A Comparative Study of Fe (II) Ion Adsorption onto Chemically Activated Banana Peel and Sawdust Bio-adsorbent

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Abstract
The adsorption capacity of ferrous ions onto bio-sorbents prepared from two different types of bio-waste of banana peel (CABP) and sawdust (CASD) treated with sulfuric acid was studied using Langmuir and Freundlich isotherms. Result shows that the optimum pH value for about 99 % Fe (II) adsorption onto the CABP and CASD was found to be 3 and 4, respectively, after 5 hours or more contact time period. Both the Langmuir and Freundlich adsorption models are fitted to remove the Fe (II) ions from aqueous solution by the bio-adsorbent of CABP and CASD. The maximum adsorption capacities for the CABP and CASD were found to be about 34 and 116 mg/g, respectively. These results showed that the CASD seems to be more effective bio-adsorbent than the CABP to remove the Fe (II) ions from drinking or/and wastewaters.

Key words: Bio-adsorbent; sawdust; banana waste; adsorption; Fe(II); sulfuric acid

Introduction
Iron is a dietary requirement for most organisms and plays an important role in many processes and is routinely detected in drinking water as well as municipal waste effluent, particularly where iron and steels are manufactured (Karthikeyan et al., 2005). It was reported that the uptake of iron ranges from about 10 to 50 mg/day and the US environmental protection agency (US EPA) has been established a secondary drinking water regulation of 0.3 ppm for iron in drinking water and more than this amount might be caused unfavorable effects on human beings (WHO, 1996). In the drinking water, iron concentration about 2 ppm or fewer amounts does not pose health hazard and hence 1–3 ppm iron amounts can be assumed to be acceptable level for drinking water. It was reported that the excessive accumulation of iron in human body causes a disorder diseases of hemato-chromatosis, cirrhosis and diabetes mellitus (Lauffer, 1992). Water pollution caused by the excess amounts of iron is a great problem in Nepal.

The use various methods like reduction, precipitation, filtration, ion-exchange, adsorption and so on are recently proved to be the most common ones to remove different contaminated metals from water sources (Aziz et al., 2004; Lastra et al., 2004; Nurchi & Villaescusa, 2008; Zaid & Mohammed, 2008). It was reported that the iron (II) was removed by using limestone filters (Aziz et al., 2004), nanofiltration and ultrafiltration (Lastra et al., 2004). Most of these methods are comparatively expensive and inefficient to remove high percentage of the contaminated metals from aqueous system. In recent years, the adsorption
process is being an efficient, cost-effective and simple to operate among all other methods (Bhattarai, 1994; Blazquez et al., 2005; Zaid & Mohammed, 2008; Duwal, 2013; Duwal et al., 2016; Moutou et al., 2018). It was reported that metals are attached onto the surface of adsorbent in the adsorption process (Sun & Shi, 1998; Basso et al., 2002; Deng et al., 2003a, 2003b; Mahvi et al., 2005; WanNgah & Hanafiah, 2008; Chen et al., 2010; Phan et al., 2010; Markandeya et al., 2015). In this context, it is very suitable to develop low cost and efficient bio-adsorbent, especially from wastage bio-materials like animal, vegetable and forest by-products for removal of heavy metals from waters (Volesky & Holan, 1995; Das, 2008). It was reported that rice husk (Kumar & Bandyopadhyay, 2006), used tea leaves (Islam et al., 2009), wheat straw (Chen et al., 2010), banana peel (Yousaf & Sajjad, 2015), chitin and chitosan (Vijayarhavan et al., 2006) as a good adsorbent, because these are easily available and less polluting substances. In this context, it is necessary to develop the more reliable adsorbent using different types of bio-adsorbents those are locally available in cheap.

The main objectives of this study are to prepare two different types of low cost bio-adsorbents of the chemically activated banana peel (CABP) and sawdust (CASD) those are prepared by treating the raw banana peel and sawdust with concentrated sulfuric acid solution and to carry out comparative studies of their removal capacity of Fe (II) ions from wastewaters using batch adsorption methods.

**Materials and Methods**

**Preparation of bio-adsorbent**

Both the banana peel and sawdust were firstly collected and sun-dried for few days followed by preliminary processes such as crushing, grinding and sieving through 300 micron sieve mesh. The preliminary prepared banana peel and sawdust powder were used as precursors for the preparation of the chemically activated banana peel and sawdust sample specimens. About 500 grams of the preliminary prepared banana peel and sawdust powder were treated with 500 mL of 2 M sulfuric acid solution for 24 hours and then it was washed several times until completely removed the free acid using distilled water. The washed materials of each banana peel and sawdust were completely dried which is called as CABP and CASD bio-adsorbent, respectively and they were separately stored in air tight sample bottles.

** Determination of Fe (II) ions in wastewater:**

The determination of iron (II) ions in wastewater was carried out using spectrophotometric method which involved the complexation of Fe^{2+} with 1, 10-phenanthroline to produce an intensely orange-red complex of ferrous tris-1, 10-phenanthroline as discussed elsewhere (Adhikari, 2013). The required concentration of the working iron (II) solution which was collected directly from the disposal wastewaters.

**Batch adsorption study:**

The absorption of the orange-red complex of ferrous tris-1, 10-phenanthroline was measured at 510 nm. The pH value ranges from 1 to 6 of the ferrous tris-1, 10-phenanthroline complex was adjusted using sodium hydroxide and hydrochloric acid solutions and the solution of the pH onto the adsorption was studied. The amount of 100 mg of each bio-adsorbent of CABP and CASD was mixed in separate conical flask with 100 mL of the ferrous tris-1, 10-phenanthroline complex at their maximum pH values (i.e., pH 3 for CABP and pH 4 for CASD). The conical flask was stirred for 3-5 hours and then it was left for 24 hours at 25 ± 1°C. The amount of the remaining iron (II) complex concentration was spectrophotometrically estimated using equation (1). Then the equation (2) was used to estimate the maximum adsorption at equilibrium (Q_e), where C_0 = C_e and Q_e = Q_0.

\[
Q_e = \frac{(C_0 - C_e) \times V}{m}
\]  

(1)

where, Q_e is the amount of Fe (II) adsorbed per unit mass of both the bio-adsorbents of CABP and CASD (mg/g) at t time, C_0 and C_e are the iron (II) concentrations (mg/L) in liquid phase initially and at time t, respectively. V (litre) is the volume of the iron (II) solution and m in gram is the mass of the dry bio-adsorbents of both CABP and CASD.

The adsorption percentage of iron (II) (R %) from the wastewater sample was estimated using following the equation (3).

\[
A \% = \frac{C_0 - C_e}{C_0} \times 100
\]  

(3)

Several experiments were carried out using 2 mg/L Fe (II) solution with 10 mg of both the bio-adsorbents of CABP and CASD separately in 100 mL of Fe (II) solution at pH of 4 for different interval of time from 10 to 1440 minutes to study the contact time effect on the removal of Fe (II) from the sampling solution. Then, both the adsorbents of CASD-iron (II) complex suspension and the CASD-iron (II) complex suspension was decanted and was separated using centrifugal machine and was analyzed for equilibrium Fe (II) concentration. The obtained data were used to evaluate the maximum adsorption capacity of Fe (II) ions from wastewater onto the bio-adsorbent of the CABP and CASD using Langmuir (equation 5) and Freundlich (equation 7) adsorption models.

\[
Q_e = \frac{Q_{max} bC_e}{(1 + bC_e)}
\]  

(4)

\[
\frac{C_e}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{Q_{max} b}
\]  

(5)
\[ Q_e = K_F C_e^{1/n} \]  
\[ \log Q_e = \log K_F + \frac{1}{n} \log C_e \]

Where, \( Q_e \) (mg/g) is the adsorption amount of Fe\(^{2+} \) ions; \( C_e \) (mg/L) is the equilibrium concentration of the Fe\(^{2+} \) ions after the adsorption process, \( Q_{\text{max}} \) (mg/g) is the maximum removal capacity, \( b \) (L/mg) is the adsorption energy, \( K_F \) and \( 1/n \) are Freundlich constants.

**Results and Discussion**

**Effect of initial pH of Fe (II) solution**

Several batch adsorption experiments were performed at different initial pH values ranging from 1.0 to 6.0 at room temperature in order to evaluate the effect of initial pH to study the adsorption of Fe (II) by both the bio-adsorbents of CABP and CASD. Fig. 1 shows the changes of the percentage removal of the Fe (II) by both the CABP and CASD bio-adsorbents as a function of initial pH of Fe (II) solution at room temperature.

![Fig. 1: Initial pH effect on the removal of Fe (II) by both the CABP and CASD](image)

It shows that the % removal of Fe (II) from wastewaters was increased with increasing the initial pH of Fe (II) solution until it becomes maximum at pH 3 for CABP and at pH 4 for CASD. Thus, the optimal pH for the removal of Fe (II) from wastewaters by the CABP is considered to be pH 3 and the CASD is considered to be pH 4 and these pH values were adjusted for further adsorption study. These results revealed that the bio-adsorbent of CASD can be used in less acidic aqueous solution than used by the CABP bio-adsorbent to remove the contaminated ferrous ions from water and wastewaters.

**Effect of Contact Time**

The contact time effect was studied by taking 40 mL of the adsorbate solution containing 2 mg/L Fe (II) in a 100 mL Erlenmeyer flask with addition of 40 mg of both the bio-adsorbents of CABP and CASD at pH 3 and pH 4, respectively. All the sets of the solutions were stirred for different time intervals ranging from 10 to 1440 minutes. Fig. 2 shows the removal efficiency of Fe (II) by both the CABP and the CASD bio-adsorbents which is found to be increased significantly with contact time for about 3 to 5 hours and it became almost constant with long contact time up to 25 hour or more. The iron (II) removal capacity of both the CABP as well as the CASD was found around 99 % after equilibrating the Fe (II)-bio-adsorbent suspension for about 3 to 25 hours. Therefore, for the batch adsorption study of the Fe (II) from wastewater sample by both the CABP and the CASD bio-adsorbents, the Fe (II)-CASD suspension was stirred for 5 hours in all adsorption studies and then the suspension was kept contact for about 24 h in this study. These results revealed that 3 to 5 hours stirring with keepin about one day of the the Fe(II)-bio-adsorbent suspension is sufficient to get an accurate results from the batch adsorption study.

![Fig. 2: Effect of contact time on removal of Fe (II) from wastewater solution by both the bio-adsorbents of CABP and CASD.](image)

**Batch Adsorption Study**

Two adsorption models of Langmuir and Freundlich were applied to study the adsorption phenomena of the contaminated Fe (II) ions from wastewater sample by both the bio-adsorbents of CABP and CASD. Fig. 3 depicts the adsorption isotherm curves for the removable of the Fe (II) by both the bio-adsorbents at above mentioned conditions of maximum pH and contact time. The result raveled that the maximum adsorption amounts of Fe (II) ions from wastewater is found to be about 31 mg/g and 106 mg/g by the bio-adsorbents of CABP and CASD, respectively. The maximum removal capacity of both the CABP as well as the CASD was found around 99 % after equilibrating the Fe (II)-bio-adsorbent suspension for about 3 to 25 hours. Therefore, for the batch adsorption study of the Fe (II) from wastewater sample by both the CABP and the CASD bio-adsorbents, the Fe (II)-CASD suspension was stirred for 5 hours in all adsorption studies and then the suspension was kept contact for about 24 h in this study. These results revealed that 3 to 5 hours stirring with keepin about one day of the the Fe(II)-bio-adsorbent suspension is sufficient to get an accurate results from the batch adsorption study.
Fig. 3: Adsorption isotherm for the removal of Fe (II) from wastewater sample by both the bio-adsorbents of CABP and CASD at room temperature.

Fig. 4: Langmuir plots for the removal of Fe (II) from wastewater by both the bio-adsorbents of CABP and CASD at room temperature.

Fig. 5: Freundlich plots for the removal of Fe (II) from wastewater sample by both the bio-adsorbents of CABP and CASD at room temperature.

Fig. 4 and 5 depict the removal of Fe (II) by both the bio-adsorbents follow both the Langmuir and Freundlich adsorption isotherms. In case of the adsorption of Fe (II) ions by the bio-adsorbent of CASD, almost unit value of the R² (i.e., 0.9996) confirmed the Langmuir adsorption isotherm model (as shown in Fig. 4) is the best fitted than that of the Freundlich adsorption isotherm model, because the R² value for the linearized Freundlich plot is found to be 0.93328 as shown in Fig. 5. On the other hand, the R² value of 0.97838 for CABP (as shown in Fig. 5) is slightly higher than that of the R² value of 0.94482 for CASD confirmed the Freundlich adsorption isotherm model is the best fitted than that of the Langmuir adsorption isotherm model in case of the adsorption of Fe (II) ions by the bio-adsorbent of CABP. The maximum adsorption capacity (Qmax) for the Fe (II) removable from the wastewater by the CABP and CASD bio-adsorbents was found to be 33.8 mg/g and 116.3 mg/g, respectively, using Langmuir plot (Fig. 4) at room temperature in above mentioned other batch adsorption conditions. On the other hand, the adsorption energies (i.e., b) for Fe (II) ions removal by CABP and CASD bio-adsorbents were found as 0.03 L/mg and 0.2815 L/mg, respectively. The Freundlich constant of 1/n, which is related to the adsorption intensity, was found to be less than 1 for both the bio-adsorbents which suggests the favorable adsorption behavior of Fe (II) ions onto both the CABP and CASD bio-adsorbents.

Conclusions

The batch adsorption experiments were performed at room temperature for a comparative study of the removal of Fe (II) from wastewaters using both the CABP and CASD as a bio-adsorbents. Following conclusions are drawn from the above results and discussion:

1. It is found that the 99 % adsorption of Fe (II) from wastewater solution onto the bio-adsorbents of CABP and CASD is dependent on the pH and the maximum uptake of Fe (II) was found in pH 3 for CABP and pH 4 for CASD.

2. Equilibrium uptake of Fe (II) was attained at about five hours or more stirring time in both cases of the uses of CABP and CASD bio-adsorbents.

3. The maximum adsorption capacities of the CABP and CASD bio-adsorbents for Fe (II) adsorption from wastewater were found to be about 34 mg/g and 116 mg/g, respectively, using adsorption isotherm equation.

4. The adsorption of Fe (II) onto both the CABP and CASD obeys both Langmuir and Freundlich isotherm models.

5. The CASD can be used as a good bio-adsorbent to remove the Fe (II) ions from wastewater or drinking water than CABP bio-adsorbent.
References

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