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Cr(III) adsorption by sugarcane pulp residue and biochar

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Abstract: A batch experiment was conducted to investigate the adsorption of trivalent chromium (Cr(III)) from aqueous solutions by sugarcane pulp residue (SPR) and biochar. The results show that Cr(III) adsorption by SPR and biochar is highly pH-dependent and Cr(III) adsorption amount increases with the increase of pH. The adsorption kinetics of Cr(III) fits well with the pseudo-second-order model. The maximum Cr(III) adsorption capacities of 15.85 mg/g and 3.43 mg/g for biochar and SPR were calculated by Langmuir model. This indicates that biochar has a larger ability for Cr(III) adsorption than SPR. The free energy change value (ΔG) reveals a spontaneous sorption process of Cr(III) onto SPR and non-spontaneous sorption process onto biochar. The entropy change (ΔS) and enthalpy change (ΔH) are found to be 66.27 J/(mol·K) and 17.13 kJ/mol for SPR and 91.59 J/(mol·K) and 30.875 kJ/mol for biochar which further reflect an affinity of Cr(III) onto SPR and biochar. It is suggested that biochar has potential to be an efficient adsorbent in the removal of Cr(III) from industrial wastewater.

Key words: Cr(III); adsorption; sugarcane residue pulp; biochar

1 Introduction

The increasing contamination of urban and industrial wastewater by toxic metal ions causes significant environmental problem [1]. In particular, chromium is one of the undesirable heavy metals because it accumulates in the food chain, affects human physiology, and causes several health problems [2]. The most common forms of chromium are hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)) which are commonly used in various industrial processes. Trivalent chromium is extensively used in the leather tanning, paints and pigment, fungicides industries and in ceramic and glass manufacture. Although Cr(III) is considerably less toxic than Cr(VI), its disposal as a dissolved species in natural waters or as sludge in soil may pose serious health risks because it can be oxidized to hexavalent chromium in the environment [3−4]. The maximum chromium contaminant level permitted in wastewater is 5 mg/L for Cr(III) [5]. Therefore, the removal of Cr(III) from wastewater arouses an attention. Typical treatment methods for Cr(III) removal from the industrial wastewater include electrocoagulation [6], iron exchanges [7], membrane separation [8], reduction [9], biosorption [10], and adsorption [11−12]. Among these methods, biosorption has been considered to be the most feasible method because biomass is cheap and capable of removing many heavy metals over a wide pH range. A variety of materials are used as adsorbents for chromium removal, such as activated carbon [13], hydrotalcite [14], cross-linked chitosan [15], fly ash [16], diatomite [17], rose [18], lignin [19], and rice full ash [20].

In China, the planting area of sugarcane accounts for 15×10^9 m^2, and sugarcane yield reaches up to 998 Mt. About 112 Mt of sugarcane pulp residue (SPR) is discharged from sugar manufactory annually, which occupies a large area for its deposition. Moreover, the discharge of residue from agricultural by-product will cause an environment problem. Therefore, it is essential to utilize this residue to eliminate environmental and limited land stresses in China. Sugarcane pulp residue contains several functional groups including hydroxylaliphatic, carboxyl, carbon and oxygen functional group [21]. It can be used to remove Ca^{2+}, Ni^{2+}, Cr^{3+}, Zn^{2+} and Cu^{2+} from waste water [22]. However, the research on the removal of chromium ions by SPR is rather scanty. Moreover, the adsorption capacity for SPR is limited and heavy metal-loaded SPR may cause further pollution along with decay of biomass

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in the environment [23]. It was reported that biochar prepared from pinewood and rice husk had good adsorption capacities with respect to lead [24]. In order to obtain high removal efficiency of Cr(III), it is important to improve adsorption ability for adsorbent. The hypotheses are that pyrolization of biomass can increase the surface area and then improve Cr(III) adsorption capacity. The outcome would help to provide a new approach for removing Cr(III) in the wastewater and recycling agricultural by-products. Therefore, the objectives of this work are: 1) quantify the effect of pH, temperature, chromium concentration and adsorbent dosage on Cr(III) adsorption; 2) Analyze the adsorption capacity of Cr(III) by SPR and biochar; 3) Investigate the adsorption kinetics and isotherm of Cr(III) on SPR and biochar.

2 Materials and methods

2.1 Sugarcane pulp residue and preparation of biochar

The SPR used in this work was collected from a sugar-refinery in Hunan Province, China. It was sun-dried and ground to pass a 0.25 mm sieve prior to experiment. The biochar were prepared from SPR. Briefly, SPR was pyrolysed in a stainless steel tube placed in an electric tubular furnace under nitrogen gas protection. The electric tubular furnace was maintained 2−3 h at a heating rate of 10 °C/min till the maximum temperature of 500 °C. Thereafter, the biochar was cooled down at room temperature and passed through a 150−600 μm sieve. 5 g SPR yields about 1 g biochar.

2.2 Adsorption of Cr(III) by SPR and biochar

The stock solutions of 1 g/L Cr(III) were prepared by dissolving 5.1250 $CrCl_3{\cdot}6H_2O$ in 1 L distilled water. 0.5 g SPR and 0.1 g biochar (equal to 0.5 g of crude SPR) were added into 15 mL of solution containing known Cr(III) concentration. The pH values of the solution were adjusted to the desired values with either 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. The SPR and biochar samples were shaken for 24 h and 4 h on a shaker at 140 r/min under the desired temperature conditions, respectively, according to the adsorption equilibrium time of Cr(III) onto SPR and biochar in the pre-experiments. After reaching the adsorption equilibrium, the adsorbent was removed by filtration. One portion of filtrate was taken for measuring the total chromium concentration. The other portion of the filtrate was taken for determining Cr(VI) concentration. All experiments had three replicates.

2.3 Kinetics of Cr(III) adsorption

0.5 g SPR or 0.1 g biochar was put into a 100 mL polyethylene plastic bottle containing 15 mL of 100 mg/L Cr(III) solution. The samples were shaken on a shaker with a speed of 140 r/min under room temperature. After 24 h, the samples were filtrated to separate the adsorbent, and the supernatant was chosen for determining the concentrations of total chromium and Cr(VI). All experiments had three replicates.

2.4 Analytical methods

The total chromium concentration in solution was determined by a flame atomic adsorption spectrophotometer (TAS-990, Beijing Purkinje General Instrument Co., Ltd.). Cr(VI) concentration in solution was measured with diphenylcarbazide colorimetric method. The Cr(III) concentration was calculated from the difference between the total chromium and Cr(VI) concentration in the filtrate. The pH values were measured by a pH meter (LeiCi, Shanghai PHS-3s with B-201-C composite electrode) with accuracy of ±0.1 pH units.

3 Results and discussion

3.1 Effect of pH on Cr(III) adsorption

The pH of a solution plays an important role in the adsorption of Cr(III) ions onto various adsorbents. The effect of pH on the adsorption of Cr(III) ions onto SPR or biochar were investigated at initial pH values ranging from 1.5 to 5.5 (Fig. 1). The results revealed that Cr(III) adsorption by SPR or biochar was highly pH-dependent. The amount of Cr(III) adsorption increased with the increase in pH values. Moreover, the effect of pH values on Cr(III) adsorption was more evident when biochar was used as adsorbent. For instances, Cr(III) adsorption capacity for biochar increased from 0.27 mg/g at the pH value of 1.5 to 5.06 mg/g at the pH value of 5.5 when initial trivalent chromium concentration was 100 mg/L, whereas Cr(III) adsorption capacity for SPR had a slight increase in the above pH range. Such sorption trend is attributed to the competition between Cr(III) and portion for the binding sites on SPR or biochar surface as well as the speciation of trivalent chromium ions [25−26]. At low pH value, an excess proton can compete with Cr(III), resulting in a low adsorption of Cr(III). Increasing the pH value can decrease the amount of the competitive H^+ ion in the system. Therefore, the Cr(III) loading becomes more probable [27]. Generally, Cr(III) coexisting as Cr^{3+}, $Cr(OH)^{2+}$ and $Cr(OH)_2^+$ is cationic ion in the solution. When pH is lower than 2, the predominant species is Cr^{3+}. At pH=4, Cr^{3+} and $Cr(OH)^{2+}$ are present in approximate distribution of 40% and 60%, respectively. At pH 5, $Cr(OH)^{2+}$ are the dominant species, accounting for nearly 70% of the chromium present. At neutral pH range (pH 6.0 and above), precipitation could not be excluded. To avoid precipitation of Cr(III), all the experiments on Cr(III) adsorption are conducted at a maximum pH value of 5.0. It can be concluded that Cr(III) is principally adsorbed as $Cr(OH)^{2+}$ form on SPR and biochar since the largest adsorption amount was observed at pH 5.0. Since no obvious adsorption of Cr(III) by biochar was detected below pH 2, Cr^{3+} was not the predominant form adsorbed by biochar.

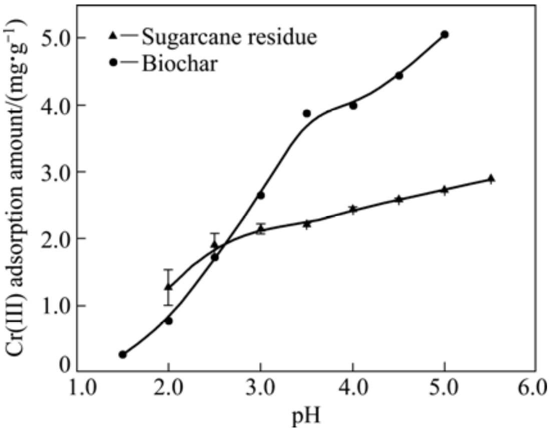

Fig. 1 Effect of pH values on adsorption of Cr(III)

3.2 Influence of initial ion concentration on Cr(III) adsorption

The initial ion concentration provides an important driving force to overcome all mass transfer resistance of metal ions between the aqueous solution and the adsorbent [28]. The adsorption amounts of Cr(III) with varying Cr(III) concentration are presented in Fig. 2. It was noted that the unit adsorption of Cr(III) on SPR and biochar increased from 1.12 to 5.59 mg/g and from 1.47 to 16.02 mg/g, respectively, with the increase of the chromium concentration in the test solution. It is obvious that Cr(III) adsorption capacity for biochar is higher than that for SPR because the biochar obtained after pyrolization of SPR has a greater specific surface area which is in favor of the Cr(III) adsorption capacity.

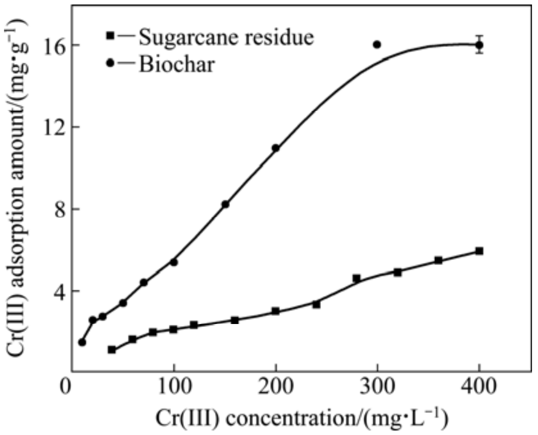

Fig. 2 Influence of initial Cr(III) concentration on adsorption of Cr(III)

3.3 Effect of temperature on Cr(III) adsorption

The effect of temperature on Cr(III) adsorption was investigated at temperature range varying from 10 °C to 60 °C. The results indicated that Cr(III) adsorption onto SPR and biochar was obviously affected by the temperature (Fig. 3). However, temperature influence on the adsorption capacity of Cr(III) for biochar was larger than that for SPR.

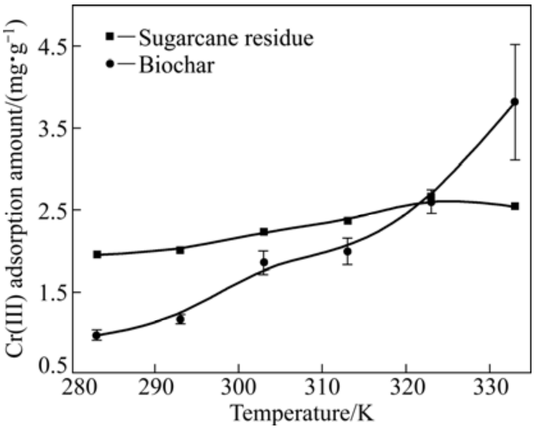

Fig. 3 Effect of temperature on adsorption of Cr(III) ions (initial Cr(III) concentration: 100 mg/L)

In this work, the thermodynamic parameters were estimated to evaluate the feasibility and nature of adsorption process [5, 29]. Thermodynamic parameters such as free energy change (ΔG, kJ/mol), enthalpy change (ΔH, kJ/mol) and entropy change (ΔS, J/(mol·K)) can be calculated as following:

$$K_c = \frac{C_a}{C_e}$$

$$\Delta G = -RT \ln K_c$$

$$\ln K_c = -(\frac{\Delta H}{RT}) + \frac{S}{R}$$

where K_c is the equilibrium constant of the adsorption process, C_a and C_e are the equilibrium concentration of trivalent chromium on SPR or biochar and in solution (mg/L), respectively, R is the gas constant (8.314×10^{-3} kJ/(mol·K)) and T is the absolute temperature (K).

The determined values of ΔG, ΔH and ΔS are listed in Table 1. The negative values of ΔG imply a spontaneous nature of Cr(III) adsorption onto SPR [30], while the positive values of ΔG imply a non-spontaneous in the nature of Cr(III) adsorption onto biochar. However, the spontaneity for Cr(III) adsorption onto biochar increases with the rise in temperature. Consequently, the equilibrium adsorption capacity of Cr(III) for biochar increased sharply with increasing temperature. In the present work, both ΔH and ΔS were positive. The

Table 1 Thermodynamic parameters for adsorption of Cr(III) on SPR and biochar

Adsorbent	$\Delta G/(\text{J}\cdot\text{mol}^{-1})$						$\Delta H/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta S/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$
	283 K	293 K	303 K	313 K	323 K	333 K		
SPR	−1 462.66	−1 715.16	−2 702.92	−3 424.27	−5 589.54	−4 776.01	17.13	66.27
Biochar	4 484.14	4 413.14	2 795.17	2 602.28	1 701.37	−95.51	30.88	91.59

positive value for enthalpy change (ΔH) [31] indicates the adsorption to be an endothermic process and the positive entropy change (ΔS) reflects an affinity of the SPR and biochar for the trivalent chromium [32].

3.4 Adsorption isotherm of Cr(III)

In order to investigate the mechanism of Cr(III) adsorption on SPR and biochar and to provide sufficient information for defining the chemical equilibrium between trivalent chromium and adsorbents, Langmuir and Freundlich isotherms were used to describe the equilibrium. The Langmuir isotherm is described as a homogeneous one assuming that all the adsorption sites have equal adsorbate affinity and that the adsorption at one site does not affect the adsorption at an adjacent site [33]. The linearized form of Langmuir equation is given as follows:

$$\frac{C_e}{q_e}=\frac{1}{q_m b}+\frac{C_e}{q_m}$$

where C_e (mg/L) is the equilibrium concentration of trivalent chromium ions in the solutions. q_e (mg/g) is the amount of adsorbed per unit mass of the SPR or biochar at equilibrium. q_m (mg/g) is the maximum monolayer adsorption capacity and b (g/L) is the Langmuir constants.

A further analysis of the Langmuir equation can be made on the basis of dimensionless equilibrium parameter, R_L [34]. The adsorption intensity (R_L) can be expressed as

$$R_L=\frac{1}{1+bC_0}$$

where C_0 (mg/L) is the initial concentration. The value of R_L lies between 0 and 1 for a favorable adsorption, while R_L>1 represents an unfavorable adsorption, and R_L=1 represents the linear adsorption, while the adsorption is irreversible if R_L=0.

The Freundlich isotherm assumes that the ion adsorption occurs on a heterogeneous surface by multilayer adsorption [35]. The linearlized form of Freundlich equation is given as follows:

$$\lg q_e=\lg k_f+\frac{1}{n}\lg C_e$$

where k_f and n are the Freundlich constants that indicate relative capacity and adsorption intensity.

Data obtained from the present work were plotted following the above two isotherms and the results are depicted in Fig. 4. The results showed that Cr(III) adsorption pattern on the SPR well followed Langmuir isotherms than Freundlich isotherms, while Cr(III) adsorption pattern on the biochar well followed Freundlich isotherms than Langmuir isotherms.

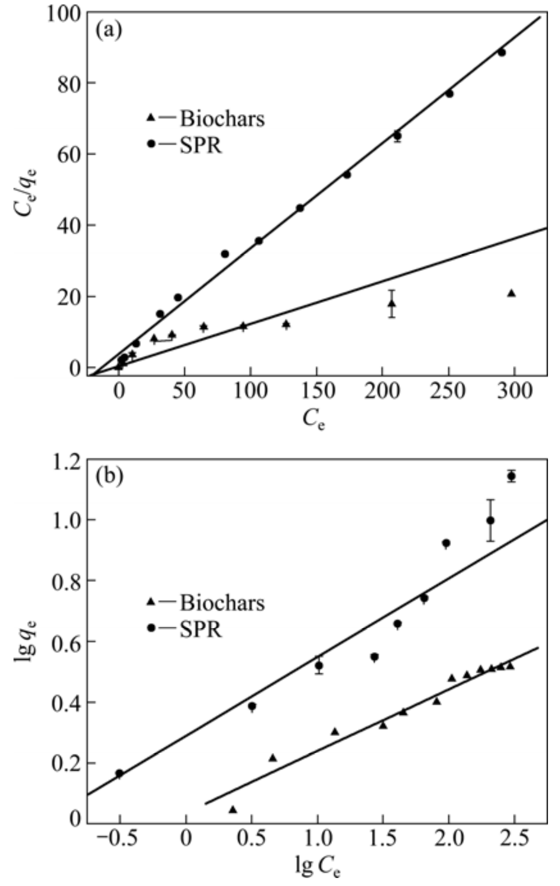

Fig. 4 Langmuir isotherm (a) and Freundlich isotherm (b) plots for Cr(III) by adsorption of SPR and biochar

The parameters obtained from Langmuir and Freundlich models are summarized in Table 2. The values of Langmuir constant q_m, a measure of the monolayer maximum adsorption capacity of SPR and biochar, are 3.43 mg/g and 15.85 mg/g, respectively, which are closer to the actual capacity (q_e) of Cr(III) of 3.29 mg/g and 15.32 mg/g, respectively. The high value of coefficient of determination (r^2=0.99 and 0.86 for SPR and biochar) revealed that these models could be regarded as sufficient to describe adsorption of Cr(III) on SPR and biochar. The dimensionless parameter (R_L), a measure of adsorption favorability, is found in the range from 0.079 to 0.009 ($0<R_L<1$) for SPR and from 0.613 to 0.038 ($0<R_L<1$) for biochar (Table 1). All R_L values were in the range of $0<R_L<1$, indicating the favorable adsorption process for Cr(III) adsorption onto SPR and biochar. In addition, the value of the Freundlich constant, *n*, further demonstrated that Cr(III) ions are favorably adsorbed by SPR and biochar because Freundlich constant varied between 1 and 10 (Table 1). The high value of k_f suggested that SPR and biochar have high affinity for Cr(III) ions [36]. Therefore, the low reversibility found here suggests that the adsorption reactions of Cr(III) ions onto SPR and biochar are of the high-affinity type [37].

Table 2 Characteristic parameters of adsorption process of Cr(III) adsorption

Adsorbent	Langmuir				Freundlich			
	q_m	b	r^2	R_L	k_f	n	r^2	$1/n$
SPR	3.43	0.070 9	0.99	0−1	1.07	4.823 9	0.95	0−1
Biochar	15.85	0.015 4	0.86	0−1	1.71	3.174 6	0.89	0−1

3.5 Adsorption kinetics of Cr(III)

The dynamic of Cr(III) adsorption process in terms of the order and the rate constant can be evaluated using the kinetic adsorption data. The adsorption process of Cr(III) in aqueous solution by adsorbents can be explained by using kinetic models and examining the rate-controlling mechanism of the adsorption process such as chemical reaction or diffusion control [38]. In the present work, pseudo-first-order kinetics model [39] and pseudo-second-order kinetics model [40] were applied to describe the adsorption of Cr(III) onto SPR and biochar as the function of initial Cr(III) concentration.

The linear form of pseudo-first-order kinetic equation is

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Correspondingly, the linear form of pseudo-second-order kinetic equation is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where k_1 and k_2 are the rate constants for the pseudo-order-second and pseudo-second-order kinetic equations, respectively. q_e and q_t are the amounts of solutes adsorbed per unit adsorbent at equilibrium and at time *t*, respectively.

The plots of $\ln(q_e - q_t)$ and t/q_t versus *t* are shown in Fig. 5 which represent the fits of pseudo-first-order kinetics and pseudo-second-order kinetics models to the adsorption of Cr(III) by SPR and biochar. The parameters determined from pseudo-first-order kinetic and pseudo-second-order kinetic models for Cr(III) adsorption are presented in Table 3.

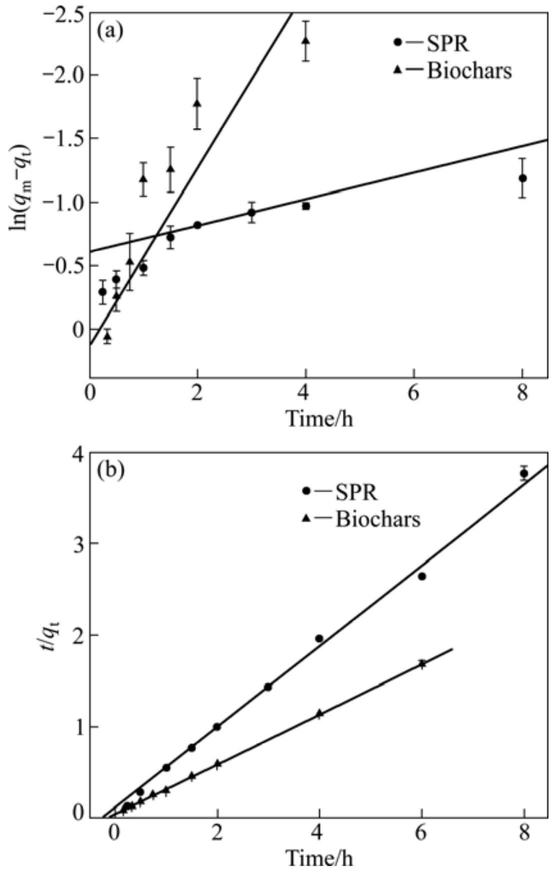

Fig. 5 Pseudo-first-order kinetic (a) and pseudo-second-order kinetic (b) fit for adsorption of Cr(III) on SPR and biochar

Table 3 Predicted kinetic parameters for Cr(III) adsorption on SPR and biochar

Adsorbent	Pseudo-first-order			Pseudo-second-order		
	q_e	k_1	r^2	q_e	k_2	r^2
SPR	0.58	0.115 3	0.93	2.20	2.929 4	0.99
biochar	1.39	0.717 1	0.60	4.91	1.020 0	0.99

When pseudo-first-order equation was used to describe Cr(III) adsorption, the equilibrium adsorption capacity (q_e) of SPR and biochar were 0.58 mg/g, 1.39 mg/g, respectively, much lower than the actual amount of equilibrium adsorption (2.13 mg/g and 4.78 mg/g). Therefore, the pseudo-first-order is an undesired model for Cr(III) adsorption on SPR and biochar. Therefore, the kinetic adsorption data of Cr(III) are further fitted by the pseudo-second-order kinetic model. It was found that the second-order equation model provided higher correlation coefficients with experimental results. This fact indicates that intra-particle diffusion is the rate-limiting factor for Cr(III) adsorption on SPR and biochar [37]. As given in Table 2, the calculated values of q_e from pseudo-second-order kinetic model for Cr(III) adsorption onto SPR and biochar (2.20 mg/g, 4.91 mg/g, respectively) are very close to the experiment values. Meanwhile, the high value of k_2 suggested that Cr(III) could be adsorbed rapidly on SPR and biochar because k_2 means the rate constant for the pseudo-second-order kinetic equation. Therefore, pseudo-second-order kinetic model could be used to describe Cr(III) adsorption of on SPR and biochar. These results were also observed in the adsorption of Cd(II) on activated carbon from olive stone[41].

4 Conclusions

1) The pH, temperature, chromium concentration and adsorbent dosage have great effects on Cr(III) adsorption by SPR and biochar and Cr(III) adsorption amount increases with the increase of pH, temperature, chromium concentration or adsorbent dosage.

2) Although SPR could adsorb Cr(III) from aqueous solution, the efficiency of Cr(III) adsorption by SPR is relatively low. However, a biochar obtained from SPR is an effective adsorbent for Cr(III) adsorption. The maximum adsorption capacity of Cr(III) by biochar was 15.32 mg/g. The results suggest that biochar is an efficient adsorbent in the removal of Cr(III) from industrial wastewaters.

3) Cr(III) adsorption by SPR and biochar can be well described using Langmuir and Freundlich models. It is found that Cr(III) sorption process onto SPR is spontaneous while onto biochar is non-spontaneous. Moreover, biochar has a larger affinity for Cr(III) adsorption than SPR.

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