

Comparative Study of Iron (III) Removal Using Charred Sugarcane Bagasse and Precipitating Agent Calcium Hydroxide

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Abstract

Comparative study of Fe(III) removal using charred sugarcane bagasse and precipitating reagent calcium hydroxide Ca(OH)_2 is presented. The effect of pH, initial metal ion concentration and contact time on the removal of iron were investigated. The optimum pH for the charred sugarcane bagasse (CSB) and the precipitant calcium hydroxide was found to be 2.5 and 3, respectively. The maximum adsorption capacity for the removal of Fe(III) was found to be 30mg/g and 20mg/g using CSB and the precipitating capacity of Ca(OH)_2 , respectively. The equilibrium time has been achieved in 50 minutes and follow pseudo second order kinetics. The experimental data were well fitted with Langmuir adsorption isotherm model.

Keywords: *Bio adsorption, Fe(III), calcium hydroxide, charred sugarcane bagasse, isotherm*

Introduction

Environment pollution by toxic metals remains a serious problem that has been focus of attention all over the world¹. Contamination of water, soil, air with hazardous and toxic chemicals plays significant problems for human health and the environment. Metals are toxic pollutants that are not biodegradable, undergo transformation, and have great environmental, public health, and economic impacts². The different forms of elements presence in the nature create a great problem. Some of the elements such as iron³, arsenic⁴, manganese⁵, and chromium⁶ are mainly present in natural water as two oxidation states. For instance, Cr(VI), As(III), and As(V) are known carcinogens, while Fe(II), Fe(III), Mn(II), Mn(VII) and Cr(III) are essential micronutrients for organisms and plants. However, they become toxic at higher levels.

Iron is the fourth most abundant element present in a variety of rock and soil minerals both as Fe(II) and Fe(III). Fe(II) is required for proper transport and storage of oxygen by means of hemoglobin and myoglobin while its oxidized forms, methemoglobin and metmyoglobin, which contain Fe(III), will not bind oxygen⁷. Iron plays great role in biological functioning such as in photosynthesis and is the limiting growth nutrient for phytoplankton in some part of the ocean⁸. Both Fe(II) and Fe(III) are important in the biosphere, serving as an active centre of a wide range of proteins such as oxidases and reductases. Water effluents from steel tempering, coal coking and mining industries for examples, contain significant quantities of iron, nickel, copper and zinc⁹⁻¹¹. The application of low-cost adsorbents obtained from agricultural byproduct widely used in the recent research as a replacement for costly conventional

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methods of removal heavy metal ions from waste water¹²⁻¹⁵. Due to the advantages of economic feasibility and environmental friendly behavior, adsorption is regarded as the best technique for removing heavy metal ions at trace levels¹⁶⁻¹⁹.

The objective of this study is to develop low-cost adsorbent from sugarcane bagasse modified by chemical treatments for the effective removal of Fe(III) ions from contaminated water. The FTIR characterization indicates that the chemically modified sugarcane has the functional groups like phenols, carboxylic acids, lactones, hydroxides etc. on the surface of adsorbent to change and increase the surface area. The adsorption capacity was greatly influenced by surface group changes.

Experimental

Preparation of Adsorbent

Locally collected sugarcane bagasse was dried and grounded using mechanical grinder which is known as raw sugarcane bagasse. Then the raw sugarcane bagasse was treated with concentrated H₂SO₄ in 1:2 (w/v). It was washed till neutrality finally dried at 70 °C and stored after keeping in desiccator and the sample is called charred sugarcane bagasse(CSB).

Chemicals

Chemicals and reagents used in the experiment were analytical grade. Exact 1000 ppm stock solution was prepared by dissolving 2.158 gram of salt NH₄Fe(SO₄)₂.12H₂O in 250 mL volumetric flask. Likewise, the solution of 1 M HNO₃, 0.1 M NaOH, 1 M HCl, 0.1 M Ca(OH)₂, KSCN solution were prepared by adding calculated mass of the requirement.

Adsorption Experiments

The pH of the working solution of Fe(III) was adjusted by adding either small amount of HCl or NaOH after adding 0.1 M of HEPES as a buffering agent. The flasks were shaken at a speed of 180 rpm in the mechanical shaker. The initial and equilibrium concentration of the metal ions were measured using spectrophotometer. The removal efficiency, A% of the metal ion was calculated from eq. (1)

$$A \% = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

The sorption capacity of metal ions is the concentration of the metal ions on the adsorbent and can be calculated based on the mass balance principle using equation (2).

$$q = \frac{C_i - C_e}{C_e} \times \frac{L}{1000} \quad (2)$$

In above equations, *q* represents the amount of metal uptake per unit mass of the adsorbent (mg g⁻¹), *L* is the volume of the test solution (mL), *W* is the dry mass of the adsorbent (g), *C_i* and *C_e* the initial and final concentrations (mg dm⁻³), respectively.

Results and Discussion

FTIR Analysis

The chemical structure of the adsorbent is of vital importance in understanding the adsorption process. FTIR technique is an important tool to identify the characteristic functional groups, which are involved in adsorption of metal ions. FTIR analysis was performed in this study to investigate the surface functional

groups of charred sugarcane bagasse before and after the adsorption of Fe (III) metal ions. The peaks range shows the functional group present in the test sample.

In this transformation, many characteristics bands are shifted at the maximum peaks and absorbance is changed. The peak observed at 3402.43 cm^{-1} is due to stretching vibration of the O-H groups. Although there is possibility of overlapping between the N-H and the O-H stretching vibrations, the strong broad band at the wave number region number of 3248.13 to 3541.31 cm^{-1} is characteristic of the NH stretching vibration the range 1141.86 to 1674.21 cm^{-1} are closely related to the NH binding, C-N stretching, and N-H rocking bands. The range 326356 to 3363.86 cm^{-1} may be due to overlapping of O-H and N-H stretching, which is consistent with the peaks at 1644 and 1047 cm^{-1} assigned to alcoholic C-O and C-N stretching vibrations.

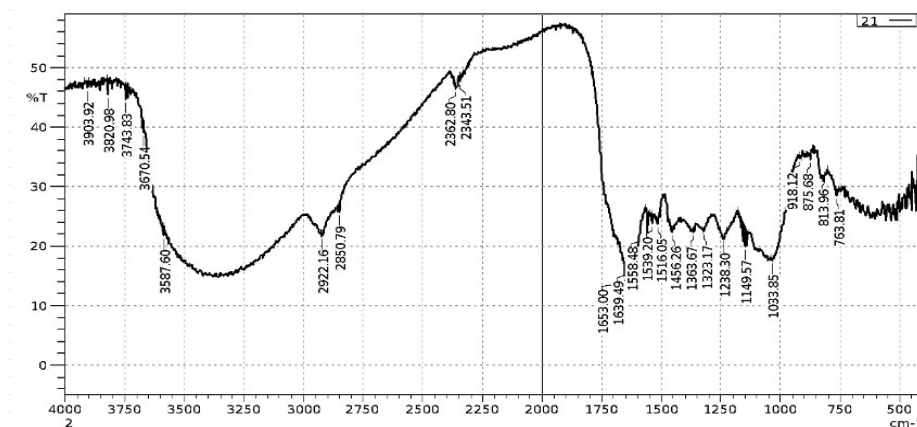


Figure 1: FTIR of charred sugarcane bagasse

Effect of pH

The pH of the solution has significant impact on the uptake of Fe (III) ions, since it determines the surface charge of the adsorbent and the degree of ionization of the adsorbate. Fig: 2 show the effect of pH on adsorption of Fe (III) ions onto CSB at initial concentration of 25 ppm at room temperature. The experiment was carried out to find the effect of pH for the adsorption of Fe (III), taking the pH range of 0.5 to 4.5. The percentage removal of Fe (III) ions by charred sugarcane bagasse increased from 8.57% to 84.61% within the pH range and maximum adsorption occurs at pH 2.5.

It was found that little sorption of Fe(III) at lower pH could be ascribed due to the hydrogen ions competing with metal ions for sorption sites. At higher H^+ concentration, the adsorbent surface becomes positively charged, thus reducing the attraction between adsorbent and metal ions. As pH increases surface charge of adsorbent become negative and thus facilitating greater metal uptake due to cations exchange mechanism. Maximum adsorption of Fe(III) at higher value of pH is due to the electrostatic attraction between negative and positive surface function of the adsorbent. The optimum pH was investigated as 2.5 for Fe(III) removal onto CSB.

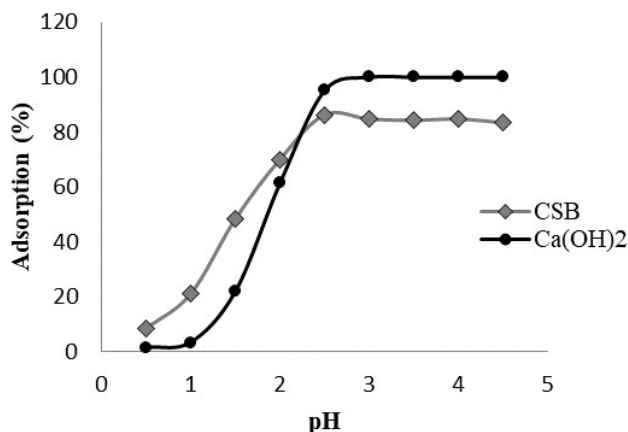


Figure 2: Effect of pH for Adsorption of Fe (III) onto CSB and Ca(OH)₂

Effect of pH on Precipitant Ca(OH)₂

Fe (III) ions are weakly acidic and hydrolyze in solution producing a less soluble complex. We know that the solubility of the salt is a function of the pH and it increases as the pH decreases. The maximum solubility is found under acidic conditions when the concentrations of the hydrolyze species became negligible. Removal of the heavy metals ions as hydroxide formation is the most common heavy metal precipitation method. The addition of calcium hydroxide is used to raise the pH for removal of Fe(III) by precipitating and settling process. Removal of Fe(III) increase with the increase in pH and the optimum removal was reached at pH 3.

Adsorption Isotherms

The surface coverage of adsorbate is a function of adsorption of adsorbents and adsorption isotherm describes the equilibrium of the adsorption of materials at a surface at constant temperature. Here isotherm studies were performed using various concentration of the metal ion ranging from 25 to 1000 mg/L. For batch adsorption experiment, 25 mg of adsorbent was equilibrated with 25 mL of synthetic Fe(III) solution in conical flask for 24 hours to attain equilibrium. All the adsorption data were tested with the Langmuir and Freundlich isotherm model using linear form as represented by equations (3) and (4).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m b} + \frac{C_e}{q_m} \tag{3}$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{4}$$

Where C_e (mg/L) is the equilibrium concentration of the metal ion in aqueous solution and q_e is the amount Fe(III) adsorbed at equilibrium (mg/g). The Langmuir constant q_m (mg/g) represents the monolayer adsorption capacity, b (L/mg) the binding constant, n (dimensionless) a constant of adsorption intensity and K_f (L/mg) is Freundlich constant characterizing the adsorption capacity. To examine the relationship between the metal sorption capacity (q_e) and the metal ions at equilibrium (C_e), the sorption equilibrium data for Fe(III) was compared to Langmuir and Freundlich isotherm models, where the

Langmuir and Freundlich constants and its correlation coefficients evaluated from the isotherm for Fe^{+++} are given in table 1. The sorption characteristics of the metal ions on the charred sugarcane bagasse followed more closely the Langmuir isotherm model than the Freundlich isotherm model. The high value of Langmuir correlation coefficient confirmed that the Langmuir isotherm is the best fitted than Freundlich isotherm onto CSB. The maximum adsorption capacity based on the experimental result is shown in Figure 3 for both charred sugarcane bagasse and calcium hydroxide respectively.

On the other hand, the theoretical maximum monolayer capacity (q_m) of the metal ion based on Langmuir adsorption equation were determined to be 0.454 mg/g and 0.769 mg/g from figure 4 for charred sugarcane bagasse and calcium hydroxide. This result is in closed agreement against each other suggesting that iron metal can be quantitatively sequestered on to charred sugarcane bagasse and calcium hydroxide. The essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant, separation factor or equilibrium parameters R_L , which is defined as by equation (5).

$$R_L = \frac{1}{1+bC_e} \quad (5)$$

The R_L value indicates the shape of the isotherm as $R_L > 1$: unfavorable, $R_L = 1$: linear, $0 < R_L < 1$: favorable, $R_L = 0$: irreversible adsorption. The value of R_L found by calculating the data of b, taking initial that concentration of sorbate and concluded that Langmuir adsorption isotherm is favorable.

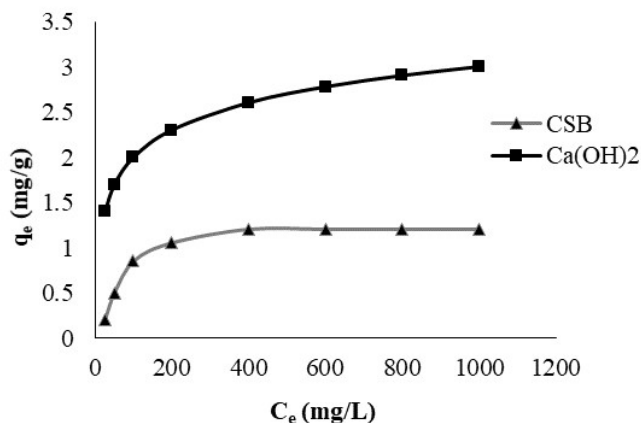


Figure 3: Adsorption isotherm for adsorption of Fe (III) onto CSB and $Ca(OH)_2$

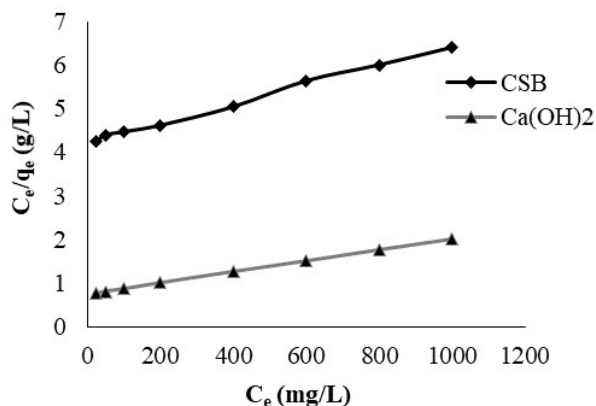


Figure 4: Langmuir Plot for Adsorption of Fe(III) ions onto CSB and Ca(OH)₂

Table 1: Langmuir Parameters for Adsorption of Fe(III)

SN	Adsorbent	Metal	Langmuir isotherm		
			q _m (mg/g)	b (L/mg)	R ²
1	CSB	Fe(III)	20	1.0001	0.995
2	Ca(OH) ₂	Fe(III)	18	0.0017	0.999

Adsorption Kinetics

The effect of contact time on the removal of Fe (III) ions from aqueous solution by modified adsorbent was studied. Adsorption kinetics of metal ions were obtained within contact times between 5 to 360 minutes for the removal of Fe (III) using CSB and precipitating reagent Ca (OH)₂. Adsorption increases with time and finally equilibrium point is attained which are shown in figure 6 and 7. Kinetic studies for the adsorption of Fe (III) was studied using different kinetic models, pseudo first order (Lagergrens 1898) and pseudo second order (Ho, 1995). The pseudo second order kinetic equation²⁰ is well fitted used as the following form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where q_t (mg/g) is the amount of adsorption at time t (min), K_2 (g mg⁻¹ min⁻¹) is the rate constant of the pseudo second order kinetics adsorption. The values of K_2 and q_e can be obtained from intercept and slope of the plot and the experimental data can be explained by the pseudo second order kinetic model, with the correlation coefficient R^2 being almost unity (0.99) for the Fe (III) ions. The experimental value of K_2 was found from the plot that is based on kinetic model as shown in Figure 8.

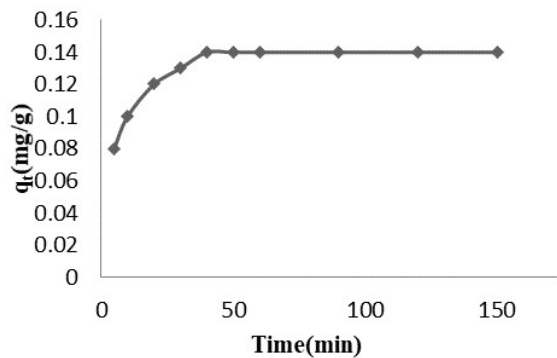


Figure 6: Adsorption Kinetics for Adsorption of Fe(III) onto CSB

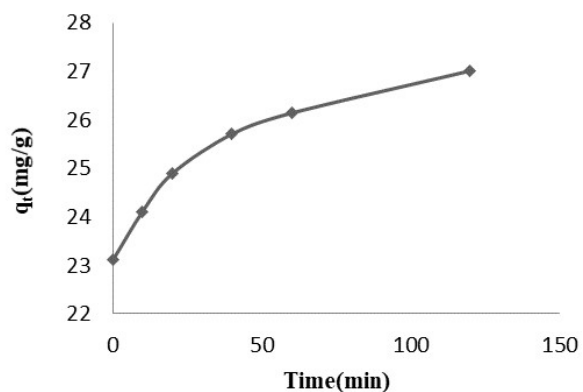


Figure 7: Kinetics for Separation of Fe(III) using $\text{Ca}(\text{OH})_2$

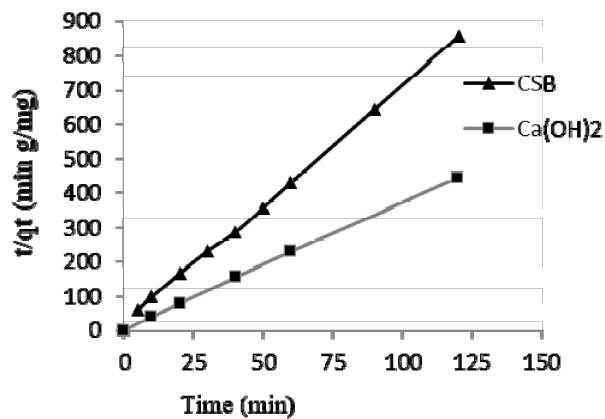


Figure 8: Pseudo Second Order Kinetics for Adsorption of Fe(III) onto CSB and $\text{Ca}(\text{OH})_2$

Pseudo second order plot of (t/qt) versus t gave perfect straight line for the removal of Fe(III) onto CSB and $\text{Ca}(\text{OH})_2$ and it proves that the adsorption reaction follows the pseudo second order kinetics model. The correlation coefficient is 0.99 conform that the adsorption reaction follows pseudo second order model. The value of correlation coefficient and the rate constant for metals and adsorbents are shown in the table. On the increasing the time the precipitating rate was increases with the initial dose 1000 mg/L. the 100% removal was found at 120 minutes and nearly to 100 at 60 minutes.

Conclusions

The studies have shown that the charred sugarcane bagasse and inorganic base calcium hydroxide can be used for the removal of Fe(III) from the aqueous solution through adsorption and precipitation. The efficiency of the adsorbent can be increased by chemical modification. The optimum pH for the adsorption of Fe(III) onto CSB is to be found 2.5 and precipitation is completed at pH 3 using precipitant $\text{Ca}(\text{OH})_2$. The maximum adsorption q_m was found 20 mg/g onto CSB and q_m 18 mg/g was found for $\text{Ca}(\text{OH})_2$ and both follow the pseudo second order kinetics. Langmuir adsorption isotherm model was found to be more fitted than Freundlich model. The equilibrium time for the adsorption was found to be 40 minutes for the adsorption of Fe(III) ions onto CSB and for complete precipitation required 120 minutes using $\text{Ca}(\text{OH})_2$.

Based on this study, it is concluded that modified sugarcane bagasse can be used as low-cost adsorbent for the removal of Fe(III) and it is superior to the inorganic precipitating agent calcium hydroxide.

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