THE STUDY OF NON-LINEAR ISOTHERMS FOR COBALT ADSORPTION

Peyman Salaryan*, Fanoos Mokari

Young Researchers Club, I.A.U, Kazerun Branch, P.O.Box168 / 73135, Kazerun, Iran

*Correspondence author. Tel; +987212230505, fax; +987212230508, Email: peyman_salaryan@yahoo.com

ABSTRACT

In this work, removal of Co (II) from aqueous solutions by Black Carbon (BC) derived from Rice Straw (RS) was studied. The parameters for adsorption process such as pH, adsorbent dose and contact time were investigated. In order to evaluate equilibrium isotherms, The Langmuir, Freundlich, Sips and Redlich–Peterson isotherms were modeled with non-linear method.The adsorption of Co (II) on BC was best described by Sips model.

INTRODUCTION

Heavy metals released into the environment are as pollutant and a result of industrial activities and technological development. These metals cause significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence nature [1].The main industrial use of cobalt (Co) is in the production of high-grade steels, alloys, super alloys, magnetic alloys, pigment, glass decolourizer, and as a drying agent in paints, varnishes, enamels, and inks[2]. The maximum concentration limit (MCL) of Co (II) for the drinking water is 2 mg/L [3]. The high levels of Co (II) cause the problems such as tremor, diarrhea and high blood pressure [3]. Thus, Cobalt containing wastewaters must be treated to lower the Co (II) to allowable limits before discharge to environment. There are conventional techniques for removal of heavy metals from aqueous solutions [4,5].However, these techniques have their own limitations include less efficiency, sensitive operating conditions and theirs high-cost. Adsorption is one of the most popular and effective processes for the removal of heavy metals from wastewater [6]. However, the high cost of activated carbon and its loss during the regenerations limits its application. As well as, activated carbon is employed more frequently for adsorption of organic compounds rather than heavy metal ions. The adsorption with low-cost adsorbent recently was used for the removal heavy metals [7]. The RS does not have any use in the south of Iran. Farmers in agricultural lands burn it as waste. However, the RC could be used as adsorbent for the removal of heavy metals. In this work, the ability of the BC from the RC as adsorbent for the removal of Co (II) was studied.

EXPERIMENTAL

All chemicals were of analytical reagent grade. The Co (Cl_2) was purchased from Merck. All of the solutions were prepared by dissolving Co (Cl_2) using dual distilled water (DDW). The RS was collected from agricultural lands in Mamasani County (Fars province, Iran). The RS was burned in free air. In order to remove impurity, the particles were washed by DDW. The particles were screened through 60-mesh (0.250mm)., The BC obtained was suspended in a 3:1 mixture of conc. H_2SO_4 and conc. HNO_3 at 20 °C for 10 hours. In order to remove extra acid the BC was washed with DDW and dried at 100 °C for 12 hours. The BC obtained was used as acidically modified black carbon (AMBC) in the adsorption experiments. All of the experiments were carried out at 20 °C.

Effect of pH

The AMBC (0.3 g) and the Co (II) solution (100 mg/L, 80 mL) were transferred to an Erlenmeyer flask. The initial pH (pH_0) of the solution was increased from 2.5 to 10 by adding

0.01M H_2SO_4 or 0.1M NaOH solution. The samples were agitated at 400 rpm for 30 min.Then the solutions were filtered through filter paper and the filtrates were analyzed to determine Co (II) content using the Atomic Absorption Spectroscopy (AAS) method with the PHILIPS PU9100X apparatus.

Effect of adsorbent dose

The effect of AMBC dose on the equilibrium uptake of Co (II) was performed by shaking of AMBC (0.1-0.6 g) with 80mL of Co (II) ion (100 mg/L) at 400 rpm for 120min. the pH was adjusted in 5.5. The final solutions were filtered and analyzed using AAS method.

Effect of contact time

The kinetic experiments were performed using Co (II) (100 mg/L, 80 mL) with 0.6 g AMBC. The experiments were controlled at pH 5.5 and the adsorption time varied from 30 to 240 min. the residual concentration Co (II) was determined with AAS method.

Adsorption isotherms

Adsorption isotherm studies were carried out using seven different initial Co (II) concentrations varying from 20 to 100 mg/L. The initial pH was adjusted in 5.5. The adsorbent dose was used 0.6 gr. The solutions were agitated at 400rpm for 150min. The volume of solutions was 80 mL.

RESULTS

Effect of pH

The effect of solution pH on the amount of the adsorption was studied by varying the initial pH under constant process parameters at equilibrium conditions. The results of Co (II) removal in the pH-effect experiment are presented in Fig.1. As seen in this figure, the pH has important effect on the removal percentage of Co (II).A sharp increase in the removal percentage for Co (II)in pH range of 2.5 to 5.5 was observed and the removal percentage of Co (II) increased up to 70%. In the pH range of 5.5–8, only a modest increase in the removal percentage of AMBC for Co (II) observed. A sharp increase in Co (II) removal above pH 8 was noted. The maximum uptake of Co (II) occurred at a pH of 5.5.At low pH, the adsorption capacity for Co (II) is very low, because large quantity of hydrogen ions competes with metal ions at sorption sites. As the pH increasing, more negatively charged surface become available thus facilitating greater metal uptake [7]. At above pH 8, metal precipitates and inhibit the metal contact with AMBC.

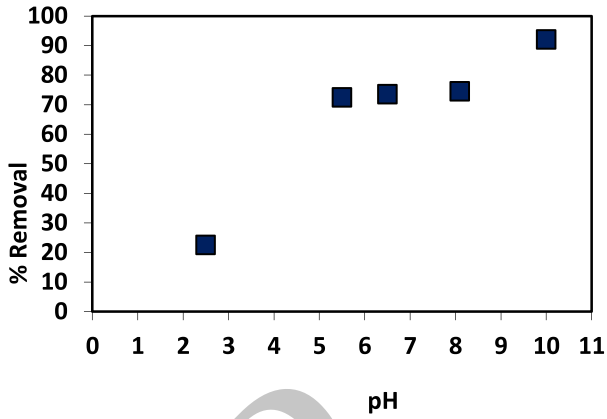

Fig.1- Effect of initial pH on the adsorption of Co (II) by AMBC.

Effect of AMBC dose

Fig.2 shows the effect of AMBC dose on the Co (II) sorption. The experiments were carried out at different doses of AMBC ranging from 0.1 to 0.6 g. when the amount of AMBC dose increased from 0.1 to 0.6 g, the Co (II) removal increased. This could be due to the available more binding sites for the adsorption of Co (II) ions .However higher removal was not showed with the increase of AMBC dose which may be due to the coverage of active sites of the AMBC at higher dose.

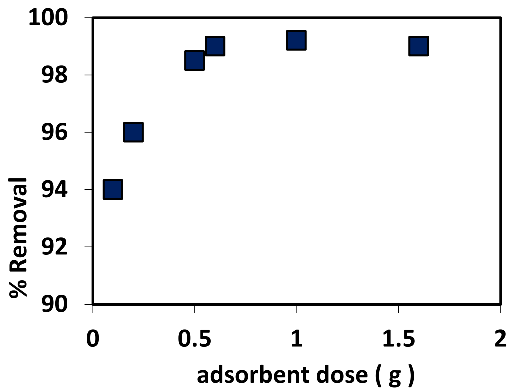

Fig.2- Effect of adsorbent dose on the adsorption of Co (II) by AMBC.

Effect of contact time

The adsorption experiments were carried out for contact times ranging from30to240 min with fixed amounts of adsorbent (0.6 g) at 20 °C while keeping all other parameters constant. The effect of contact time on the removal percentage of Co (II) is shown in Fig.3.The removal percentage increases with the increase of contact time. As seen from Fig.3, the removal percentage increased from 77% to 89% with the increase of contact time from 30 to 60 min. According to obtained data, the highest value of the removal of Co (II) ion on the AMBC was reached for 150 min.

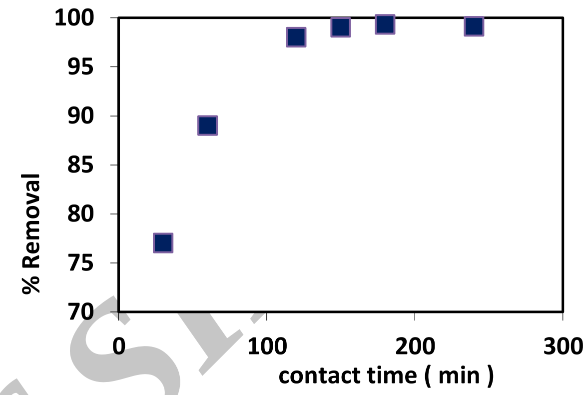

Fig.3- Effect of contact time on the adsorption of Co (II) by AMBC

Adsorption isotherms

The *Chi-square analysis* was frequently used to determine the best-fitting isotherm equations. The *Chi-square analysis* was expressed [8]:

$$\chi^2=\Sigma((q_e-q_{e,m})^2/q_{e,m}) \qquad (1)$$

Where q_e equilibrium capacity (mg/g) obtained from the experimental data and $q_{e,\ m}$ was the equilibrium capacity obtained by calculated from model (mg/g).If data from the model were similar to experimental data, χ^2 would be a small number, if they were different, χ^2 would be a large number. In addition, the correlation coefficient (r^2, values close or equal to 1) was used for the best fitting isotherm equations.

Different isotherm models were used to describe the Co (II) adsorption onto the AMBC.

The Langmuir isotherm is represented as follows[9]:

$$q_e=q_{max}K_LC_e/(1+K_LC_e) \qquad (2)$$

Where q_e is the concentration of adsorbate in solid phase at equilibrium (mg/g), C_e is the concentration of adsorbate in liquid phase at equilibrium (mg/L), q_{max} (mg/g) is the maximum adsorption capacity and K_L (L/mg) is the Langmuir constant.

The Freundlich isotherm is represented as follows[10]:

$$q_e=K_FC_e^{1/n} \qquad (3)$$

Where K_F((mg/g) (L/mg) $^{1/n}$) and n are the Freundlich constants.

The Sips equation is given as follows[11]:

$$q_e=q_{max}(K_sC_e)^{\gamma}/(1+(K_sC_e)^{\gamma}) \qquad (5)$$

Where γ is the parameter characterizing the heterogeneity of system and K_s is a constant.

The Redlich- Peterson isotherm has the following form[12]:

$$q_e=K_{RP}C_e/(1+aC_e^{\beta}) \qquad (6)$$

Where K_{RP} (L/g), a (L/mmol) and β are Redlich-Peterson constants.

Analysis of isotherms

Equilibrium studies were performed to evaluate the best-fit isotherm models for explaining the adsorption of Co (II) onto AMBC.The plots of non-linear form of Langmuir, Freundlich, Sips and Redlich–Peterson adsorption isotherms of Co (II) ions obtained at 20°C, ar epresented in Fig.4 and 5. Table 1 shows all of the isotherm model parameters for the adsorption of Co(II) ions onto AMBC. The values χ^2 and r^2show that the adsorption of Co (II) ions onto AMBC is fitted well to Sips isotherm than the other models. From the analysis of Sips isotherm, the maximum adsorption capacity (q_{max}) of AMBC was obtained at 10.771 mg/g. The parameter γ was obtained 1.688.

CONCLUSION

The Co (II) adsorption was studied under different pH, adsorbent dose and contact time. The studies of non-linear isotherms of the adsorption were investigated. The following conclusions can be extracted from this study:

1) The maximum adsorption of Co (II) from aqueous solutions occurred at pH 5.5, 0.6 g adsorbent dose and 150 min contact time.
2) The Sips adsorption isotherm adequately fit the experimental data.

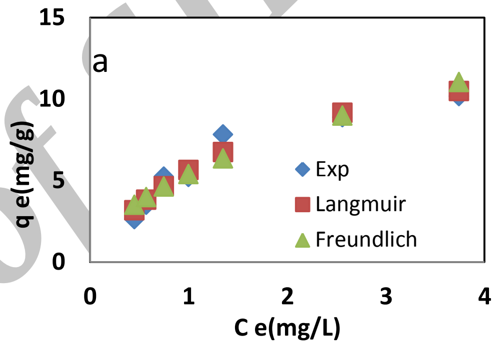

Fig4. Langmuir and Freundlich isotherms.

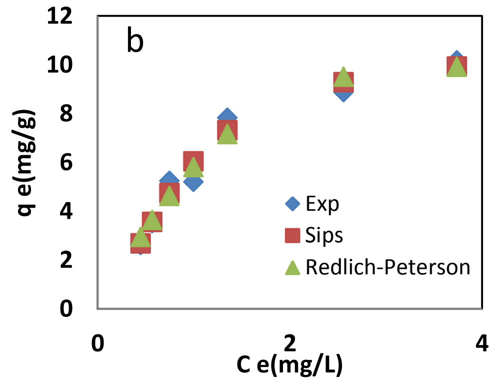

Fig5. Sips and Redlich-Peterson isotherms.

Table1. Isotherm parameters

Isotherm	parameters	
Langmuir	q_{max}(mg/g)	15.309
	K_L (L/mg)	0.581
	r^2	0.992
	χ^2	0.426
Freundlich	K_f((mg/g) (L/mg) $^{1/n}$)	5.388
	n	1.844
	r^2	0.986
	χ^2	0.78
Sips	q_{max}(mg/g)	10.771
	K_s	1.154
	γ	1.688
	r^2	0.995
	χ^2	0.230
Redlich-Peterson	K_{RP}	6.824
	a	0.175
	β	1.667
	r^2	0.994
	χ^2	0.299

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Nomenclature

r^2 is the correlation coefficient

χ^2 is the value related to the Chi-square analysis

$q_{e,\ m}$ is the equilibrium capacity obtained from isotherm model (mg/g)

C_e is the concentration of adsorbate in liquid phaseat equilibrium (mg/L)

q_{max} is the maximum adsorption capacity(mg/g)

K_L is the Langmuir constant(L/mg)

K_F is the Freundlich constant((mg/g) (L/mg) $^{1/n}$)

n is the Freundlich constant

γ is the parameter characterizing the heterogeneity of system

K_s is The Sips constant

K_{RP} is the Redlich-Peterson constant(L/g)

A is the Redlich-Peterson constant(L/mmol)

β is the Redlich-Peterson constant