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Investigation on the Removal of Fe (II) from Wastewater onto Chemically Activated Sawdust

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Abstract: *The adsorption of the bio-sorbent of the chemically activated sawdust (CASD) with concentrated sulfuric acid 1:1 (w/v) was carried out for studying the removable kinetics of Fe (II) ions from industrial wastewater and the applicability of Langmuir and Freundlich isotherms was tested. The adsorption kinetics of the Fe (II) ions onto the CASD was studied using pseudo-first order, pseudo-second order and second order kinetics equations. Result shows that the optimum pH for Fe (II) adsorption onto the CASD was found to be 4 and the adsorption efficiency was found to be about 99 % and the maximum adsorption capacity was found to be 116 mg/g. These results showed that the CASD may be an attractive alternative for treatment of the industrial wastewater contaminated by Fe (II) ions.*

Keywords: *Activated sawdust, isotherms, pH, Fe (II), adsorption kinetics, pseudo-second order, sulfuric acid.*

1. Introduction

It was reported that the use various techniques for removing metals from waste waters [1]. Reduction, precipitation, filtration, ion-exchange, adsorption and so on are the most common techniques for removing the metal from the metal contaminated aqueous environments. Different techniques have been used to remove iron ions form water and wastewater [2-4]. It was reported that the iron (II) was removed by using limestone filters [2], nanofiltration and ultrafiltration [3]. These operations are affected by different parameters such as temperature, pH, and oxygen flow. Moreover, most of these technologies are comparatively expensive and inefficient in reducing metal ion levels in effluent to concentrations that are required by governmental legislation. Among all methods, the adsorption is a cost-effective technique and simple to operate [4]. In this context, it is very suitable to develop low cost and efficient adsorbent, especially from wastage bio-materials like animal, vegetable and forest by-products for removal of heavy metals from wastewaters [5, 6]. It was reported that rice husk [7], olive stone [8], clay minerals [9-12], used tea leaves [13], wheat straw [14], banana peel [15, 16], chitin and chitosan [17] as a good adsorbent, because these are easily available and less polluting substances. It was reported that metals are attached onto the surface of adsorbent in the adsorption process [18-26].

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 [27]. 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 [28]. 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 [29]. Water pollution caused by the excess amounts of iron is a great problem in Nepal. 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 aims of this study are to prepare a low cost bio-adsorbent from the CASD, to increase the adsorption capacity of Fe (II) from wastewater, to study the effect of initial pH, initial concentration of the bioadsorbate and contact time, to study the kinetics of the removal of Fe (II) from wastewater and to investigate the maximum adsorption capacities of the CASD.

2. Materials and Methods

2.1. Preparation of CSD Bio-adsorbent

The sawdust collected from five different saw mills around Patan areas of Kathmandu valley was firstly mixed and then sun-dried it for few days followed by preliminary processes such as crushing, grinding and sieving through 300 micron sieve mesh. Thus, the preliminary prepared sawdust powder was used as a precursor for the preparation of the chemically activated sawdust sample specimen. About 500 grams of the preliminary prepared sawdust powder was 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 material was completely dried which is called as CASD bio-adsorbent and stored in air tight sample bottle.

2.2. Determination of Fe (II) Ions in Wastewater

The commonly used method for the spectrophotometric determination of iron (II) ions in sampled wastewater 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 in detail elsewhere [30]. The required concentration of the working iron (II) solution which was collected directly from the disposure wastewaters from Iron and steel Industry of Nepal.

2.3. Batch Adsorption Study

The absorption of light by the orange-red complex of ferrous tris-1, 10-phenanthroline was measured and 510 nm was found to be the λ_{max} of the iron (II) complex. 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 effect of the pH onto the adsorption was studied. The amount of 100 mg of CASD was mixed with 100 mL of the ferrous tris-1, 10-phenanthroline complex at the initial pH 4 and was equilibrated in a conical flask, as a maximum adsorption of the iron (II) complex was confirmed. The conical flask was stirred for 3 hours and then it was left for 24 hours at 25 ± 1°C. The amount of the remaining iron (II) complex concentration was estimated using spectrophotometer at 510 nm in this study using equation (1) and then the equation (2) was used to estimate the Q_e at equilibrium where $C_t = C_e$ and $Q_t = Q_e$. The details about the bath adsortption study was described elsewhere [15].

$$Q_t = \frac{(C_o - C_t) \times V}{m} \tag{1}$$

$$Q_e = \frac{(C_o - C_e) \times V}{m} \tag{2}$$

where, Q_t is the amount of Fe (II) adsorbed per unit mass of CASD (mg/g) at t time, C_o and C_t 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 CASD bio-adsorbent.

The percentage removal of iron (II) (R %) from the solution was estimated using following the equation (3).

$$R\ \% = \frac{C_o - C_t}{C_o} \times 100 \tag{3}$$

Several experiments were carried out using 2 mg/L Fe (II) solution with 10 mg of the CASD 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 the adsorbent 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 verify the three kinetic models of the pseudo-first order, pseudo-second order and second order. On the other hand, Langmuir (equation 5) and Freundlich (equation 7) adsorption models were applied to evaluate the maximum Fe (II) ions removable capacity of the adsorbent of CASD.

$$Q_e = \frac{Q_{max} b C_e}{(1 + bC_e)} \tag{4}$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max}.b} \tag{5}$$

$$Q_e = K_F C_e^{1/n} \tag{6}$$

$$\log Q_e = \log K_F + 1/n \log C_e \tag{7}$$

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_{max} (mg/g) is the maximum removal capacity, b (L/mg) is the adsorption energy, K_F and 1/n are Freundlich constants.

3. Results and Discussion

3.1. 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 in the removal of Fe (II) from wastewaters by the CASD bio-adsorbent. Figure 1 shows the changes of the percentage removal of the Fe (II) by the CASD as a function of initial pH of Fe (II) solution at room temperature. 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 3.5 to 4.0. Thus, the optimal pH for the removal of Fe (II) from wastewaters by the CASD is considered to be 4.0 and this pH value was adjusted for further adsorption study in this research work.

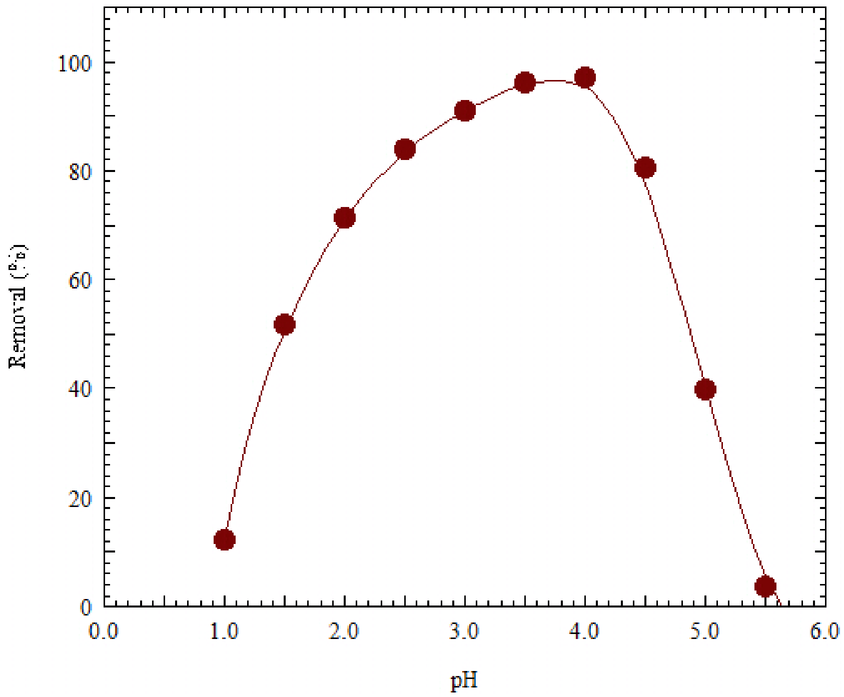

Figure1. *Effect of the initial pH on removal of Fe (II) from by the CASD*

3.2. Batch Adsorption Study

Two adsorption models of Langmuir and Freundlich were applied to study the removable of contaminated Fe (II) ions from wastewater sample by the bio-adsorbent CASD. Figure 2 depicts the adsorption isotherm curve for the removable of the Fe (II) by the CASD at above mentioned conditions. The result raveled that the maximum adsorption amounts of Fe (II) ions from wastewater is found to be about 106 mg/g of the bio-adsorbent of CASD from the adsorption isotherm data. The Langmuir constants (i.e., Q_{max} and b) and Freundlich constants (K_F and n) were calculated using the linearized Langmuir (equation 5) and Freundlich (equation 6) equations, respectively. Figures 3 and 4 depict the removable of Fe (II) by the CASD follows both the Langmuir and Freundlich models adsorption isotherms.

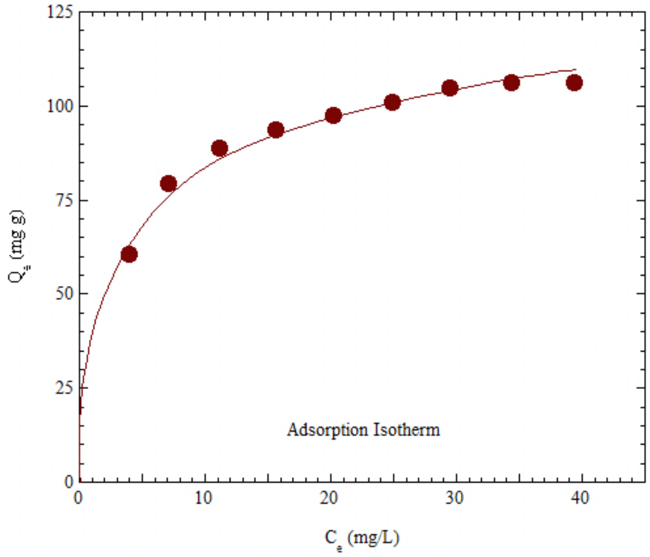

Figure2. *Adsorption isotherm for the removal of Fe (II) from wastewater sample by the CASD at room temperature*

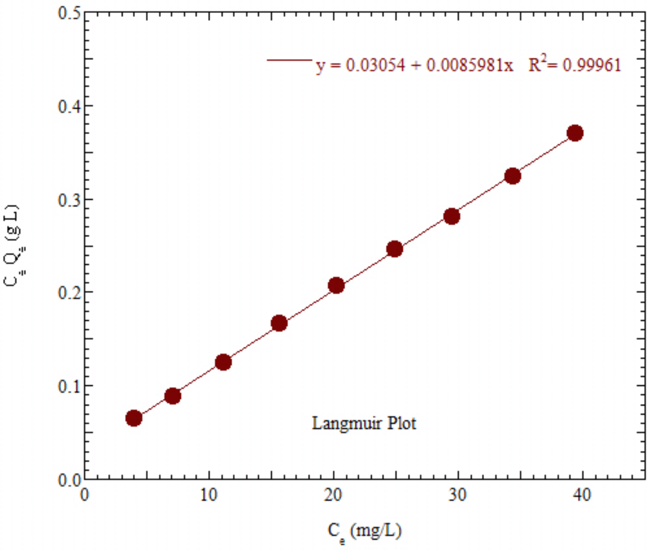

Figure3. *Langmuir plot for the removal of Fe (II) from industrial wastewater sample by the CASD bio-adsorbent at room temperature*

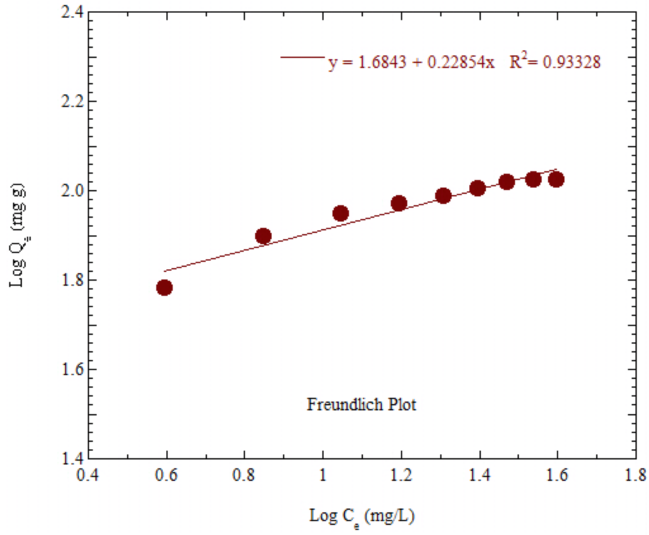

Figure4. *Freundlich plot for the removal of Fe (II) from industrial wastewater sample by the CASD bio-adsorbent at room temperature*

Almost unit value of the R^2 (i. e., 0.9996) confirmed the Langmuir adsorption isotherm model is the best fitted than that of the Freundlich adsorption isotherm model, because the R^2 value for the linearized Freundlich plot is found to be 0.93328 as shown Fig. 4. The maximum adsorption capacity (Q_{max}) for the Fe (II) removable from the wastewater by the CASD bio-adsorbent was found to be 116.3 mg/g using Langmuir plot (Fig. 3) at room temperature in pH 4. On the other hand, the adsorption energy (i. e., b) for Fe (II) ions removal by the CASD was found as 0.2815 L/mg. The Freundlich constant of 1/n, which is related to the adsorption intensity, was found to be less than 1 (i. e., 0.22854). It suggests the favorable adsorption behavior of Fe (II) ions by the CASD bio-adsorbent. The K_F value was calculated as 48.34 mg/g.

3.3. Effect of Contact Time

The effect of contact time was studied by taking 40 mL of the adsorbate solution containing 2 mg/L Fe (II) in a 100 mL Erlenmeyer flask with 40 mg of the CASD bio-adsorbent at pH 4. The solution was stirred for different time intervals ranging from 10 to 1440 minutes. Figure 5 shows the removal efficiency of Fe (II) by the CASD which is increased significantly with contact time for about 5 hours and it became almost constant with long contact time. The iron (II) removal capacity of CASD was found 99.05 % after 24 hours contact time. Therefore, for the batch adsorption study of the Fe (II) from wastewater sample by CASD bio-adsorbent, 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 the studies. From this experimental data, it was studied the adsorption kinetics which will be discussed subsequently.

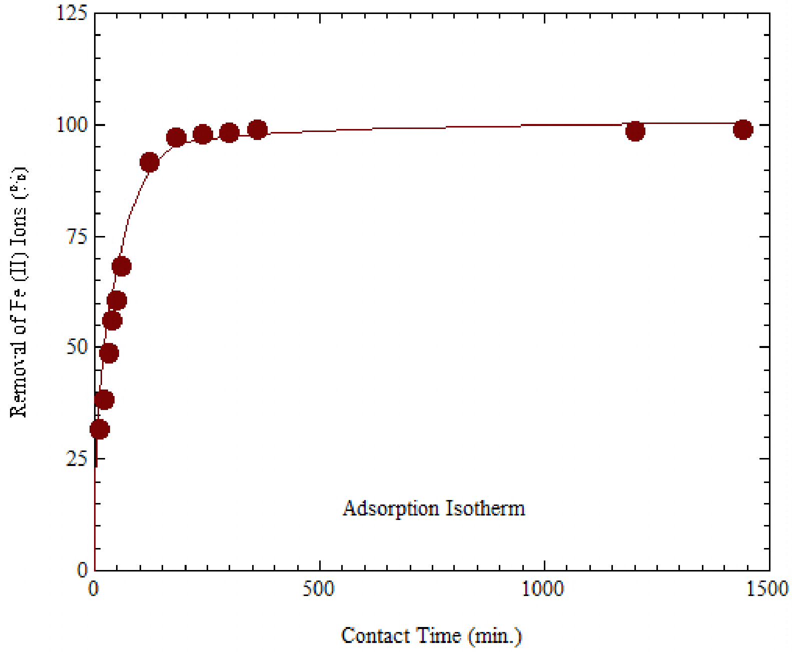

Figure5. *Effect of contact time on removal of Fe (II) from industrial wastewater sample solution by the CASD bio-adsorbent*

3.4. Adsorption Kinetics

Pseudo-first order, pseudo-second order and second order kinetic models were used to study the kinetics of the adsorption process. The pseudo-first order kinetic model was proposed by Lagergren and rate constant is determined by equation (8) as given below.

$$\log (Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303} t \tag{8}$$

Where, Q_e (mg/g) and Q_t (mg/g) are the amount of adsorbed Fe^{2+} ions at equilibrium and time t (min.), respectively and K_1 (min^{-1}) is the pseudo first order adsorption rate constant. The K_1 and Q_e were calculated from the slope and intercepts of plot of log ($Q_e - Q_t$) versus t, as shown in Fig. 6. Similarly, the kinetics of Fe (II) ions removal by the CASD was studied using linearized form of the pseudo-second order kinetics equations as given in equation (9) which was proposed by Ho and McKay [31].

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{9}$$

Where, Q_e (mg/g), Q_t (mg/g) and t (min.) have the same meaning as mentioned in equation (8) and K_2 ($g/mg^{-1}.min^{-1}$) is the rate constant of the pseudo second order adsorption kinetic. The plot of t/Q_t versus t, as shown in Fig. 7 gives K_2 and Q_e values.

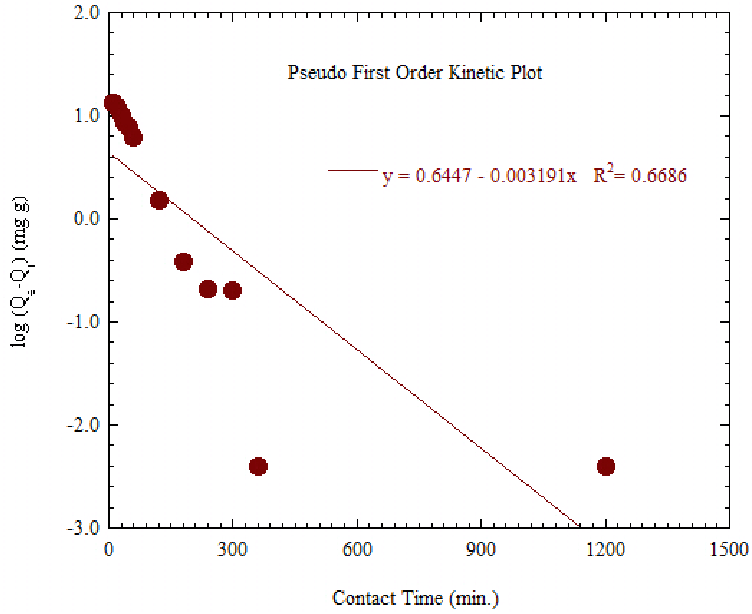

Figure6. *Pseudo first order kinetic plot for the adsorption of Fe (II) from industrial wastewater sample onto the CASD bio-adsorbent at room temperature*

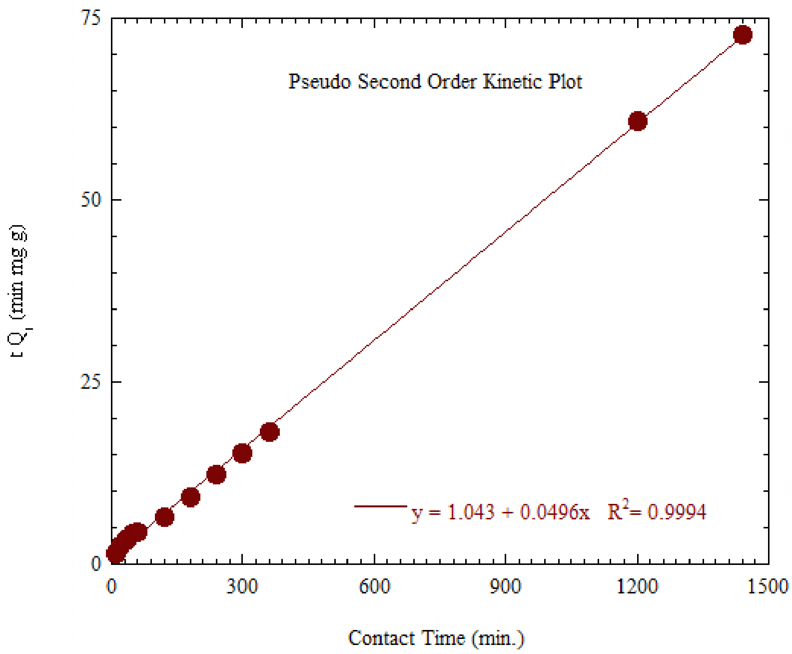

Figure7. *Pseudo second order kinetic plot for the adsorption of Fe (II) from industrial wastewater sample onto the CASD bio-adsorbent at room temperature*

The linear coefficient of determination (i.e., R^2 = 0.9998) value is near unity, which shows that the pseudo second order model can be applied for the adsorption of Fe (II) onto the CASD and also confirmed the chemisorptions of metal ions [32]. It is meaningful to mention here that the second order kinetic model of adsorption cannot be applied for the removal of Fe (II) onto the CASD from the result shown in Fig. 8.

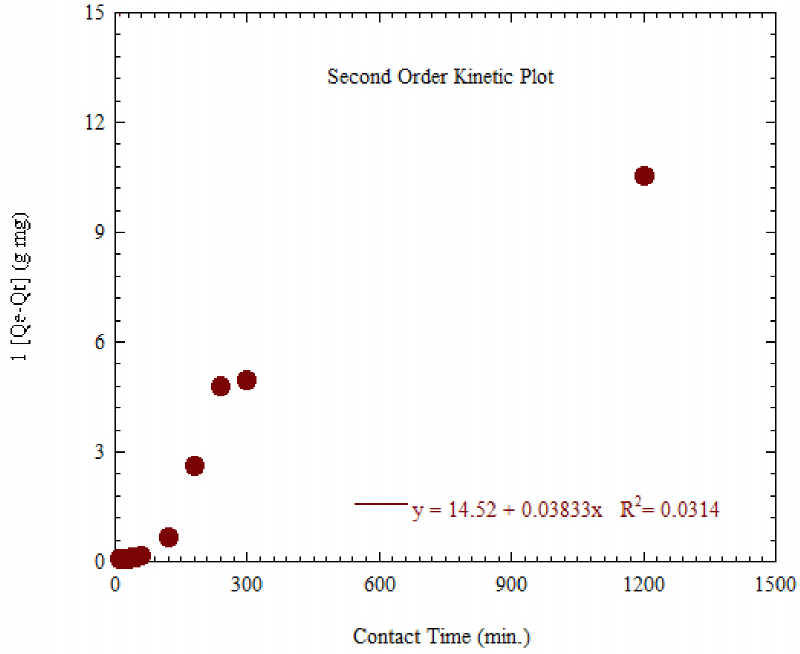

Figure8. *Second order kinetic plot for the adsorption of Fe (II) from industrial wastewater sample onto the CASD bio-adsorbent at room temperature*

4. Conclusions

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

1. It is found that the percent removal of Fe (II) from wastewater solution by the bio-adsorbent of CASD is dependent on the pH and the maximum uptake of Fe (II) was found in pH 4.
2. Equilibrium uptake of Fe (II) was attained at about five hours or more stirring time.
3. The maximum adsorption capacity of the CASD bio-adsorbent for Fe (II) removal from wastewater was found to be about 116 mg/g using adsorption isotherm equation.
4. The removal of Fe (II) by the CASD obeys both Langmuir and Freundlich isotherm models. However, the Langmuir isotherm model is the best fitted than the Freundlich isotherm model.
5. The removal of Fe (II) from the wastewater by the CASD follows the pseudo-second order rate kinetic, although the pseudo-first order and second order kinetic model was not found to be followed.
6. The CASD can be used as good bio-adsorbent for long time to remove the heavy metals from wastewater or drinking water.

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