



Synthesis and Characterization of Epichlorohydrin-Crosslinked Lumbang (*Aleurites moluccana*)-Derived Activated Carbon Chitosan Composite as Cr(VI) Bioadsorbent

Angelo Patrick R. Bautista¹, Derick Erl P. Sumalapao^{2,3*}
and Nelson R. Villarante¹

¹Department of Physical Sciences and Mathematics, College of Arts and Sciences, University of the Philippines Manila, Manila, Philippines.

²Department of Biology, College of Science, De La Salle University, Manila, Philippines.

³Department of Medical Microbiology, College of Public Health, University of the Philippines Manila, Manila, Philippines.

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/2017/38259

Editor(s):

- (1) J. David Puett, Professor, Department of Biochemistry and Molecular Biology, University of Georgia, Athens, USA.
(2) George Perry, Dean and Professor of Biology, University of Texas at San Antonio, USA.

Reviewers:

- (1) Nüket Tirtom, Celal Bayar University, Turkey.
(2) Julian Cruz-Olivares, Autonomous University of State of Mexico, Mexico.
Complete Peer review History: <http://www.sciencedomain.org/review-history/22318>

Original Research Article

Received 20th November 2017
Accepted 6th December 2017
Published 16th December 2017

ABSTRACT

Lumbang (*Aleurites moluccana*) activated carbon chitosan composite crosslinked with epichlorohydrin was synthesized for batch adsorption of toxic Cr(VI) ion from an aqueous solution. The synthesized biosorbent was characterized by instrumental techniques such as FTIR and SEM. The surface morphology of the adsorbent had a porous texture with round- and elliptical-shaped voids as adsorption sites for the adsorbate. Some functionalities including –OH and –NH₂ groups were identified on the surfaces. The synthesized activated lumbang-biocharcoal chitosan composite crosslinked with epichlorohydrin adsorbent at the optimized conditions adsorbed 93% of Cr(VI) ion. The investigated adsorption phenomenon described a chemisorption process due to the functional groups identified and the high porosity of the adsorbent surfaces.

*Corresponding author: E-mail: derick.sumalapao@dlsu.edu.ph;

Keywords: *Lumbang; Aleurites moluccana; chromium; carbon-chitosan composite; SEM; FTIR; chemisorption; epichlorohydrin crosslinking.*

1. INTRODUCTION

High amount of wastes and toxic pollutants produced by different industries along with improper disposal subsequently led to the contamination of natural water. One of these toxic pollutants is chromium (Cr) which is present in wastewaters as Cr(VI) in the form of oxyanions [1]. Depending on pH and Cr concentration, Cr(VI) at 25°C exists in different forms [2,3]. Cr(VI) is very toxic to living organisms compared to Cr(III) because of its high solubility [4] and ingestion of Cr(VI) at concentrations higher than 0.1 mg/L caused health disorders [5]. The hexavalent chromium causes damage to the DNA by forming inter-strand crosslinks, DNA-protein crosslinks, strand breaks, chromium adducts and radical-DNA adducts, and impairs the normal function of DNA as a template in replication and transcription [6]. Due to its threat on health and environmental contamination, monitoring of its concentration in wastewater systems is imperative and for subsequent removal of such pollutant.

In the removal of toxic metal ions, several methods were employed such as precipitation, adsorption, ion exchange, and membrane processes. Adsorption is recognized as an efficient method for the removal of pollutants from wastewater. Several improvements and innovation of this process have been developed including utility of biosorbents [7,8] because of the diversity of the readily available sorbent materials. However, with the high cost of adsorption studies, researchers modified the surface properties of various adsorbents, such as activated carbon, for better adsorption capacity. One of the commonly used coating material for activated carbon is chitosan.

Chitosan is obtained from the deacetylation of the natural biopolymer chitin abundantly present in the cell walls of insects, crustaceans, and fungi. Chitosan is very useful and effective in water remediation in adsorbing heavy metal ions, dyes, and proteins [9] due to its hydrophilic, biodegradable, non-toxic, biocompatible, and antimicrobial characteristics. Moreover, uncrosslinked chitosan has been used as a coating on several adsorbents such as ceramic alumina [10], polyvinyl chloride [11], bamboo [12], perlite [13], and sand [14] to improve adsorption capacity in the removal of heavy metals and dyes.

In a search for a better alternative adsorbent with high adsorption capacity, this study investigated the utility of epichlorohydrin-crosslinked lumbang-derived activated carbon chitosan composite as an efficient, safe, and cheap Cr(VI) biosorbent in aqueous solutions. The outer shells of lumbang (*Aleurites moluccana*) were used for activated carbon generation using traditional and low-cost method, and the activated carbon chitosan composite crosslinked with epichlorohydrin composite was prepared, synthesized, and partially characterized using SEM and FT-IR. Given how toxic heavy metals from industrial sources pollute surface waters, this present study provides possible applications in industries producing high amounts of heavy metal wastes and a feasible method in the reduction of agricultural wastes in addressing serious environmental pollution.

2. MATERIALS AND METHODS

2.1 Adsorbent Synthesis

2.1.1 Biocharcoal and activated carbon preparations

The seeds of lumbang (*Aleurites moluccana*) 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. Using the traditional burrow method, pyrolysis was performed for 5 h. The collected charcoal was cooled, washed thoroughly with deionized water, pulverized into smaller particle sizes (0.149 - 0.250 mm), and soaked in 25% CaCl₂ for 24 h. Using deionized water, the activated biocharcoal was washed thoroughly and oven dried at 100°C for 6 h.

2.1.2 Activated carbon-chitosan composite and epichlorohydrin crosslinking

The activated carbon was coated with chitosan [15]. In a liter of 0.4 M oxalic acid solution, 25 g chitosan (75% minimum deacetylation) was added while continuously stirring at 45 - 50°C. 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 100°C for 24 h. Using a manual grinder, the dried composite was reduced to smaller sizes (0.250 - 0.420 mm) with pH adjusted to neutrality, and oven dried again.

Under continuous stirring and at 50°C, a neutral solution of 40 mM epichlorohydrin (Sigma-Aldrich) was added in the composite for crosslinking.

2.2 Adsorbent Characterization

2.2.1 Bulk density and proximate analysis

Dried composite adsorbents were placed in 10-mL cylinders and filled to a specific volume. Initial and final weights of the cylinders were obtained, the bulk density was calculated by dividing the mass (g) of the dried composite material with the volume (cm³) of the dried composite adsorbents.

Analysis of ash content, crude fat, crude fiber, crude protein content, and moisture content was performed by the Biotech Central Analysis Laboratory, University of the Philippines Los Baños, Laguna, Philippines.

2.2.2 Scanning electron microscopy

The surface morphology of the composite was visualized by Analytical Services Laboratory, University of Santo Tomas, Manila, Philippines.

2.2.3 Surface Chemistry

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.

2.3 Biosorption Studies

2.3.1 Chromium ion stock solution and concentration quantification

A 0.424 g of K₂Cr₂O₇ 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 [16]. 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.

2.3.2 Batch adsorption experiments

Adsorption experiments [17] were performed in triplicates using 15-mL conical flasks. Agitation and incubation were done using SHZ-82A water bath.

2.3.3 Adsorption efficiency

The removal efficiency (E) of the adsorbent on Cr(VI) was calculated using the formula:

$$E (\% \text{ removal}) = \frac{\text{initial concentration} - \text{final concentration}}{\text{initial concentration}} \times 100$$

The Cr(VI) removal efficiencies of lumbang charcoal (LC), lumbang-activated charcoal (LAC), chitosan (CH), lumbang-activated charcoal chitosan (LAC-CH) composite, and lumbang-activated charcoal chitosan composite crosslinked with epichlorohydrin (LAC-CH-ECH) were compared under the optimal conditions.

3. RESULTS AND DISCUSSION

3.1 Characterization of the Composite

3.1.1 Bulk density and proximate analysis

The bulk density of the biosorbent was 0.46 g/cm³ which is above the established value of 0.40 g/cm³ for highly porous adsorbents. The presence of moisture in the adsorbent is expected due to its high surface area and adsorptive nature. Low percentage of ash indicates that the low-cost method of pyrolysis is an effective adsorbent preparation while low percentages of fat and protein are expected due to biomass pyrolysis. Moreover, there is a high crude fiber content found in the adsorbent (Table 1).

3.1.2 Surface morphology and chemistry

Scanning electron microscopy (SEM) was used to observe the surface morphology of the activated carbon chitosan composite crosslinked with epichlorohydrin adsorbent. Microstructures of the surface images of the adsorbent were captured before and after adsorption of Cr(VI) ions and high porosity was observed on these surfaces because of the evaporation of bound chemicals upon activation (Fig. 1). The surfaces and pores were clear before adsorption (Figs. 1a, 1c). After the adsorption, an accumulation of adsorbate residues was observed around and inside the adsorbent pores suggestive of Cr(VI) adsorption in aqueous solutions (Figs. 1b, 1d).

The FTIR spectra of the LAC-CH-ECH adsorbent before and after sorption of Cr(VI) identified the presence of functional groups and the changes

that occurred after adsorption (Fig. 2). The peak around 3417 cm^{-1} indicates the free hydroxyl group and amines while peaks observed at 2922 cm^{-1} and 2855.10 cm^{-1} can be associated with the C-H stretching vibration. Peaks around 1615 cm^{-1} correspond to C=O stretching of the amide group. Amine peaks are not visible in the spectra due to the overlap with the peaks of hydroxyl groups. The shift in peaks after adsorption corresponding to the $-\text{NH}$ bending vibrations of the $-\text{NH}_2$ groups reveals that this functional group is responsible for Cr(VI) adsorption on the adsorbent (Table 2).

Table 1. Proximate analysis of biosorbent with values reported as means \pm standard deviations

Moisture (%)	5.07 ± 0.02
Ash (%)	1.67 ± 0.02
Crude Fat (%)	3.51 ± 0.01
Crude Fiber (%)	72.43 ± 0.34
Protein (%)	1.81 ± 0.00

3.2 Adsorption Capacities

Comparison on adsorption capacities of the different prepared adsorbents from lumbang was

performed using the optimized conditions [17] for the crosslinked activated carbon chitosan composite in the removal of Cr(VI) ion (Table 3). The synthesized composite adsorbed 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 30°C , and agitation speed of 160 rpm [17].

Adsorption performance, including the rate and capacity, is affected by several factors such as the application process and the physical nature, source, and composition of the adsorbent. The activated carbon has higher removal percentage due to its more porous structure compared to the native charcoal. Chitosan yielded a 79.70% removal due to the interaction of its glucosamine groups with the Cr(VI) ion, consequently coating the chitosan into the activated carbon had resulted in a significant improvement in the adsorption (97.20% removal, $p < 0.05$). However, the crosslinked activated carbon chitosan composite yielded a relatively lower percentage removal (93.52%, $p > 0.05$) when compared to the uncrosslinked composite which suggests that crosslinking had resulted to the loss of free NH_2 functionality.

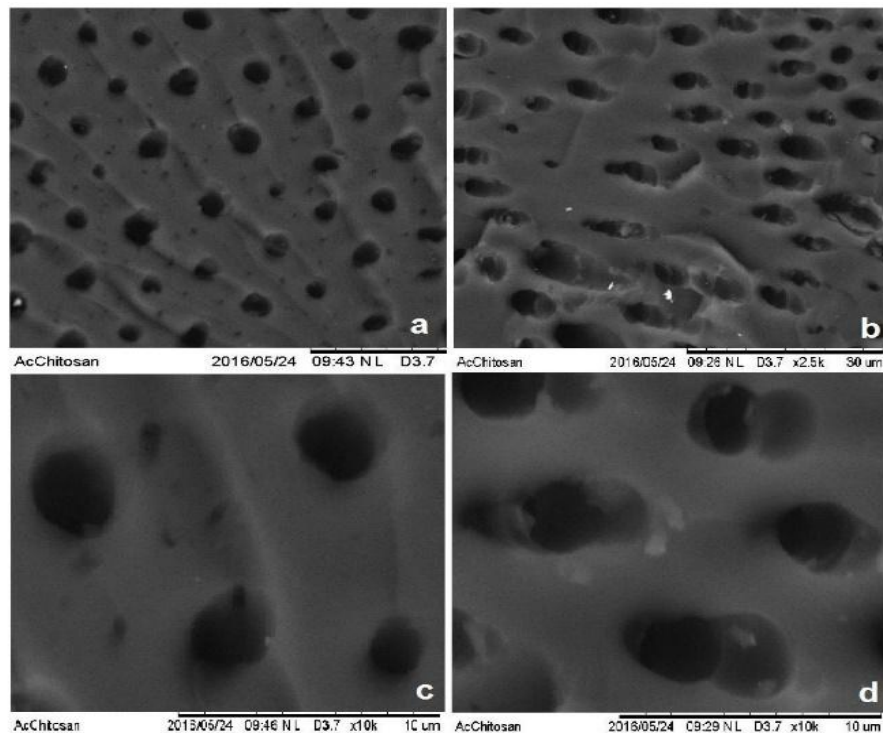


Fig. 1. Visualization of the activated carbon chitosan composite crosslinked with epichlorohydrin biosorbent material before (a, c) and after (b, d) adsorption process using scanning electron microscopy

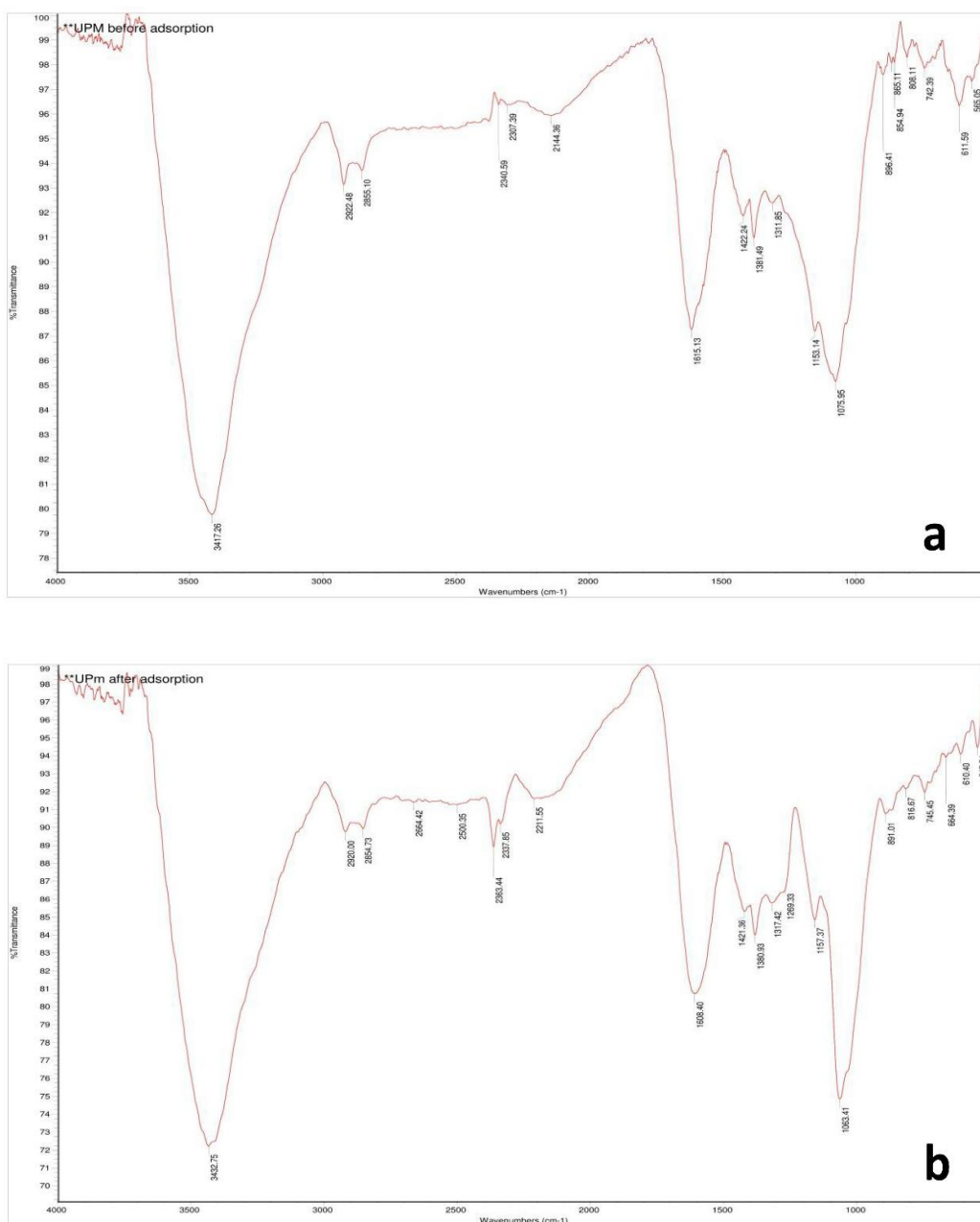


Fig. 2. FTIR spectra of lumbang-activated charcoal chitosan composite crosslinked with epichlorohydrin before (a) and after (b) adsorption process

Table 2. Comparison of peaks of lumbang-activated charcoal chitosan composite crosslinked with epichlorohydrin before and after adsorption process

Before adsorption peaks (cm ⁻¹)	After adsorption peaks (cm ⁻¹)	Functional group
1615.13	1608.49	C=O Stretch Amide Group
2855.10	2854.73	C-H Stretch
2922.48	2920.00	C-H Stretch
3417.26	3432.75	O-H Stretch, N-H Stretch

Table 3. Comparison on adsorption capacities of the different adsorbents in the removal of Cr(VI) ions

Adsorbent material	Percentage removal (mean \pm standard deviation)
Lumbang charcoal	1.45 \pm 0.95 ^a
Lumbang-activated charcoal	5.41 \pm 2.88 ^a
Chitosan	79.70 \pm 0.77 ^b
Lumbang-activated charcoal chitosan composite	97.20 \pm 0.51 ^c
Lumbang-activated charcoal chitosan composite crosslinked with epichlorohydrin	93.52 \pm 0.51 ^c

Means with the same superscript letters do not differ at 5% level of significance using Bonferroni test

It is evident that surface modification of biocharcoal can improve its adsorption capacity. A similar result was obtained in the batch adsorption removal of Cr(VI) using coconut shell charcoal activated with nitric acid and coated with chitosan [18]. Moreover, when chitosan was used as a coating material for acid treated biocharcoal from palm shell, Cr(VI) removal was improved by about 22% for adsorbent coated with chitosan at optimum Cr(VI) concentration of 20 mg/L and adsorbent dosage of 13-18 g/L [19]. Crosslinking of untreated biocharcoal may not necessarily improve the efficiency of this adsorbent for the removal of Cr(VI). However, crosslinking of adsorbent with epichlorohydrin can improve the rigidity and efficiency of adsorbent especially in its reusability [20].

In the present study, activation of the biocharcoal transformed the adsorbent into an extremely porous structure thus having a very large surface area available for adsorption. The pore size distribution properties dictate carbon's potential performance in removing contaminants from water, which is usually derived from charcoal, a raw material that has long been used as an adsorbent for water filtration [21]. However, 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 as epichlorohydrin predominantly reacts with the hydroxyl group in chitosan, consuming only about 18% of the amino groups present [22].

4. CONCLUSION

A highly modified adsorbent using lumbang (*Aleurites moluccana*) biocharcoal, chitosan, and epichlorohydrin was successfully synthesized. Surface activation of the biocharcoal with CaCl₂ and crosslinking with chitosan and epichlorohydrin has greatly improved the removal of 50 ppm Cr(VI) from aqueous solution at the optimum pH of 3, adsorbent dosage of 3 g/L, and reaction time of 75 min. Surface characterization by SEM showed porous texture with round and elliptical adsorption sites. FTIR spectra indicates the chemical shifting of the -OH, -NH and -C=O functional groups which are usually involved in binding with Cr(VI) metal ion.

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.

REFERENCES

- Kongsricharoen N, Polprasert C. Electrochemical precipitation of chromium (Cr) from an electroplating wastewater. *Water Science and Technology*. 1995; 31(9):109-117.
- Ramos L, Hernandez LM, Gonzalez MJ. Sequential fractionation of copper, lead, cadmium and zinc in soils from near Donana National Park. *J Environ Qual*. 1994;23:50-57.
- Kotas J, Stasicka Z. Chromium occurrence in the environment and methods of its speciation. *Environ. Pollut*. 2000;107(3): 263-283.
- Selvaraj K, Manonmani S, Pattabhi S. Removal of hexavalent chromium using distillery sludge. *Bioresource Technology*. 2003;89(2):207-211.
- Lalvani S, Wiltowski T, Hübner A, Weston A, Mandich N. Removal of hexavalent chromium and metal cations by a selective and novel carbon adsorbent. *Carbon*. 1998;36(7-8):1219-1226.
- Standeven AM, Wetterhahn KE. Chromium(VI) toxicity: Uptake, reduction, and DNA damage. *Int J Toxicol*. 1989;8: 1275-1283.

7. Chen A, Liu S, Chen C, Chen C. Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin. *Journal of Hazardous Materials*. 2008; 154(1-3):184-191.
8. Sumalapao DEP, Distor JR, Domingo NTS, Dy LF, Villarante NR. Biosorption kinetic models on the removal of congo red onto unripe calamansi (*Citrus microcarpa*) peels. *Oriental Journal of Chemistry*. 2016; 32(6):2889-2900.
9. Laus R, Costa T, Szpoganicz B, Fávère V. Adsorption and desorption of Cu(II), Cd(II) and Pb(II) ions using chitosan crosslinked with epichlorohydrin-triphosphate as the adsorbent. *Journal of Hazardous Materials*. 2010;183(1-3):233-241.
10. Boddu VM, Abburi K, Talbott JL, Smith ED, Haasch R. Removal of arsenic(III) and arsenic(IV) from aqueous medium using chitosan-coated biosorbent. *Water Research*. 2008;42:633-642.
11. Popuri SR, Vijaya Y, Boddu VM, Abburi K. Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads. *Bioresour Technol*. 2009;100(1): 194-199.
12. Zhang Y, Xing Z, Duan Z, Li M, Wang Y. Effects of steam activation on the pore structure and surface chemistry of activated carbon derived from bamboo waste. *Applied Surface Science*. 2014; 315:279-286.
13. Swayampakula K, Boddu VM, Nadavala SK, Abburi K. Competitive adsorption of Cu(II), Co(II), and Ni(II) from their binary and tertiary aqueous solutions using chitosan-coated perlite beads as biosorbent. *Journal of Hazardous Materials*. 2008;170:680-689.
14. Wan M, Kan C, Rogel BD, Dalida MLP. Adsorption of copper(II) and lead(II) ions from aqueous solution on chitosan-coated sand. *Carbohydrate Polymers*. 2010;80(3): 891-899.
15. Hydari S, Shariffard H, Nabavinia M, Parvizi M. A comparative investigation on removal performances of commercial activated carbon, chitosan biosorbent and chitosan/activated carbon composite for cadmium. *Chemical Engineering Journal*. 2012;193-194:276-282.
16. Clesceri LS, Greenberg AE, Eaton AD. Standard methods for the examination of water and waste water. 20th Ed. American Public Health Association, Washington; 1998.
17. Villarante NR, Bautista APR, Sumalapao DEP. Batch adsorption study and kinetic profile of Cr(VI) using lumbang (*Aleurites moluccana*)-derived activated carbon-chitosan composite crosslinked with epichlorohydrin. *Oriental Journal of Chemistry*. 2017;33(3):1111-1119.
18. Babel S, Kurniawank TA. Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*. 2004;54: 951-967.
19. Nomanbhay SM, Palanisamy K. Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic Journal of Biotechnology*. 2005;8(1):43-53.
20. Auta M, Hameed BH. Coalesced chitosan activated carbon composite for batch and fixed-bed adsorption of cationic and anionic dyes. *Colloids and Surfaces B: Biointerfaces*. 2013;105(2010):199-206.
21. Heijman S, Hopman R. Activated carbon filtration in drinking water production: Model prediction and new concepts. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 1999;151(1-2): 303-310.
22. Saifuddin N, Nur YAA, Abdullah SF. Microwave enhanced synthesis of chitosan-graft-polyacrilamide molecular imprinting polymer for the selective removal of 17 β -estradiol at trace concentration. *Science Alert*; 2011.

© 2017 Bautista et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:
<http://sciedomain.org/review-history/22318>