the reported work of Sureshkumar Halnor et al [27] and R. S. Shelke et al [28].

Effect of Temperature

Temperature plays a major role in the adsorption of heavy metals on the surface of adsorbent. Adsorption study was carried out in different temperature range (293-333 K) and remaining parameters were kept constant and found that adsorption increases with increase in temperature from 293-313 K and decreases from 323-333 (**Fig. 5**). The increased in adsorption from 293-313 K indicates endothermic adsorption. It has been reported that the increase in uptake with temperature is mainly due to an increase in the number of adsorption sites created by the breaking of some of the internal bonds near the edge of the crystal [29]. The decrease in adsorption with increase in temperature is due to the increase in solubility of the adsorbate with increase in temperature, or the mobility of the large ions increases with increasing temperature [27].

Effect of pH

Solution pH is one of the most important parameter for adsorption of heavy metals from aqueous solution and was studied at different pH values and it was found that the amount of metal adsorbed increases with increasing pH (**Fig. 6**). At a low pH adsorption of iron was less; the H^+ ions are much larger than ions of iron on the surface of the powder which limits the access of iron ions on the surface of grains of the adsorbent. When the pH increases, the effect of competition from H^+ ions decreases and the positive charged ions take their place on the surface [30-32].

Adsorption Isotherms

The adsorption isotherm is a graphical representation of amount of substance adsorbed against the residual concentration of the adsorbate and adsorbent doses were analyzed using Langmuir and Freundlich isotherm in order to find the adsorption capacity of PJLP [22].

Freundlich Adsorption isotherm

The Freundlich equation was applied to describe the analytical results on adsorption. It was an empirical result agrees quite well with Langmuir equation and experimental data over a moderate range of adsorbate concentration. It is represented by the equation [33],

$$\log x/m = \log k + 1/n \log C_{eq} \qquad (4)$$

Where, C_{eq} is the equilibrium concentration (mg/L) and x/m is the amount adsorbed per unit mass of adsorbent (mg/g). Plotting log x/m vs log C_{eq} a straight line was obtained with a slope of 1/n, and log k is the intercept. The k value was found to be 9.85. The value of 'n' was calculated to be 1.1784. As the value of 'n' is 1 < n < 10, shows favorable adsorption of Fe (II) on PJLP.

Langmuir Adsorption Isotherm

Langmuir equation was also applied for adsorption equilibrium. The Langmuir treatment is based on the assumption that maximum adsorption corresponds to monolayer of adsorbate molecules on the adsorbent surface that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface [22].

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \qquad (5)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/L), Q_0 is the monolayer adsorption capacity (mg/g) and b is a constant related to the free energy of adsorption.

The linear plot of Ce/qe vs Ce shows that the adsorption obeys Langmuir adsorption model. Q_0 and b respectively were determined from the Langmuir plots and found to be 53.92 mg/g and 0.18 mg/L. The essential characteristic of Langmuir isotherm were expressed in terms of a dimensionless constant separation factor or equilibrium factor R_L, which is defined by

$$R_L = 1/ 1+bC_0 \qquad (6)$$

Where, b is the Langmuir constant and C_0 is the initial concentration of Fe (II).

R_L is indicative of the nature of the isotherm and is enlisted below as [26, 27],

R_L Value	Type of Isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$O < R_L < 1$	Favorable
$R_L = O$	Irreversible

In present study R_L value observed was between 0 and 1 indicate favorable adsorption of Fe (II) on PJLP. R_L value in the present study was 0.0040.

Thermodynamic Parameters

Thermodynamic parameters such as free energy, enthalpy and entropy of adsorption were calculated and found that ΔG was negative and showed spontaneous nature of adsorption process, ΔH was negative and showed exothermic nature of adsorption process, ΔS was positive and showed the increasing randomness at solid/liquid interface during the adsorption of iron. All these values demonstrate a spontaneous and favorable adsorption process.

Application to Industrial Wastewater

The suitability of the PJLP adsorbent for the removal of Fe (II) with respect to Industrial waste water was evaluated. Adsorption experiments were conducted with Industrial waste water samples S_1, S_2 and S_3 containing Fe (II). **Table 1** and **2** gives the details of the Industrial waste water samples applied for this study before and after adsorption experiments. The concentration of Fe (II) in S_1, S_2 and S_3 were determined by AAS. The percentage of Fe (II) removal in each sample was determined by usual procedure. The results are shown in Table 2. From which it is evident that Fe (II) removals were 88.06, 87.91 and 83.92 % from S_1, S_2 and S_3 respectively. It has been observed that 88.06% removal of Fe (II) could be achieved with an adsorbent dose of 1 g/100 mL.

Table 1 Concentration of iron in industrial waste water before adsorption

Name of sample /Name of metal ion	S_1 Co (ppm)	S_2 Co (ppm)	S_3 Co (ppm)
Fe	13.58	16.47	14.3

Conclusions

The present study shows that the nitric acid treated Prosopis Juliflora Leaf Powder (PJLP) is an efficient, low-cost adsorbent for the removal of toxic Fe (II) from aqueous solution and industrial waste water. The adsorption of Fe (II) was found to be dependent on contact time, adsorbent dose, and initial concentration of adsorbate, temperature and pH. The equilibrium adsorption data showed significant correlation to Langmuir and Freundlich adsorption isotherms and the adsorption was followed second order kinetics. Value of R_L indicates this adsorption process is favorable. Adsorption with low cost adsorbent is not only cheaper but requires less maintenance and supervision. With the application of very small dose of adsorbent (1 g/100 mL), it is possible to remove about 88% Fe (II) from industrial waste water. It is suggested that the use of this adsorbent for removal of Fe (II) from industrial waste water is an effective and low cost process.

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Table 2 Concentration of iron in industrial waste water after adsorption

Name of sample	Industrial waste water (mL)	Amount of adsorbent (g)	Time (min)	O.D.	Conc.(Ce)	Co-Ce	% Removal
S_1	100	1	50	0.189	1.62	11.95	88.06
S_2	100	1	50	0.232	1.98	14.48	87.91
S_3	100	1	50	0.268	2.29	12.00	83.92

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