Removal of Cr (III) Ions from Wastewater using Sawdust and Rice Husk Biochar Pyrolyzed at Low Temperature

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Abstract

Sorption capacity of two different biochar (saw dust and rice straw) was evaluated in the recovery of chromium from wastewater. The optimum pH was 5-7 for recovery of Cr(III). Optimum yield was received after 1 hour contacting time with an adsorbent dose of 1 g/L and initial concentration was ∼20 mg/L. Cr(III) ions were transported to biochar surface through adsorption and intra-particle diffusion process. Langmuir and Freundlich kinetic parameters indicated that the affinity of the sorbent towards the uptake of Cr(III) ions and adsorptions were favorable. According to FTIR analysis of Cr(III) ions bound to active sites either electrostatic attraction or complexation mechanism. These results indicated that carbonyl, hydroxyl, amine and halides are the main adsorption sites in saw dust and rice straw biochar and these functional groups complexes with Cr(III) ions in the aqueous solution and changed the chemical environment of the functional groups in the biochar.

1. Introduction

Chromium is highly toxic heavy metal that widely attracted industrial contaminant, released mainly from leather tanning, textile, metal processing, paint and pigments, dyeing and steel fabrication industries [1]. The hexavalent and trivalent forms of chromium is often present in natural waters that contaminated from industrial waste. Chromium present in trivalent and hexavalent forms in the natural environment while Cr(III) produces mononuclear species $Cr(OH)^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_4^{-}$, neutral species $Cr(OH)_3^{0}$ and polynuclear species $Cr_2(OH)_2$ and $Cr_3(OH)_4^{5+}$[2, 3]. The Cr(VI) is present in solution as CrO_4^{2-} and $Cr_2O_7^{2-}$ at normal pH, but when pH values are reduced below 3 then Cr exists in the form of $HCrO_4^{-}$[4-6]. According to WHO, the maximum discharge limits for chromium in wastewater is 1.0 mg/L and maximum allowable limit in drinking water is 0.05 mg/L. In fact there is no safe level for drinking water and even a very dilute content can be caused adverse health effects. Heavy exposure of hexavalent chromium causes cancer in the digestive tract and lungs and may cause gastric pain, nausea, vomiting, severe diarrhea and hemorrhage [7].

Since Cr species are highly toxic when present in natural waters, more attention was given to remove such contaminants using chemisorptions methods and biosorption methods. Recent years, biosorption methods were extensively used for removal of heavy metals from contaminated water since such methods have been proven to be an efficient technique for the sequestration of pollutants in wastewater [8-10]. Such methods are usually low cost as the absorption materials are mostly by-product of agricultural and other industrial wastes [9]. However in most early studies were investigated the removal of more toxic form of Cr(VI) while few attempts were made on the removal of the trivalent Cr using biochar [2]. Therefore, this study was aimed to investigate the efficiency of different bio-residues to remove chromium (III) from contaminated water. Biochar that produced from sawdust and rice straw were used as the adsorptive material in this study. Pyrolyzing temperature was selected as 400°C since it considered as an optimal condition that producing biochar for effective sorbent [11, 12].

2. Materials and methods

Boichars were produced by sawdust and rice straw at the temperature of 400 °C under low oxygen condition. Pyrolyzed materials were then washed thoroughly with deionized water in order to remove any remaining dirt. Dried material were then grounded and mechanically sieved to a particle size of <0.125 mm that were used for the adsorption experiments. Adsorption experiments were carried out by using batch technique to obtain equilibrium data that were performed at different pH, contacting time and initial concentrations to obtain equilibrium isotherms for known concentrations of Cr(III) solutions. A stock solution of 1000 mg/L Cr(III) were prepared using $Cr(NO_3)_3 .9H_2O$ and diluted to various initial experimental concentrations. 0.1 g of the powdered biochar samples were added with 100 ml of a metal ion solution whose concentration was 5 mg/L. All adsorption experiments were performed at room temperature (27±1.0°C) and agitated at 600 rpm. All batch isotherm tests were replicated three times and all the observations were recorded in triplicate and average values are reported. Continuous nitrogen purging were performed in all experimental procedures and oxygen free deionized water (<0.05 mS/cm) were used for the solution preparations. The solutions were then filtered using 0.45 µm nylon fiber membrane filters and the total chromium concentration in solution was determined by a flame atomic adsorption spectrophotometer (Varian 240FS).

The absorption experiment variables were set as a function of initial pH of the solution, contact time and initial metal concentrations in order to obtain the optimum adsorption conditions. After selecting the optimum conditions, kinetic parameters and sorption characteristics of inexpensive, nontoxic adsorbents were studied. The amount of Cr(III) removed or adsorbed and the removal percentages (%) of Cr(III) were calculated using mass balance equations;

$$q = \frac{(C_o - C_f)v}{m} \text{ ---(1)}$$

$$Removal\ Percentage\ (\%) = \frac{(C_i - C_f) * 100}{C_i} \text{------------(2)}$$

where the q is the amount mg/g of Cr(III) adsorbed, C_0 and C_f are the initial and final concentrations of Cr(III) (mg/L), V is the volume of solution and m is the weight of the biochar used for the experiment.

Material characterization and the possible involvement of functional groups in biochars were carried out using Furrier Transformation Infrared Spectroscopy (FT-IR) (Thermo Scientific Nicolet iS-10) that were run from 500 and 4000 cm^{-1}at a resolution of $4cm^{-1}$and samples were directly mounted on the diamond base using a transparent polyethylene film.

3. Results and discussion

3.1. Influence of contacting time to Cr(III) metal ions

Chromium adsorption capacity was higher with saw dust biochar (8.5 mg/g) while 5.5mg/g adsorption capacity was achieved by rice straw biochar (Figure 1). The varied adsorption capacity obtained for different biochars was mainly related with the contents of the functional groups on the biochars. The greatest content of the functional groups on the saw dust biochar led to the largest adsorption capacity for Cr(III), and the relatively lower contents of the functional groups on the rice straw biochars led to the lower adsorption capacity for Cr(III) ions. Formation of surface complexes between Cr^{3+} and the functional groups on the saw dust biochar was one of the main mechanisms for higher Cr(III) adsorption in the solution.

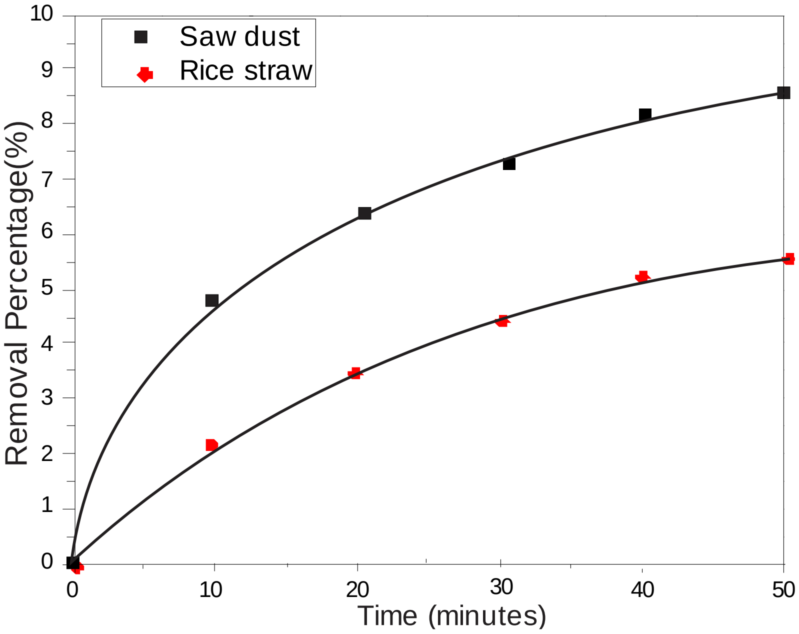


Figure 1 Removal of Cr(III) ions with contacting time

3.2. Effect of pH onCr(III) adsorption

The pH of a solution consider as an important parameter in the adsorption of Cr(III) ions onto various adsorbents. The effect of pH on the adsorption of Cr(III) ions onto biochars were investigated at initial pH ranging from 3.0 to 9.0. The results revealed that Cr(III)ions adsorption by biochars were highly pH-dependent. The amount of Cr(III) adsorption increased with the increase in pH from 3 to 6 and then gradually decreased with increased of pH (Figure 2). The effect of pH values on Cr(III) adsorption was also more evident when rice straw biochar was used as adsorbent. For instances, Cr(III) removal percentage (%) for rice straw biochar increased from 35% at the pH value of 3 to 87% at the pH value of 6 and then decreased to 19 at the pH 9 when initial Cr (III) concentration was 6.5 mg/L, whereas Cr(III) removal percentage (%) for saw dust biochar had a slight increase from 30% to99% in the above pH range from 3 to 6 and decreased as rice straw biochar upto 76%.

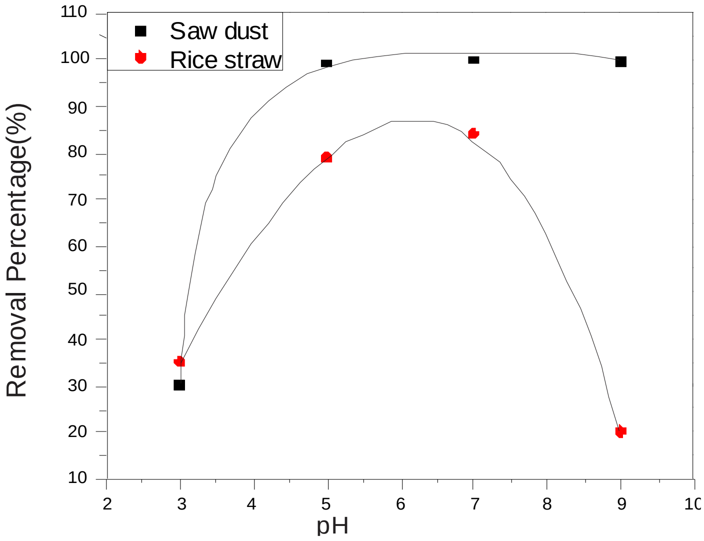


Figure 2. Variation of removal percentage(%) of Cr(III) ions with pH

At lower pH, excess proton can compete with Cr (III) reducing the adsorption of Cr (III) ions on to biochar surface. Cr(III) produced $Cr(OH)^{2+}$, $Cr(OH)_2^+$ ions in the solution due to excess proton which can compete with Cr(III) (Mohan et al 2006). When metal binding sites on biochar became positively charged and adsorption was low due to repelling Cr(III) cations. Removal of Cr(III) ions was optimum when pH increases above 5 for both sawdust and rice straw biochar. When pH is increased above 6, Cr (III) is precipitated by forming $Cr(OH)_3$. Since more hydroxyl groups are in rice straw biochar surface when pH higher than 7, adsorption was reduced due to production of polynuclear species $Cr_2(OH)_2$ and $Cr_3(OH)_4^{5+}$[2, 3].

3.3. Influence of initial ion concentration on Cr (III) adsorption

Highest removal was observed at low concentrations of chromium ion solution. At the first 15 minutes it was observed rapid uptake of chromium ions by both biochar and then gradually decreased with time. Therefore, more metal ions were left un-adsorbed in solution at higher concentration levels [13]. These results may be explained on the basis that the increase in the number of ions competing for the available binding sites and also because of the lack of active sites on the adsorbent at higher concentrations.

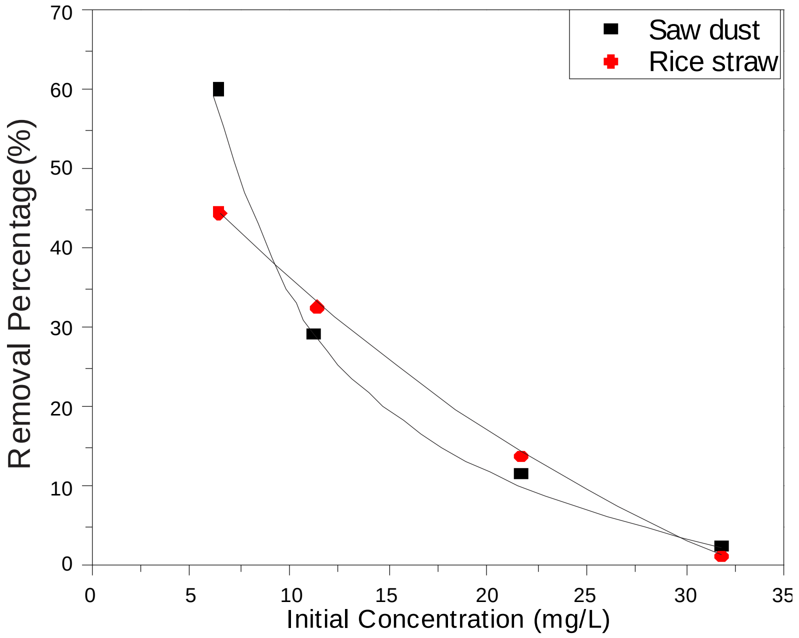


Figure 3. Variation of removal percentage (%) of Cr(III) ions with initial metal concentrations

3.4. Sorption dynamics of Cr (III) ions

Kinetics of adsorption is an important characteristic in defining the efficiency of adsorption. In order to explain the kinetics of biosorption pseudo second order kinetics model also was applied.

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2\text{------------(3)}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t\text{------------(4)}$$

Where, *K2* is the pseudo-second order rate constant. The slope and intercepts of the plot of t/q_t vs t (Figure 4) for adsorption of Cr(III) metal ions on saw dust and rice straw biochar were used to determine the value of K_2 and q_e respectively. Values of correlation coefficient (R^2) and calculated values of K_2 and q_e were (Table 1) indicated that pseudo-second order model is suitable to explain our experimental data. Values of K_2 for removal of Cr(III) ions for rice straw and saw dust biochar were 2.96, -0.038 respectively.

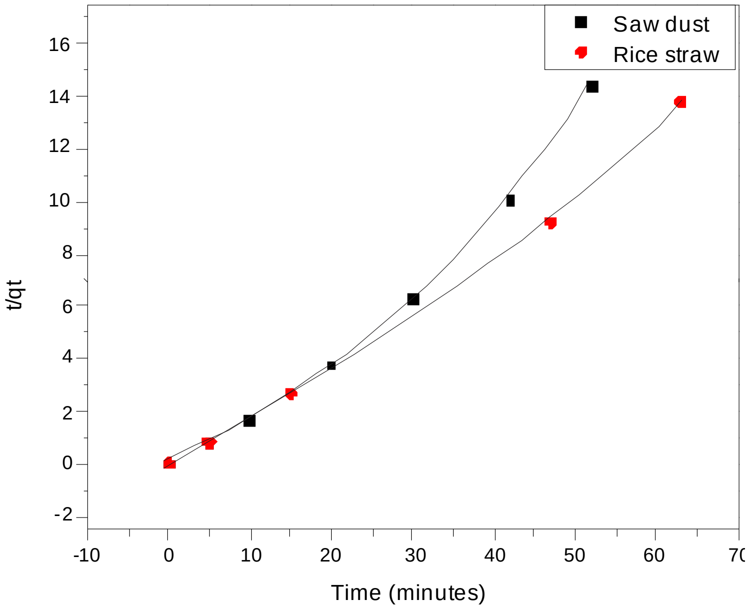


Figure 4. The graph of Time t vs t/qt for Cr(III) ions

Table 1. Adsorption parameters of Cr(III) ions

isotherm models	Parameters	Saw dust biochar	Rice straw Biochar
Pseudo 2nd	K_2	-0.038	2.96
	q_e	4.03	5.81
	R^2	0.981	0.987
Langmuir	K_L	-0.0007	0.44
	q_{max}	43.48	26.31
	R^2	0.995	0.978
	R_L	0.991	0.069
Freundlich	K_F	14.05	14.13
	n	1.12	1.19
	R^2	0.983	0.936

3.4.1. Adsorption mechanism

Metal ions can be transported from aqueous phase to the solid phase by the intra-particle transport phenomenon. The intra-particle transport is supposed to be the rate controlling step. The rate of particle transport through this mechanism is slower than adsorption on the exterior surface site of the adsorbent. The amount of adsorbed species varies proportionately with a function of retention time. The equation can be expressed as [14].

$$q_e = K_d t^{1/2} + C \text{---------}(5)$$

Where K_d is the constant coefficient, the initial rate of intraparticular diffusion (mg/L. $min^{1/2}$). The transport of the adsorbents in aqueous solution through the biochar particle interface into the pores of the biochar particles, surface of the adsorbents, is responsible for adsorption.

Figure 5 illustrates the diffusion of Cr(III) ions within the saw dust and rice straw biomass as a function of time. Chromium ion was transported through saw dust biochar with several stages while rice straw showed adsorption process is the main control process. Chromium ion transports through saw dust biochar by a both adsorption and inter-particle diffusion process.

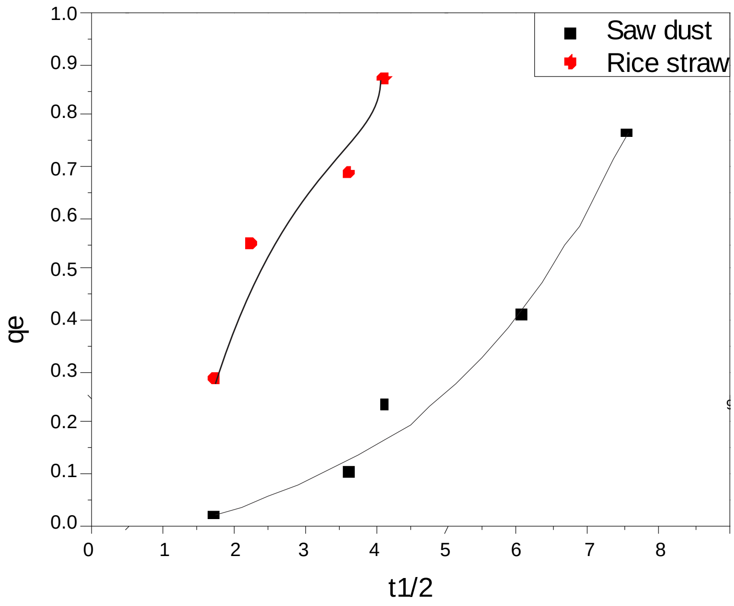


Figure 5. The graph of qe vs$t^{1/2}$ for Cr(III) ions

3.4.2. Adsorption isotherms

The most common representation of the adsorbate concentration and quantity of material adsorbed is the adsorption isotherm graph of the amount adsorbed against the equilibrium concentration, at a specific temperature. These isotherm models have been used to describe the distribution of metal ions between the solid phase (adsorbent) and liquid phase (solution) when equilibrium was reached. The nature of the interaction between the adsorbate and adsorbent can be determined from the isotherm shape [15].

3.4.2.1. Langmuir Isotherm

This model is applicable in the cases where only one molecular layer of adsorbate is formed at the adsorbent surface which remains constant even at higher adsorbate concentrations.

Langmuir isotherm (linear form) is expressed as following [16];

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{K_L}{q_{max}} \quad \text{--------------- (6)}$$

Essential features of the Langmuir isotherm was expressed in terms of a dimensionless constant separation factor R_L (Equilibrium Parameters) that is given by

$$R_L = \frac{K_L}{K_L + C_i} \quad \text{---------------- (7)}$$

Where q_{max} is the monolayer adsorption capacity of the adsorbent (mg/g) it is the maximum amount adsorbed, K_L is the Langmuir adsorption constant (L/mg), C_e is the equilibrium metal ion concentration in the solution (mg/L) and q_e is the equilibrium metal ion concentration on the adsorbent (mg/g).
Values of q_{max} and K_L are calculated respectively from the slope and the intercept of plot of Ce/qe vs. Ce, as shown in Figure 6. Value of Langmuir parameters and R^2 were summarized in Table 1. Maximum adsorption capacities were showed by saw dust biochar for Cr(III) ions. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites. Monolayer adsorption is distinguished by the fact that the amount adsorbed reaches a maximum value at a moderate concentration; this corresponds to complete coverage of the adsorbent surface by a monomolecular layer of adsorbate ([15]. The separation factor (R_L) for saw dust and rice straw biochars were 0.991 and 0.069 for Cr(III) ions. Therefore, the results show that saw dust and rice straw biochars have potentials as good sorbent for Cr(III) ions that follows monolayer adsorption isotherms.

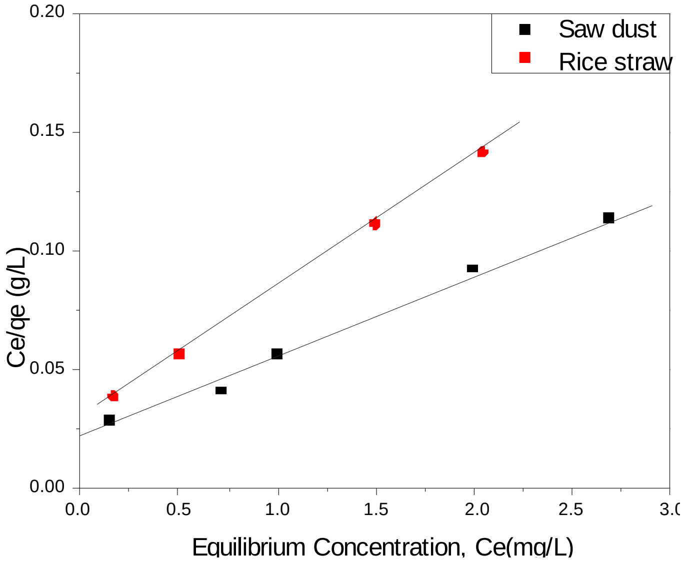


Figure 6. The graph of Ce/qe vs Ce for Cr(II) ions

3.4.2.2. Freundlich Isotherm

The Freundlich isotherm model is widely used to describe adsorption characteristics for the heterogeneous surface[17] and assume monolayer capacity, but accompanied with interaction between adsorbed molecules. The Freundlich model can be chosen to estimate the adsorption intensity of the sorbent towards the sorbate [18]. The Freundlich linear form is given by the following equation.

$$q_e = K_F C_e^{1/n}\text{---------}(8)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e\text{--------------}(9)$$

where K_F is a constant related to the adsorption capacity of the adsorbent and the constant 1/n indicates the intensity of the adsorption.

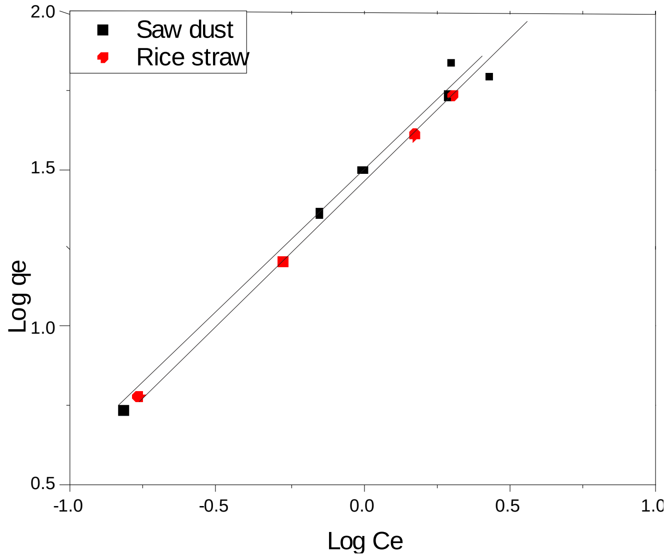
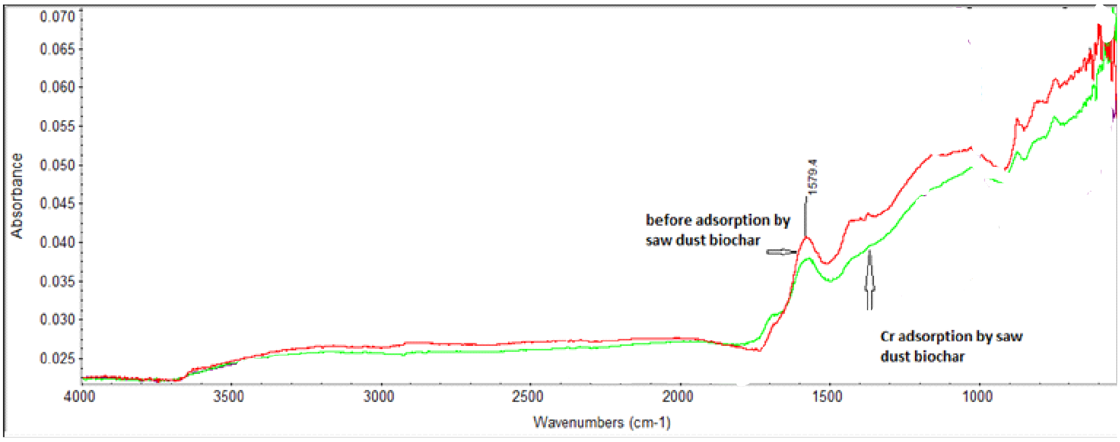


Figure 7. The graph of Log Ce vs Log qe for Cr(III) ions

The K_F is an approximate indicator of adsorption capacity, while *1/n* is a function of the strength of adsorption in the adsorption process [19]. If n = 1 then the partition between the two phases are independent of the concentration while 1/n <1 indicates a normal adsorption and 1/n>1 indicates cooperative adsorption [20]. However, K_F and *n* are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models. The obtained values of 1/n and K_F are calculated from the slope and the intercept of the plot of log C_e vs log q_e.(Figure 7). Freundlich parameters together with R^2 were summarized in Table 1. The values indicated the affinity of the sorbent towards the uptake of both ions and adsorptions of the metal ions were favourable.



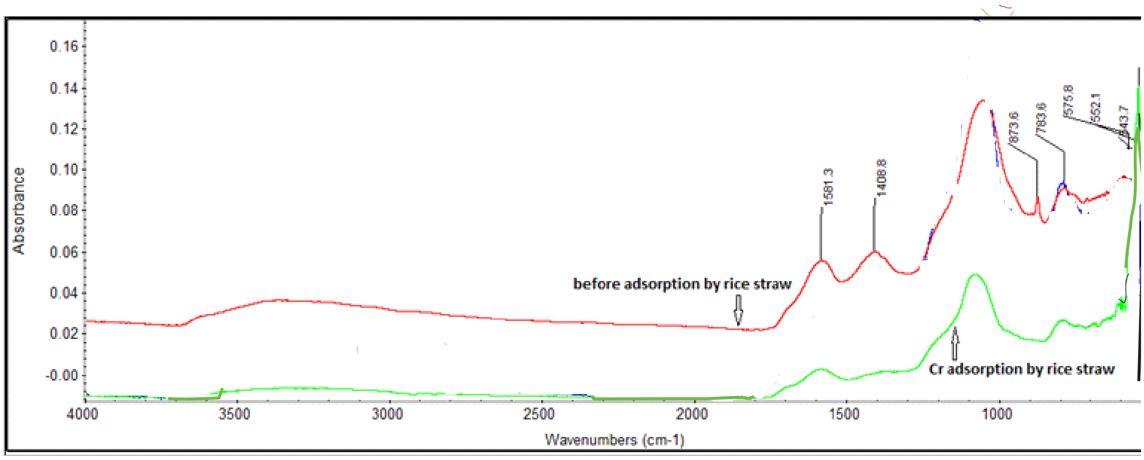


Figure 8 FT-IR Spectra of Rice Straw and Saw Dust biochar After Adsorption Cr(III) ions

The biochar obtain from byproducts of biomass are low cost materials that were pyrolysed in moderate temperature of 400° C. FT-IR spectra obtained for biochar are characteristics with different oxygen containing surface groups of C-O; C=O and C-OH and other lignocellulose materials since the materials were pyrolysis at lower temperature.Absorption bands observed at 1581 and 1408 cm^{-1} are typical for C-C bonds, 1054 cm^{-1} for CO-C stretching, 3360 cm^{-1} for hydroxyl (–OH) stretching and 575 cm^{-1} for alkyl halide groups. The spectrum of rice straw biochar was characterized by four bands (Figure 8) at wave numbers 1581, 1408,1054, 873, 783, 575, 552 and 543cm^{-1} that are attributed to, C=C ring, stretching of secondary hydroxyl, aliphatic CH_2 deformation, and aromatic C=C ring or COO– group stretching, respectively [21, 22]. The FTIR spectrum of the saw dust biochar was identified functional groups at 1579 cm^{-1} for NH amine, 1031 cm^{-1} for aliphatic amine, and 628, 602, 597, 584, 572 and 562 cm^{-1} for alkyl halide groups. A peak at 586 cm^{-1} has been formed for alkyl halide group, two peaks at 872 cm^{-1} and 757 cm^{-1} for CH aromatic active sites and other two peaks appeared at 3202 cm^{-1} and 2833 cm^{-1} corresponds to the stretching vibration of -OH and the extension vibration of -NH [21]. The band at 2833 cm^{-1} can be assigned to CH stretching.

The peak at 1579 cm^{-1} in saw dust biochar was assigned to aromatic C=C ring stretching or NH amine shifted to 1568.9 cm^{-1} due to Cr(III) adsorption. The band 1031cm^{-1} shifted to 1030cm^{-1} after Cr(III) adsorption by hydroxyl groups and aliphatic amine in sawdust biochar. Alkyl halide bands at 628, 602, 597, 584, 572, 562 and 552 cm^{-1} have been shifted and new peaks in 617, 580, 566, 554 $cm^{-1}$and 544cm^{-1} formed. The band for CO-C stretching in rice straw biochar at 1054 cm^{-1} has been shifted to 1081.7cm-1 due to Cr(III) adsorption and band located at 575, 552, 543 for alkyl halide groups has been shifted to 598cm^{-1}.

Cr(III) metal ions bound to these active sites of the biosorbents through either electrostatic attraction or complexation mechanism ([21]. The electrostatic attraction is between metal ion and carbonate group. Meanwhile, the complexation mechanism involved electron pair sharing between electron donor atoms (O and N). These results indicated that carbonyl, hydroxyl, amine and halides are the main adsorption sites in saw dust and rice straw biochar and these functional groups complexed with Cr(III) ions in the aqueous solution changed the chemical environment of the functional groups and thus led to a shift in the peak positions of the biochar functional groups in the FTIR spectra.

4. Conclusion

The results of this study reveals that the percentage removal of Cr(III) ions were dependent on the pH of the solution and the initial metal concentration. The contact time necessary for maximum adsorption was found around 50 minutes. The optimum pH was ranged between 5 to 7 for Cr(III). Kinetic studies yielded an optimum equilibrium time of 50 minutes with an adsorbent dose of 1 g/L and initial concentration ∼20 mg/L for Cr(III) ions. It can be concluded that metal ions in aqueous solution were transported to biochar surface through adsorption and intra-particle diffusion process. The sorption values indicated the affinity of the sorbent towards the uptake of Cr(III) ions and adsorptions of the metal ions were favorable. FTIR analysis revealed that Cr(III) metal ions bound to active sites of the biosorbents in different biochars through either electrostatic attraction or complexation mechanism. These results indicated that carbonyl, hydroxyl, amine and halides are the main adsorption sites in saw dust and rice straw biochar and these functional groups complexed with Cr(III) ions in the aqueous solution and changed the chemical environment of the functional groups in the biochar. The results showed that rice straw and saw dust biomass can be used to remove Chromium ions from contaminated water.

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