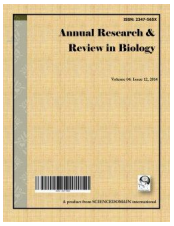

Annual Research & Review in Biology

22(5): 1-9, 2018; Article no.ARRB.38998
ISSN: 2347-565X, NLM ID: 101632869

Adsorption Isotherm and Thermodynamic Profile of Hexavalent Chromium onto Lumbang (*Aleurites moluccana*) Activated Carbon Chitosan Composite Crosslinked with Epichlorohydrin

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/ARRB/2018/38998
Editor(s):
(1) Saleha Sadeeqa, Incharge Institute of Pharmacy, Lahore College for Women University, Pakistan.
(2) George Perry, Dean and Professor of Biology, University of Texas at San Antonio, USA.
Reviewers:
(1) Imran Ali, Jamia Millia Islamia, India.
(2) Farid I. El-Dossoki, Port Said University, Egypt.
Complete Peer review History: http://www.sciencedomain.org/review-history/22819

Original Research Article

Received 26th December 2017
Accepted 15th January 2018
Published 23rd January 2018

ABSTRACT

Adsorption isotherm and thermodynamic profile of hexavalent chromium onto lumbang (*Aleurites moluccana*) activated carbon chitosan composite crosslinked with epichlorohydrin were studied. The optimum conditions were identified at pH 3, contact time of 75 min, adsorbent dose of 3 g/L, initial concentration of 60 ppm, and 30ºC temperature resulted to a removal efficiency of 93%. The composite has a round and elliptical adsorption sites, contains –OH and $–NH_2$ functional groups, and has increased stability with epichlorohydrin crosslinking. The adsorption process is best characterized by the Langmuir isotherm suggesting a monolayer adsorption nature of Cr(VI). The

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adsorption kinetics obeyed the pseudo-second order model and the adsorption process is exothermic. The investigated adsorption phenomenon described a chemisorption process, with 21.32 kJ mol^{-1} mean free energy, due to the functional groups identified and the high porosity of the adsorbent surfaces.

Keywords: Adsorption isotherm; thermodynamics; carbon chitosan composite; chromium; lumbang; Aleurites moluccana.

1. INTRODUCTION

Chromium (Cr) is present in wastewaters as Cr(VI) [1] in oxyanion forms [2,3]. Cr(VI) has high solubility, is toxic to living organisms [4], and causes health disorders when ingested beyond 0.1 mg/L [5]. Because of the environmental and health concerns, various methods were employed to monitor and remove the concentration of Cr(VI) in wastewater systems. Of the different methods for the removal of pollutants from wastewater, adsorption remains the most efficient and cost-effective. The use of low-cost biosorbents [6,7] have been given increasing attention for these can reduce the cost of an adsorption system significantly [8].

In some cases, adsorbents are coated by chitosan, a derivative of chitin [9] and an amino polysaccharide [10], because of the high sorption capacities of modified chitosan for metal ions. Moreover, activated carbon which is usually derived from charcoal has long been used as an adsorbent for water filtration [11]. However, high cost of adsorption studies using activated carbon led researchers to develop modified activated carbon varieties that allow higher adsorption while using smaller amount of the pure activated carbon such as preparation of a carbon composite made by adding activated carbon on a chitosan gel [12]. Studies have also obtained composites of activated biocharcoal from cocoa husk [13] and palm shell [14] with chitosan. Furthermore, many have opted to crosslink chitosan with glutamate [15], genipin [16], glutaraldehyde [17], and glycine [18] to increase its mechanical stability and decrease its solubility. The crosslinking mechanism has not yet been fully elucidated, but possible structures have been proposed based on their reactivity with the functional groups present in chitosan. Hence, the present study investigated the utility of epichlorohydrin-crosslinked lumbang (*Aleurites moluccana*) activated carbon chitosan composite as an efficient and economic biosorbent for the removal of Cr(VI) in aqueous solutions. Surface chemistry and thermal analysis of the composite, biosorption kinetics, adsorption isotherm, and thermodynamic profile of the composite were also examined. Given that pollution of surface water by toxic heavy metals from industrial sources is a serious environmental and health concern, this study promises to provide useful applications in industries producing high concentrations of heavy metal ions as wastes and a useful method in the reduction of agricultural wastes being utilized in the treatment of contaminated bodies of water.

2. MATERIALS AND METHODS

2.1 Synthesis of Biosorbent, Carbon Activation, and Crosslinking

Synthesis of the biosorbent and activation of biocharcoal were performed as mentioned in the previous studies [7,19]. Lumbang (*Aleurites moluccana*) seeds were obtained from the College of Forestry, University of the Philippines Los Baños, Philippines. The shells were separated from the nuts and washed several times, sundried for a day, and subsequently pulverized into small pieces. Pyrolysis was performed for 5 h using the traditional burrow method. The collected charcoal was cooled, washed thoroughly with deionized water, pulverized into smaller particle sizes (0.149 - 0.250 mm), and soaked in 25% $CaCl_2$ for a day. Using deionized water, the activated biocharcoal was washed thoroughly and oven dried at 100°C for 6 h.

The activated carbon was coated with chitosan [12]. In a liter of 0.4 M oxalic acid solution, 25 g chitosan (75% minimum deacetylation) was added while continuously stirring at 45ºC - 50ºC. Subsequently, 50 g of activated biocharcoal was added, mixed thoroughly for 2 h using a mechanical blender, and the obtained slurry was oven dried at 100ºC for 24 h. Using a manual grinder, the dried composite was reduced to smaller sizes (0.250 mm-0.420 mm) with pH adjusted to neutrality, and oven dried again. Under continuous stirring and at 50ºC, a neutral

solution of 40 mM epichlorohydrin (Sigma-Aldrich) was added in the composite for crosslinking.

2.2 Surface Chemistry and Thermal Analysis of the Composite

As mentioned in the previous study [19], the surface morphology of the composite was visualized using scanning electron microscopy by Analytical Services Laboratory, University of Santo Tomas, Manila, Philippines. The determination on the presence of functional groups on the surface of the adsorbent before and after adsorption was done using Thermo Scientific Nicolet 6700 FT-IR by the Chemistry Department, De La Salle University, Manila, Philippines.

In the present study, differential scanning calorimetry was employed for the thermal analysis of the composite. Thermal analysis of activated carbon, activated carbon chitosan, and activated carbon chitosan composite was performed using Perkin Elmer DSC 400 calorimeter at the Chemistry Laboratory, University of the Philippines Manila, Philippines.

2.3 Biosorption Studies

A 0.424 g of $K_2Cr_2O_7$ was dissolved in deionized water to prepare a 1000 ppm Cr(VI) stock solution. The change in Cr(VI) concentration due to adsorption was determined [20]. A purple-violet colored complex was developed in the reaction between Cr(VI) and 1,5-diphenylcarbazide in acidic condition and the resulting solutions were analysed using Perkin Elmer Lambda 2000 UV-Vis spectrophotometry at 540 nm.

Adsorption experiments, as performed in the previous study [7], were done in triplicates using 15-mL conical flasks. Agitation and incubation were done using SHZ-82A water bath.

2.4 Adsorption Isotherm

Adsorption isotherms are necessary for the design of adsorption systems reflecting the equilibrium relationship between the amount adsorbed and of adsorbate in the solution. Results will provide information about the capacity of the adsorbent such as the amount of adsorbent needed to remove a unit mass of the adsorbate under the specified conditions. Experimental values obtained from the present study were analyzed using the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich adsorption isotherms.

3. RESULTS AND DISCUSSION

3.1 Surface Chemistry and Thermal Analysis of the Composite

As revealed in the previous study [19], the synthesized biosorbent has a bulk density of 0.46 g/cm^3 which is above the established value of 0.40 g/cm^3 [21] for highly porous adsorbents. Moreover, the surface morphology of the activated carbon chitosan composite crosslinked with epichlorohydrin adsorbent showed highly porous structures with an accumulation of the metal around and inside the adsorbent pores [19], while the FTIR spectra of the composite identified the presence of several functional groups such as O-H, C-H, C=O, –NH, and –NH_2 [19].

In the present study, the differential scanning calorimetry thermogram detailed the effect of chitosan coating and epichlorohydrin crosslinking in the activated carbon (Fig. 1). Common endothermic peaks present in the samples were observed at temperatures of about 73.27ºC, 77.49ºC and 65.62ºC indicating the crystallization temperature due to the loss of water. Appearance of a similar exothermic peak was observed in the non-crosslinked and crosslinked chitosan coated activated carbon at 300.53ºC and 301.32ºC, respectively. This common peak did not appear in the uncoated activated carbon possibly due to the decomposition of chitosan coated in the activated carbon. The effect of crosslinking can be observed due to the increase in stability prior to complete decomposition at the exothermic peak. Epichlorohydrin-crosslinked chitosan has a higher adsorption capacity [22] since epichlorohydrin predominantly reacts with the hydroxyl group in chitosan, consuming only about 18% of the amino groups present as compared to glutaraldehyde-crosslinked chitosan since glutaraldehyde reacts with the amino groups to form an imine, while epichlorohydrin reacts with the hydroxyl groups to form an ether bond [23].

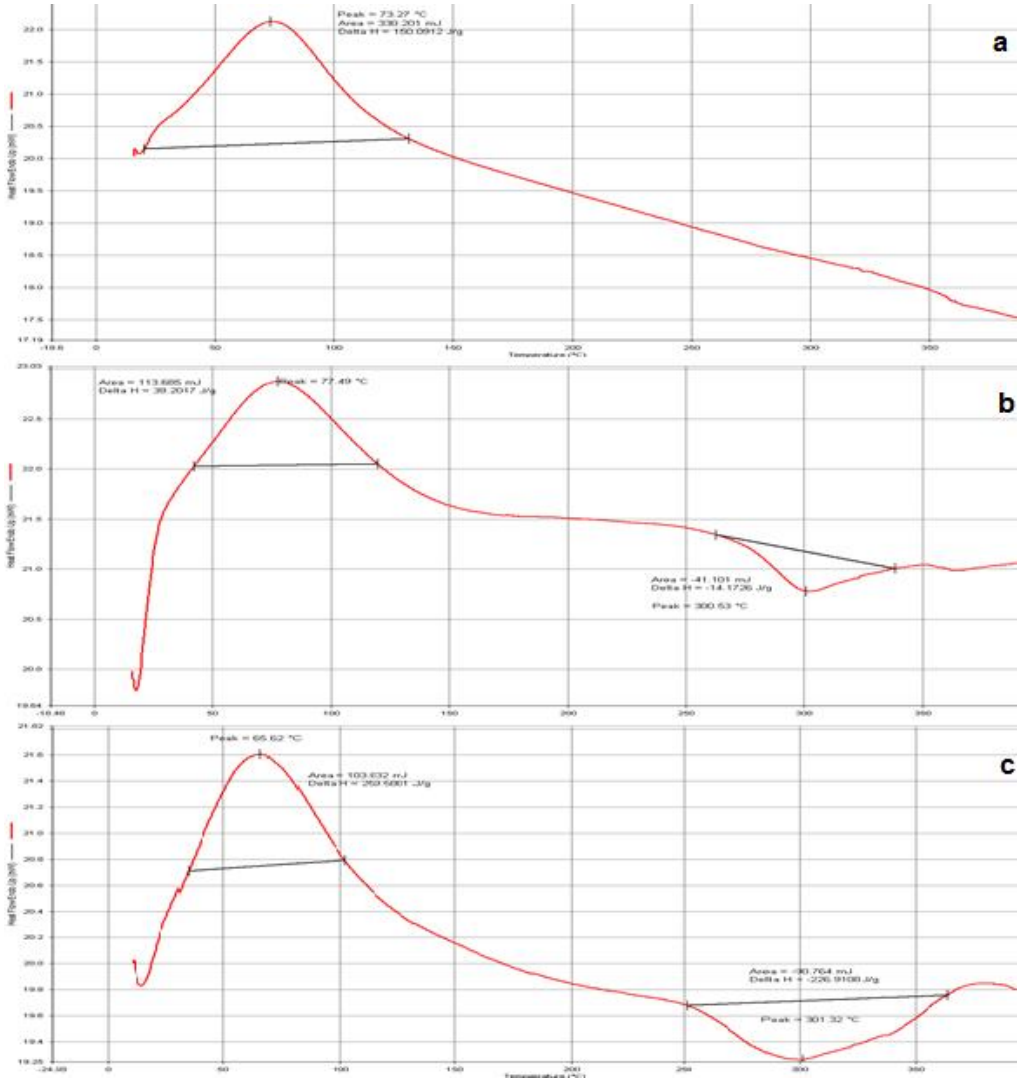

Fig. 1. Differential scanning calorimetry profile of (a) activated carbon, (b) activated carbon chitosan, (c) activated carbon chitosan crosslinked with epichlorohydrin

3.2 Adsorption Capacities and Kinetic Studies

In the previous study [7], comparison on adsorption capacities of the different prepared adsorbents from lumbang was performed using the optimized conditions for the crosslinked activated carbon chitosan composite in the removal of Cr(VI) ions. The synthesized composite adsorbed 93.52% Cr(VI) at the optimized conditions of pH 3, contact time of 75 min, metal concentration of 50 ppm, adsorbent dosage of 3 g/L, temperature of 30ºC, and agitation speed of 160 rpm [7,19]. Moreover, the adsorption process behaved under a pseudo-second order kinetic model [7] suggesting that the adsorption process was affected by intraparticle diffusion and was a combination of physisorption and chemisorption processes [7].

3.3 Adsorption Isotherms and Thermodynamics Study

3.3.1 Langmuir isotherm

For nonlinear adsorption process, Langmuir isotherm is employed and is applicable over a wide range of values exhibiting limiting or maximum adsorption capacities [24]. It is also applicable for monolayer adsorption onto a finite number of identical sites [25] as this model assumes that the adsorption activation energy is

the same at all sites and there is no interaction between the adsorbed ions [26]. The Langmuir equation is expressed as

$$\frac{Ce}{qE} = \frac{Ce}{Qo} + \frac{1}{Qo\beta}$$

where, qE (mg/g) is the concentration of the adsorbate in the adsorbent at equilibrium, Ce (mg/L) concentration of the adsorbate in the solution at equilibrium, Qo (mg/g) is the maximum adsorption capacity of the adsorbent, and β (L/mg) is the Langmuir constant. The adsorption isotherm profile using Langmuir equation is generated by plotting Ce against Ce/qE (Fig. 2a). The efficiency of adsorption (R_L) can be computed by using the Langmuir parameters Qo and β, and substituted to the equation

$$R_L = \frac{1}{1 + \beta\, Co}$$

If R_L = 0, it indicates an irreversible adsorption; R_L = 1 suggests a linear adsorption; R_L > 1 is an unfavorable, while 0 < R_L < 1 suggests a favorable adsorption process [27].

3.3.2 Freundlich isotherm

Freundlich isotherm considers variations of energy at different adsorption sites, identifies adsorption through a heterogeneous surface, and describes multilayer adsorption mechanism [28]. This isotherm is only applicable on high adsorbate concentrations since low-concentration environment does not meet the requirements of Henry's law. This isotherm also shows that the amount adsorbed increases with increasing concentration as shown by the equation

$$qE = K_f Ce^{1/n}$$

where K_f (mg/g) indicates adsorption capacity and 1/n is the adsorption intensity. Batch equilibrium data can be applied to this isotherm by converting to its linear form

$$\ln qE = \ln K_f + \frac{1}{n} \ln Ce$$

The parameters of Freundlich isotherm is obtained by plotting ln qE against ln Ce (Fig. 2b). Adsorption is considered satisfactory when the computed n falls between 1 to 10 [26]. If the value of 1/n is less than one, then it indicates a normal adsorption, while a value greater one means cooperative adsorption.

3.3.3 Temkin isotherm

Temkin isotherm assumes that the heat of adsorption decreases linearly rather than logarithmically [25] as implied in the Freundlich isotherm. Adsorbate-adsorbate interaction is given importance in this isotherm rather than concentration, the decrease in heat of adsorption is associated by the adsorbate-adsorbate interaction. The linear form of Temkin is:

$$qE = k_1 \ln(k_2) + k_1 \ln(Ce)$$

where $k_1 = \frac{RT}{b}$ (L/mg) is the heat of adsorption, and k_2 is a dimensionless Temkin constant. Parameters of Temkin isotherm were obtained by plotting qE against ln Ce (Fig. 2c).

3.3.4 Dubinin-Radushkevich

The porosity of the biomass and apparent energy of adsorption can be characterized by Dubinin-Radushkevich isotherm [29]. The linear equation of the isotherm is

$$\ln qE = \ln qT - 2(Bd)RT \ln\left(1 + \frac{1}{Ce}\right)$$

where Bd is related to free energy of sorption per mole of the adsorbent, and qT is the isotherm constant which relates the rate of sorbate sorption to the adsorbent. Isotherm constants of this equation can be computed by plotting ln qE against RT ln (1 + 1/Ce) (Fig. 2d). The higher the qT value, the higher the adsorption capacity. This approach is employed to determine the physical and chemical adsorption of metal with its mean energy. The apparent energy of adsorption (E) from this isotherm can be calculated by using the equation [30]

$$E = \frac{1}{(2Bd)^{\frac{1}{2}}}$$

Using the different adsorption isotherms on the experimentally obtained data, the parameters of these different isotherms were determined (Table 1). The Langmuir isotherm plot shows a maximum monolayer coverage capacity (Qo) of 11.96 mg/g with a Langmuir isotherm constant (β) of 1.32 L/mg. The separation factor R_L was within the range (0,1) in all concentrations which indicates a favorable equilibrium adsorption. The

adsorption process is well characterized by the Langmuir isotherm, with coefficient of determination close to unity (R^2 = 0.9946). However, when adsorption capacity was assessed using Freundlich isotherm, the adsorption capacity K_f has a value of 6.13 and an n of 5.60. Since the value of 1/n is less than 1, this indicates a normal adsorption process, as a favorable sorption process is observed when n lies between 1 to 10 [31]. Assessment on the adequacy on the goodness of fit of Freundlich isotherm revealed an R^2 value of 0.9168. Moreover, using Dubinin-Radushkevich isotherm, the mean free energy (E) of the system was found to be 21.32 kJ/mol. The value of the mean free energy (E) of adsorption for the Dubinin-Radushkevich isotherm indicates whether the adsorption process is physisorption, an ion exchange, or a strong chemical adsorption. An E value less than 8 kJ/mol signifies physisorption, whereas between 8 and 16 kJ/mol suggests an ion exchange, and over 16 kJ/mol a stronger chemical adsorption than ion exchange [32,33,34]. Hence, the adsorption process described in this study is a strong chemical adsorption process than a physisorption adsorption mechanism or an ion exchange.

Table 1. Isotherm parameters for adsorption of Cr(VI) onto lumbang activated carbon chitosan composite crosslinked with epichlorohydrin at pH 3

Isotherm	Parameter estimates	
Langmuir	R^2	0.9946
	Qo	11.9617
	β	1.3228
	R_L	0.0594
Freundlich	R^2	0.9168
	Kf	6.1331
	n	5.6022
Temkin	R^2	0.9055
	k_1	2.0577
	k_2	8.0141
Dubinin-Radushkevich	R^2	0.8733
	Bd	0.0011
	qT	13.6959
	E	21.3201

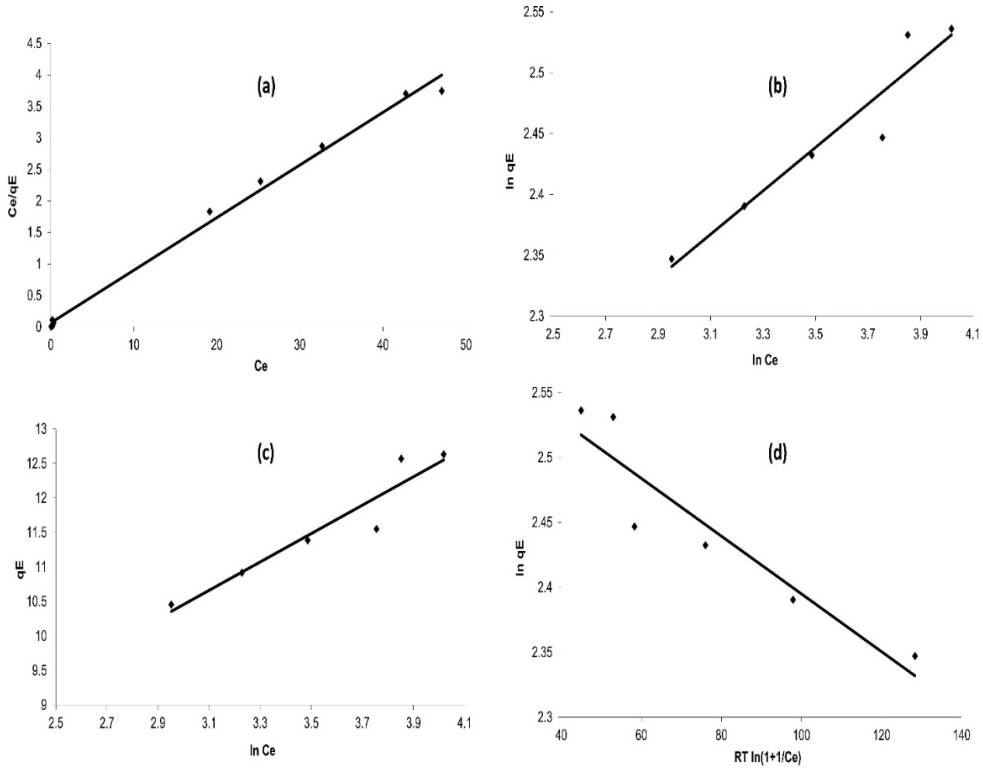

Fig. 2. Adsorption isotherm profile using (a) Langmuir, (b) Freundlich, (c) Temkin and (d) Dubinin-Radushkevich isotherm equation

3.3.5 Thermodynamics study

The nature of adsorption of Cr(VI) ions to the adsorbent was also predicted by thermodynamics principles. The Gibbs free energy and thermodynamic parameters were computed using the equation

$$\ln K = \frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R}$$

And, this equation was employed to determine the thermodynamic parameters, ΔH and ΔS, by plotting ln K vs 1/T. The obtained linear equation has an adequate fit (R^2 = 0.9210), and using the obtained values for the slope and y-intercept, the Gibbs free energy was calculated using the equation

$$G = \Delta H - T\Delta S$$

with ΔH = 1591.54, ΔS = 11.73, and Gibbs free energy of -1964.41 at 303.15 K indicating an exothermic adsorption process.

4. CONCLUSION

Adsorption isotherm and thermodynamic profile of Cr(VI) onto lumbang (*Aleurites moluccana*) activated carbon chitosan composite crosslinked with epichlorohydrin were studied. The optimum conditions were identified at pH 3, contact time of 75 min, adsorbent dose of 3 g/L, initial concentration of 60 ppm, and 30ºC temperature resulted to a removal efficiency of 93%. The composite has a porous texture with round and elliptical adsorption sites, contains –OH and–NH_2 functional groups, and has increased stability with crosslinking. The Langmuir isotherm model gives best fit with the equilibrium adsorption data suggesting a monolayer adsorption nature of Cr(VI). The adsorption kinetics obeyed the pseudo-second order model and the adsorption process was exothermic. The investigated adsorption phenomenon described a chemisorption process due to the functional groups identified and the high porosity of the adsorbent surfaces.

ACKNOWLEDGEMENT

This work was funded by the UP System Enhanced Creative Work and Research Grant (ECWRG-2015-2-021).

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history/22819