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Research Article

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Studies on albizia procera legumes for effective removal of Fe (II) and Mn (II) from aqueous solution

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ABSTRACT

Contamination of water supplies with metals is a constant area of concern. Nationally and internationally, the challenge to remediate hazardous metal-containing waste streams from present or former mining operations, industrial sites, and ground waters is immense. Adsorption has proved to be an excellent way to treat industrial waste effluents, rendering significant advantages like the low-cost, availability, profitability, ease of operation and highly efficient compare to activated carbon. The present study was aimed to utilize albizia procera legume as an adsorbent like activated charcoal for removal of toxic heavy metals like Fe(II) and Mn(II) from waste water. First time the attempt was made to use albizia procera legume substrate as an effective adsorbent for removal of Fe(II) and Mn(II) from the waste water. The adsorption isotherms were obtained in a batch reactor; various parameters like pH, agitation time, temperature, metal ion concentration and doses of substrate were studied. It is observed that, the process of uptake followed first order rate adsorption and obeyed Freundlich model of adsorption. It has *good adsorption capacity for Iron (II) and Manganese (II) at 4.5 pH with optimum agitation time of 30 min even at low concentration. It successfully removed 83-85% of Fe(II) and Mn(II) in one batch. The method could be successfully employed for removal of toxic metals from industrial effluents that could solve the problem of disposal of plant waste materials.*

Key words: Albizia procera; adsorption, Iron, Manganese, Freundlich adsorption.

INTRODUCTION

Discharge of metal containing effluents into water has been a cause of major concern. Traditional treatment methods are proving to be ineffective and expensive. In the past century there has been a rapid expansion in the chemical industry. This has led to an increase in the complexity of toxic effluents. Several industrial processes generate metal containing wastes. Heavy metal contamination has been a critical problem mainly because metals tend to persist and accumulate in the environment [1]. Adsorption of heavy metals from aqueous solution is a relatively new process that is very promising in the removal of contaminants from aqueous effluents. Industrial waste constitutes the major source of various kinds of metal pollution in natural water [2-5]. Heavy metal ions are reported as priority pollutants owing to their mobility in natural water ecosystems and their toxicity [6, 7]. 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. Heavy metals removal from aqueous solutions has been traditionally carried out by chemical precipitation [8]. Numerous methods exist to remove detrimental metal ions from aqueous solutions. Activated carbon has been the most used adsorbent, nevertheless it is relatively expensive. In order to obtain cheaper adsorbents, lignocelluloses materials have been studied [9]. The presence of copper, zinc, cadmium, lead, mercury, iron, nickel and other metals, have a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded.

Various methods of treatment for removal of heavy metals from industrial wastewater have been reported in literature [10]. Amongst these methods; precipitation, ion exchange and adsorption are the most common. 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 [11]. The application of bio-sorption in environmental treatment has become a significant research area in the past 10 years. Bio-sorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. An adsorbent material derived from low-cost agricultural wastes was employed effectively for the removal and recovery of heavy metal ions from waste-water streams [12-19]. The major advantages of bio-sorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels, use of inexpensive biosorbent materials, high efficiency; minimization of chemical and biological sludge; regeneration of biosorbent; no additional nutrient requirement and possibility of metal recovery [20]. The cost effectiveness of bio-sorption technology would guarantee the strong penetration of the large market of heavy metal polluting industries. In the present, huge efforts have been made to the development of new adsorbents and to improve existing adsorbents. Many investigators have studied the feasibility of using low-cost agro-based waste materials [21, 22]. Many conventional techniques such as chemical precipitation, membrane filtration, electrolysis, ion exchange and carbon adsorption are executed for the removal of heavy metals but at low concentrations. These techniques fail in certain cases, also they are not cost-effective. For this reason, low-cost adsorbents have been expounded for the removal of heavy metals from aqueous solutions.

The paper we present with experimental results on low cost and easily available *albizia procera legumes* as a adsorbent for the removal of heavy metals, Fe(II) and Mn(II) from wastewater. For our exclusive knowledge, this is the first time we are reporting *albizia procera legumes* as adsorbent for the removal of Fe(II) and Mn(II) from wastewater, The results are quite encouraging and efficient removal is possible and is comparable with high cost activated charcoal.

EXPERIMENTAL SECTION

2.1. Preparation of metal ions aqueous solution

All the chemicals, ferrous ammonium sulfate, o-phenonthroline, hydroxyl amine hydrochloride, and potassium periodate used were of analytical grade purchased commercially and were used without further purification. The metal ion solutions of Fe (II) and Mn (II) were prepared from ferrous ammonium sulfate and potassium permanganate respectively in double distilled water. The glass wares used were leached with conc. HNO_3 and dried in an oven at 50 ^{0}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 *albizia procera* legumes were collected and dried at room temperature in the air, grinded with grinder and sieved through a 500 μm mesh. 2 g of the *albizia procera legumes* substrate were mixed with 5 ml of 0.25 N sulfuric acid and 20 ml of 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 ^{0}C for 24 hrs. The modified *albizia procera legumes* substrate was used for final adsorption experiments of the waste water treatment.

RESULT AND DISCUSSION

3.1. Effect of pH

The effect of pH on the adsorption of Fe(II) and Mn (II) ions on *albizia procera legumes* substrate has been studied in the pH range of 2.5 – 9.5 at room temperature and at fixed initial sorption concentration of 1.0×10^{-4} M shown in Fig. 1. 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[23]. Hence, pH 4.5 was selected for all studies.

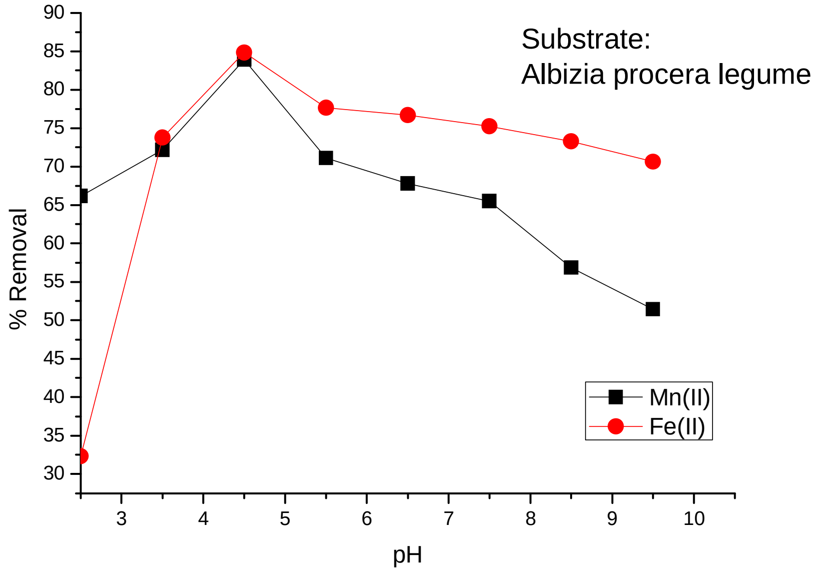

Fig. 1. Effect of pH on adsorption of Fe(II) and Mn(II)

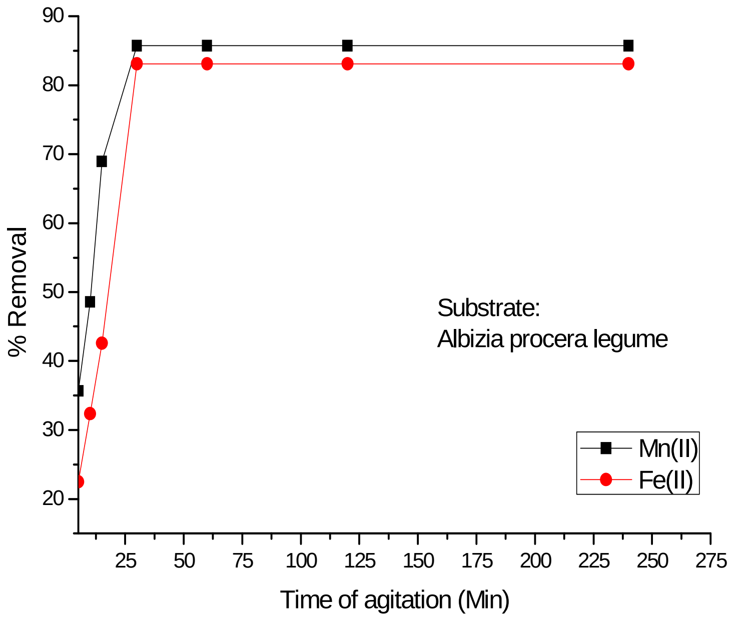

Fig. 2. Effect of agitation time on removal of Fe (II) and Mn(II)

3.2. Effect of time

The adsorption of metal ion by *albizia procera legumes* substrate for different interval of time was studied. The time of agitation was varied from 5 min to 24 hrs. It was observed in all cases that up to 30 minutes, adsorption increases at a fast rate and attains saturation (Fig. 2). Hence, 30 minutes time was chosen for all batch experiments.

3.3. Effect of temperature

The effect of temperature on adsorption of Fe (II) and Mn(II) ions by modified *albizia procera legumes* substrate has been investigated by conducting set of experiments at variable temperature ranging from 30 to 70 ^{0}C at a step of 10 ^{0}C. The initial concentration of precursor Fe(II) and Mn (II) ions in the solution was kept at 1.0 × 10^{-4} mol dm^{-3} at 4.5 pH. It was observed that with the increase in temperature the uptake of metal ions decreased from 83 to 23 % at the equilibrium as shown in Fig. 3. This fact is supported by Freundlich model of adsorption isotherm.

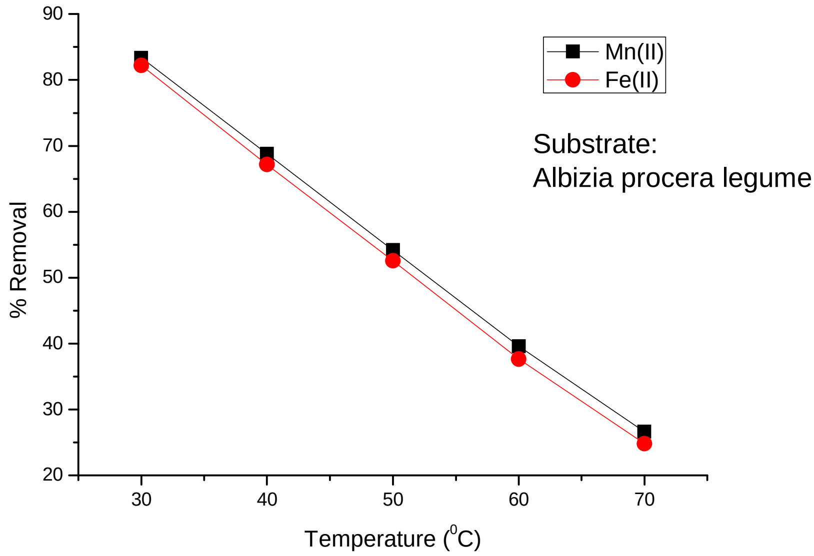

Fig. 3. Effect of temperature on removal of Fe (II) and Mn(II)

3.4. Effect of concentration

The adsorption of the metals ions by modified *albizia procera legumes* substrate were also carried out using various concentration of metal ions precursor solutions at room temperature and using predetermined agitation time of 30 min. The Freundlich (F) model was chosen to estimate the adsorption intensity of the *albizia procera legumes* substrate. The amount of Fe^{2+} and Mn^{2+} removed by modified *albizia procera legumes* substrate during the series of batch investigations were determined and presented in Fig. 4. From these experiments it was evident that extent of adsorption varies directly with concentration till saturation is reached. Beyond critical point the rate of adsorption reaches to the saturation level even after using high concentration of metal ion solution. Thus at higher concentration Freundlich adsorption isotherm is not applicable.

Freundlich equation was applied in the form of $\log \frac{x}{m} = \log k + \frac{1}{n} \log C$. Fig. 5 shows a plot of *log C* against *log x/m* which confirms a straight line which indicates Freundlich adsorption isotherm. The constants $\frac{1}{n}$ and *log K* was determined from the slope and intercept, respectively reported in Table 1.

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

Species	Metal ion	***1/n***	***K***
Albizia procera	Fe(II)	0.2496	30.4649
	Mn(II)	0.1364	35.2776
Activated charcoal [24]	Fe(II)	0.4597	2.3955
	Mn(II)	0.7466	1.1413

The fractional value of *1/n* indicates the surface of adsorbent is of heterogeneous type with an exponential distribution of energy sites. Since the value of 1/n is less than 1, it indicates favorable adsorption. A smaller value of 1/n indicates better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent [25] The higher numerical values of *K* confirm the significant affinity of Fe (II) and Mn(II) ions for *albizia procera* legume substrate.

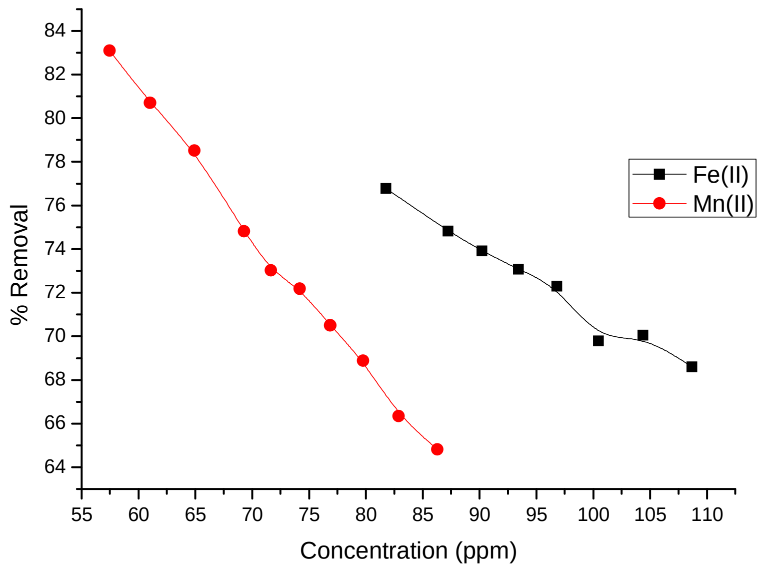

Fig. 4. Effect of concentration on removal of Fe (II) and Mn(II)

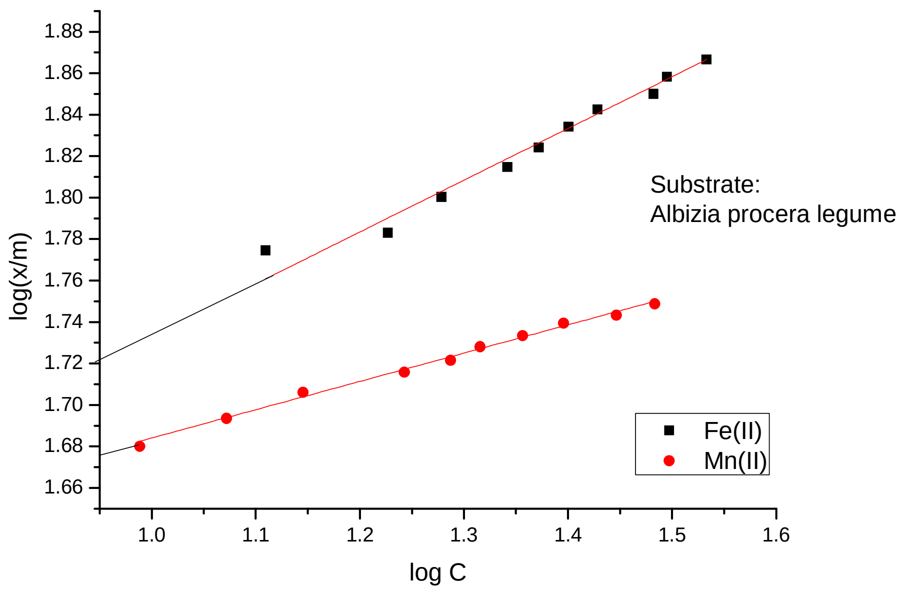

Fig. 5. Freundlich adsorption isotherm for Fe(II) and Mn(II)

3.5. Effect of adsorbent doses

The effect of adsorbent doses on removal of Fe(II) and Mn(II) are depicted in Fig. 6. It was observed that removal of Fe(II) and Mn(II) ions increases with increase in the adsorbent dose in all experimental runs. Fe(II) and Mn(II) concentration was fixed at 72.36 and 57.60 ppm respectively. An adsorbent dose was varied from 0.5 g/100ml to 4.5

g/100ml in aqueous solution at their optimum pH value. However, with the further increase in adsorbent doses, there was no appreciable change in Fe (II) and Mn(II) removal.

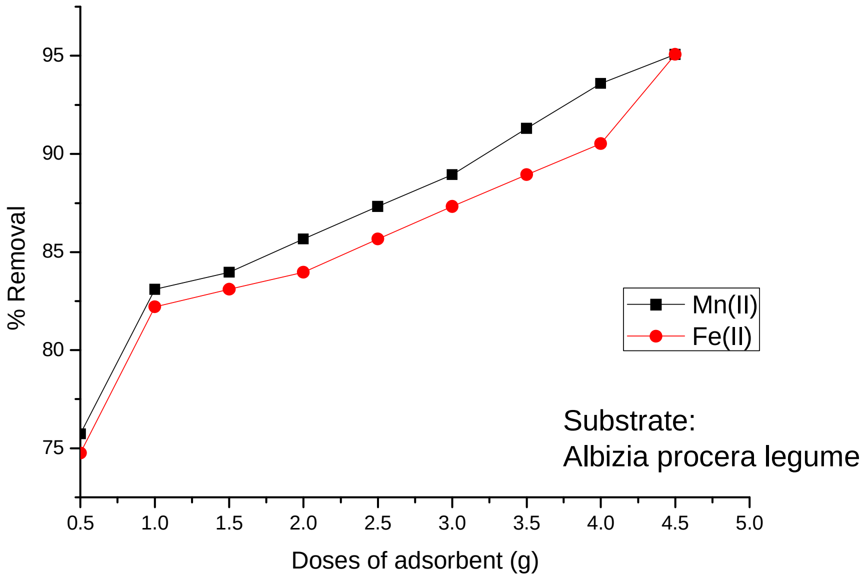

Fig. 6. Effect of adsorbent doses on removal of Fe (II) and Mn(II)

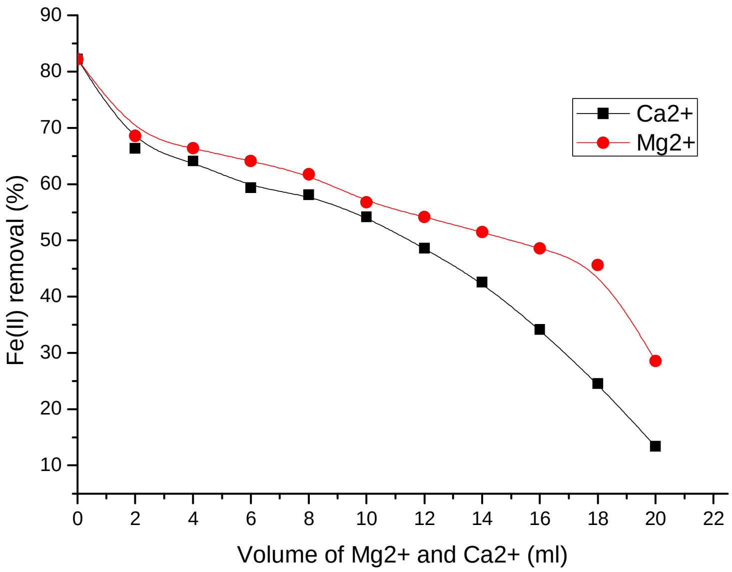

Fig. 7. Effect of co-metals Ca^{2+} and Mg^{2+} on Fe (II) adsorption by *albizia procera* legume

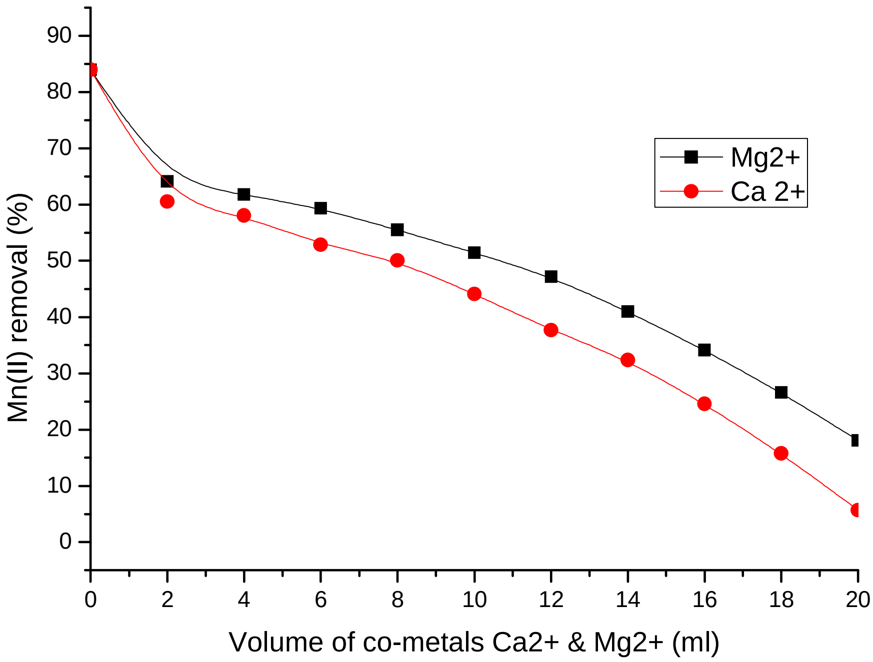

Fig. 8. Effect of co-metals Ca^{2+} and Mg^{2+} on Mn (II) adsorption by *albizia procera* legume

3.6 Effect of co-metal ions

The effect of co-metals Ca(II) and Mg(II) on adsorption of Fe (II) and Mn(II) ions by modified *albizia procera* legume seed shell substrate has been investigated by conducting set of experiments at variable concentration of Ca(II) and Mg(II) ranging from 2 mg/L to 40 mg/L at 30 ^{0}C. In first set of experiment variable concentration of Ca(II) ions mixed with fixed concentration of Fe(II), later on variable concentration of Mg(II) ions was homogenized with the same initial concentration of Fe(II) ions for adsorption study. Similar adsorption was studied for Mn(II) ion.The initial concentration of precursor Fe(II) and Mn (II) ions in the solution was kept at 1.0×10^{-4} mol dm^{-3} at 4.5 pH. It was observed that with the adsorption of Fe(II) and Mn(II) decreases with increasing in the concentration of co-metal ions (Fig. 7 & 8), This proves that *albizia procera* legume not only effectively removes heavy metal ions but co-metal ions as well.

CONCLUSION

The present investigations clearly shows that *albizia procera* legume substrate used here have considerable capacity to bind toxic metal ions. Formaldehyde modified *albizia procera* legume substrate shows highest removal for Fe(II) and Mn(II) at pH 4.5 and at agitation time of 30 minute. Numarical value of Freundlich isotherm parameter for *albizia procera* legume substrate and activated charcoal indicated that *albizia procera* legume substrate has more binding capacity compare to activated charcoal. The substrate materials are not only cheap, inexpensive, and easily available but 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. Application of this adsorbent to wastewater treatment is expected to be economical and efficient.

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