Removal of Lead and Cobalt from Pharmaceutical Effluent: Efficiency of Activated Coconut Shell and Commercial Activated Carbon

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Authors' contributions

This work was carried out in collaboration between all authors. Author UMM designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors SM and MI managed the analyses of the study. Author MB managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Zinc Chloride, Sodium Sulphate and Boric acid were used as activating agents for coconut shell. The activated carbons prepared from the mentioned activating agents labelled AC_1, AC_2, and AC_3 were tested for their adsorptive capacities compared with commercially activated carbon (CAC) made from wood, a product of Calgon for their removal of lead and cobalt from pharmaceutical effluent. The percentage removal of Cobalt and lead onto activated carbons from coconut shell was investigated in a batch system by considering the effects of contact time and pH. Adsorption processes in the study indicate that the sorption of lead and cobalt with AC_1, AC_2 and AC_3 were higher than with CAC. Contact times of 60 and 90 min were found to be the optimum for Cobalt and lead respectively. The adsorption kinetic data were analysed with pseudo first-order, pseudo

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second-order, Natarajan and Khalaf first-order and Elovich models. The results indicated that the second order model best described the adsorption kinetic data. The proximity of generated data to those reviewed in literatures is an indication that activated carbons from coconut shell have the potential for the adsorption of cobalt and lead from pharmaceutical effluent.

1. INTRODUCTION

Ecological effects and human disasters in the last decades have arisen majorly from industrial wastes causing environmental degradation [1,2]. The discharged effluents from industries constitute toxic substances which are detrimental to the health of man and living organisms in the environment [3,4]. Most often, effluents from industrial activities are not treated properly and hence are discharged into the water bodies and get accumulated in the human system through food chain [5].

In Nigeria, the increase in pharmaceutical manufacturing companies has enhanced pharmaceutical wastes. Most of these pharmaceutical effluents contain potential toxic metals such as lead, mercury, cadmium, nickel, chromium and other toxic organic chemicals which are released into the environment [6,7].

In attempt to free the environment from the menace of toxic metals which are frequently discharged, conventional and non conventional methods have been employed, such as chemical reduction, ion-exchange mechanisms, coagulation, adsorption on silica, alumina, zeolite composites and activated carbon [8,9]. These conventional methods are expensive to explore, having inadequate efficiencies at low metal concentration. These limitations have caused a drive to the quest for an alternative method. Adsorption using activated carbon had been reported as efficient and economical viable method for the removal of toxic metals from wastewater [10]. This research attempts to employ the method of adsorption using activated carbons from the agricultural waste (coconut shell) impregnated with activating agents and compare their adsorptive capacities with the industrially made commercial activated carbon on the removal of Co(II) and Pb(II) ions from pharmaceutical effluent.

2. MATERIALS AND METHODS

2.1 Sample Collection and Preparation

The coconut shell was collected from Kontagora old Market in Niger State, Nigeria. The coconut shell was washed at the point of collection to remove debris. The sample was dried at ambient temperature, and then oven dried at 105°C, pounded and finally sieved with a 2 mm mesh size sieve. 5.0 g of the sample was measured into a clean weighed crucible, incinerated in a Muffle furnace set at 600°C for 5 min, then transferred into a container, washed with ice water bath and the excess was drained off. The carbonized sample was further washed with 0.1 M HCl to remove the surface ash, followed by hot and cold distilled water to remove the acidic residue [11]. The carbonized sample was again sun dried, oven dried at 100°C for 1 hour. This process was repeated until a substantial amount of the carbonized sample was obtained [12,13].

The carbonized sample was divided into three parts. The first, second and third portions were mixed with 5.0 cm^3 of 1 M activating agents ($ZnCl_2$, Na_2SO_4 and H_3BO_3) in the crucibles and allowed to stand for 2 hours, incinerated in a Muffle furnace set at 800°C in a muffle furnace for 10 min, cooled in ice-water, washed with 0.1 M HCl followed by hot and cold distilled water to remove residual acid. Washing was continued until the pH of the supernatant fell within 6 to 7 and the excess water was drained off, sun dried and oven dried at 100°C. These prepared adsorbents were labelled AC_1, AC_2 and AC_3 for $ZnCl_2$, Na_2SO_4 and H_3BO_3 respectively. The adsorbents were then oven dried at 100°C prior to analysis. This process was repeated until sufficient activated carbon was obtained and stored in an air tight container for sorption studies [14].

2.2 Digestion of Wastewater

The pharmaceutical effluent was collected into polythene bottle from the pharmaceutical company in Minna. 5.0 cm^3 of concentrated nitric acid was added to the effluent. The addition of acid is to prevent metals from adhering to the walls of the container [15]. 10.0 cm^3 of the pharmaceutical effluent was digested with 5.0 cm^3 of concentrated HNO_3 and 2.0 cm^3 of HCl (5:2). The content was placed in a fume cupboard where the digestion process took place until the volume reduced to about 5 cm^3. 15.0

cm^3 of deionised water was added and filtered using Whatman filter paper No 45. The final solution (filtrate) was made up to 50 cm^3 of the volumetric flask with deionised water.

2.3 Adsorbent Characterization

The bulk density was determined using the method of Ahmedna et al. [16]. 25 cm^3 cylinder was filled to a given specific volume with the activated charcoal samples. The cylinder was trapped for at least 1-2 min to compress the sample and then weighed .The bulk density of the adsorbents was calculated using the equation:

$$Bulk\ density\ (gcm^{-3}) = \frac{weight\ of\ activated\ carbon\ (g)}{volume\ of\ packed\ dry\ material\ (cm^3)} \quad (1)$$

The percentage Burn off was calculated using the equation:

$$\%\ Burn\ off = \frac{W_0 - W_1}{W_0} \times 100 \quad (2)$$

W_0 = weight of char after pyrolysis, washing and drying (g)
W_1 = weight of carbon after activation, washing and drying (g) [17].

$$\%\ Yield = \frac{W_1}{W_0} \times 100 \quad (3)$$

W_0 = Original mass of precursor on a dry basis (g)
W_1 = Weight of carbon after activation, washing and drying (g) [18].

pH and conductivity were determined using a pH meter and conductivity meter respectively at room temperature [19]. The pH was determined by dissolving 0.5 g of sample in 30 cm^3 of initial concentration of 5 mg/l metal ion solution in different conical flasks. The pH of each solution in the flasks were adjusted to values 2, 4, 6 and 8 by adding 1 M HNO$_3$ and 1 M NaOH solutions. The mixture was agitated using a shaker for 45 min, then filtered and the filtrate was used for pH and conductivity determination. The pH was determined using the pH meter and the conductivity was also measured using conductivity meter at room temperature.

The ash content was determined by weighing 5.0 g of the sample into an empty pre-weighed crucible, introduced into a Muffle furnace set at 500°C for 3 hours until grayish white ash was obtained. The contents was removed and allowed to cool at room temperature in a desiccator before re- weighing [20].

$$Ash\ (\%) = \frac{W_2 - W_0}{W_1 - W_0} \times 100 \quad (4)$$

Where W_0 is the weight of empty crucible (g), W_1 is the weight of crucible and sample (g) and W_2 is the weight of crucible and ashed sample (g).

2.4 Batch Adsorption

Adsorption was performed in batch mode. In each case, 2.0 g of the activated carbon was weighed and mixed with 40 cm^3 of digested pharmaceutical effluent in a beaker. These were allowed to stand for the time intervals of 30, 60, 90, 120 and 150 min at a room temperature. The solution was filtered using Whatman filter paper No 45 and the filtrate was analyzed for the metal ions concentration by atomic absorption spectrophotometer type Variance - 240 [18].

$$Adsorption\ capacity\ (q_e) = \frac{C_i - C_f}{W} V \quad (5)$$

$$Adsorption\ capacity\ (q_t) = \frac{C_i - C_t}{W} V \quad (6)$$

Where q_t is the adsorption capacity at time t (mg/g), V is the volume of the metal solution (L), C_i is the concentration of metal ion before interaction with activated carbon (mg/L), C_t is the concentration of metal ion after interaction with the activated carbon (mg/L), W is the weight of the activated carbon (g) [21].

2.5 Adsorption Kinetics

Pseudo first-order, pseudo second-order, Natarajan and Khalaf first-order and Elovich models were applied using the prepared activated carbons (AC$_1$, AC$_2$ and AC$_3$) and the commercial activated carbon (CAC) was equally used. Thus the equations below were employed at appropriate points.

Pseudo first- order equation:

$$Log(q_e - q_t) = logq_e - \frac{K_1}{2.303} t \quad (7)$$

Pseudo second-order equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Natarajan and Khalaf first-order equation:

$$\text{Log}\left(\frac{C_t}{C_i}\right) = \frac{K_{1N}}{2.303t} \tag{9}$$

Elovich model equation:

$$q_t = \frac{1}{\beta}\ln(\propto \beta) + \frac{1}{\beta}\ln(t) \tag{10}$$

Where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), K_1 is the adsorption rate constant for the first-order (min^{-1}), K_2 is the adsorption rate constant for second-order $(gmg^{-1}min^{-1})$, $\propto$ is the initial adsorption rate $(mgg^{-1}min^{-1})$, β is the desorption constant (gmg^{-1}).

3. RESULTS AND DISCUSSION

3.1 Characteristics of Activated Carbon

The percentage ash content of the activated carbons prepared from the sampled coconut shell labelled AC_1, AC_2 and AC_3 were 6.78%, 6.91% and 6.88% respectively. This result shows that the ash content of the adsorbents were low which indicate high carbon yield. The percentage burn off was not too high and this is an indication that there was high percentage yield and as a result less chars were released due to less burn off. It was also observed that the bulk density of AC_1, AC_2 and AC_3 were low and this could be linked to the corrosive effect of the chemicals on the biomass during pore formation [22]. The pH of the various activated carbons were 4.97 (AC_1), 6.87 (AC_2) and 5.84 (AC_3), this trend is closed to the study of Kobya et al. [22]. The Conductivity values for the activated carbons were low which indicate that the ash content of the carbon was low since the conductivity values of activated carbon depends on the ash content [22].

3.2 Effect of Contact Time

Contact time was varied from 30 to 150 min as shown in Figs. 1 and 2. The increase in the percentage removal was observed though optimum values at 60 and 90 min for Pb(II) and Co(II) ions respectively. Higher percentage Pb (II) ion removal by all the adsorbents (AC_1, AC_2 and AC_3) was observed. The initial faster rate of metal ions sorption may be explained by the large number of sorption sites available for adsorption processes. Further increase of contact time beyond these optimum times

generally resulted to adsorption of metal ions [23]. The slower adsorption rate at the end is probably due to the saturation of active sites and attainment of equilibrium. Similar result has been reported by Lawal et al. [24] for the uptake of Pb(II) ions onto the seed husk of *Calophyllum inophyllum*.

Table 1. Characteristics of the activated carbon produced using the activating agents

Parameter	AC_1	AC_2	AC_3
Ash content (%)	6.78	6.91	6.88
% burn off	43.90	54.10	57.20
% yield	56.10	45.90	42.80
Bulk density (g/cm^3)	0.38	0.42	0.43
pH	4.97	6.87	5.84
Conductivity (μs/cm $^{-1}$)	3.50	3.50	3.40

3.3 Effect of pH on the Removal of Metal ions

pH is an important parameter for adsorption of metal ions from wastewater because it affects the solubility of metal ions as well as degree of ionization of the adsorbate. The results obtained were presented in Figs. 3 and 4.The adsorption of cobalt and lead ions were found to be strongly dependent on the pH of the solution. It was observed that the optimum value for the adsorption of cobalt and lead ions were at pH 4 which is acidic. At low pH, there was excessive hydroxonium ion (H_3O^+) of the active sites on the adsorbents (AC_1, AC_2 and AC_3) powder surface [25]. The H^+ is released from the active sites and adsorbed metal ions are generally increased. Also, at higher pH greater than 4, the metal ions (Pb^{2+} and Co^{2+}) were very small and this formed metal hydroxide (OH^-). This formation became significant mechanism in the metal ions removal processes since species were adsorbed at the surface of adsorbents by ion exchange mechanism. This is in accordance with the findings of Pehlivan and Arslan [26] and Asrari et al. [27].

3.4 Kinetic of Adsorption

The adsorption kinetic models described how the adsorbed molecules were distributed between the liquid phase and the solid phase when adsorption process reaches an equilibrium state [21]. The results obtained in this study were tested with four kinetic equations (Pseudo first-order, Pseudo second-order, Nataranjan and Khalaf first-order and Elovich model as shown in Table 2. The result showed that the equilibrium

data fitted pseudo second-order most compared with pseudo first-order, Natarajan Khalaf first-order and Elovich models tested. The confirmation between experimental data and the model predicted values were expressed by the correlation coefficient, R^2. A relatively high R^2 value indicates that the model successfully describes the adsorption kinetic.
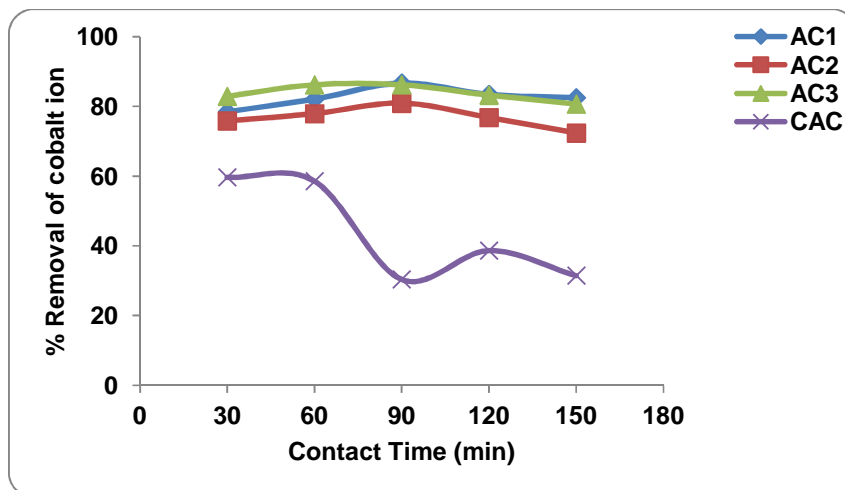

Fig. 1. Effect of contact time on the removal of cobalt ion

Table 2. Kinetic rate models for the adsorption of Co(II) and Pb(II)

| Kinetic	Parameter	Cobalt (Co)			Lead (Pb)		
		AC_1	AC_2	AC_3	AC_1	AC_2	AC_3
First-order	q_e(mg/g)	0.085	0.09	0.001	0.033	0.032	0.028
	K_1	4.24×10^{-4}	3.44×10^{-4}	4.54×10^{-4}	4.34×10^{-4}	2.34×10^{-4}	3.23×10^{-4}
	R^2	0.543	0.215	0.144	0.478	0.032	0.433
Second-order	q_e(mg/g)	9.89×10^{-4}	4.03×10^{-3}	2.91×10^{-3}	3.49×10^{-3}	5.97×10^{-3}	6.79×10^{-3}
	K_1	29.88	14.89	16.48	42.54	10.7	9.34
	R^2	0.974	0.915	0.905	0.909	0.904	0.963
Natarajan and Khalaf	R^2	0.119	0.135	0.201	0.491	0.775	0.289
Elovich	R^2	0.683	0.181	0.211	0.48	0.047	0.033
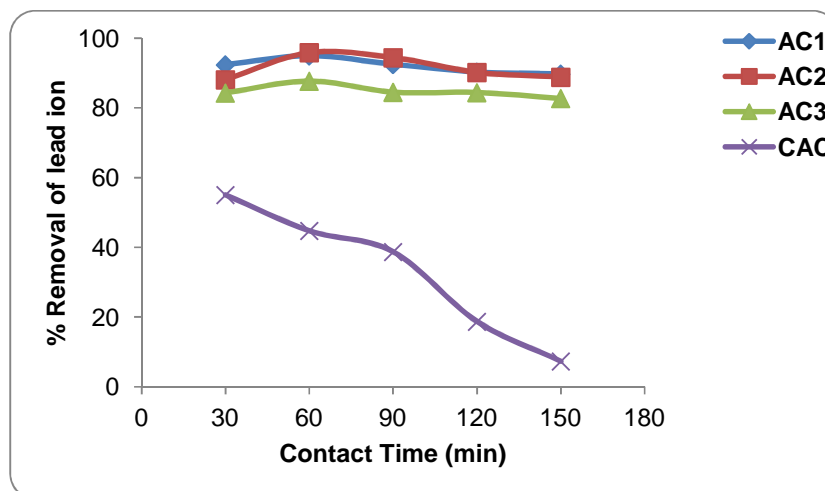
Fig. 2. Effect of contact time on the removal of lead ion
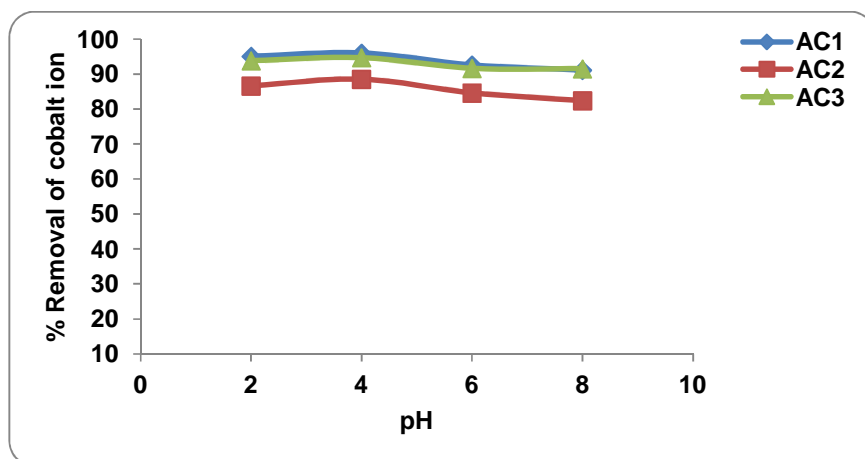
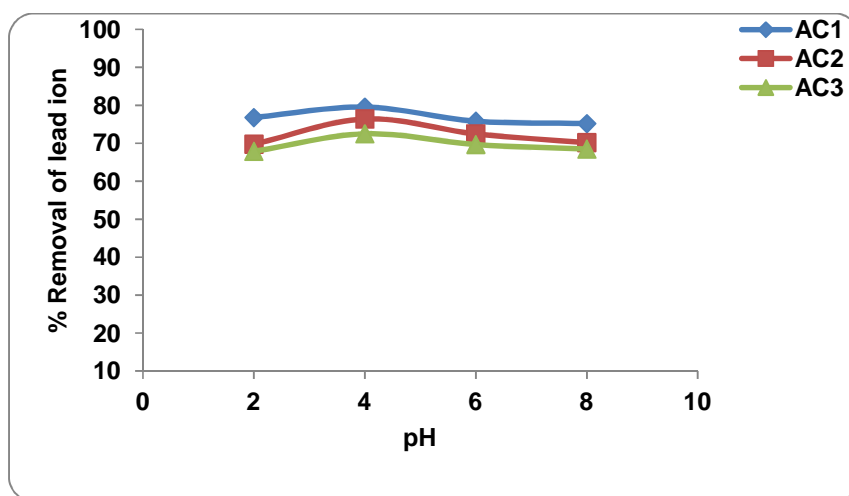**Fig. 3. Effect of pH on the removal of cobalt ion**

Fig. 4. Effect of pH on the removal of lead ion

The correlation coefficient values for the second-order for Co(II) and Pb(II) ions were higher than the R^2 value of Apricot shell studied by Khazaii et al. [28]. The observed fast rate of biosorption kinetic were in line with biosorption of metals which involve non-energy mediated reaction where metal removal from solution is purely a physicochemical interaction between biomass and metal solution [29,30].

4. CONCLUSION

Based on this study, it is evidence that agricultural waste material (coconut shell) can be effectively used in the removal of cobalt and lead ions from pharmaceutical effluent. The removal of the heavy metal ions is time and pH dependant as the percentage adsorption increases with increase in pH values of the solution up to particular values until the precipitation start to prevail. Activated carbons (ACs) adsorbed Co(II) and Pb(II) ions to a greater extent with respect to contact times than commercially activated carbon (CAC). Pseudo second-order gave the best correlation coefficient (R^2) values onto the surface of adsorbents. The results indicate that the activated carbons are promising materials which can be used for removal of potential toxic metals from pharmaceutical wastewater.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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REFERENCES

1. Abdel-shafy RI, Abdel-Basir SE. Chemical treatment of industrial waste water. Environmental Management Health. 1999;2:19-23.

2. Sridhar MKC, Olawuyi JF, Adogame LA, Okekearsu OCO, Linda A. Lead in the Nigeria environment, problems and prospects, 11th Annual International Conference on heavy metals in the environment. University of Michigan School of Public Health. 2000;862.

3. Adriano DC. Trace elements in terrestrial environment. Biochemistry bioavalability and risks of metals. Springer Verlag. 2001;867.

4. Adebisi SA, Ipinromiti KO, Amoo IA. Heavy metals content of effluents and receiving waters from various industrial groups and their environs. Journal of Applied Science. 2007;2(4):345-348.

5. Odiete WO. Impacts associated with water pollution in environmental physiology of animals and pollutions. Diversified Resources Ltd, Lagos 1st ed. 1990;187-219.

6. Ayodele JT, Momoh RU, Amin M. Determination of heavy metals in sharada Industrial effluent in water Quality monitoring and Environmental status in Nigeria, proceeding of the National seminal on water Quality monitoring and status in Nigeria, powered by Federal Environmental Protection Agency and National Water Resources Institute, October 16th- 18th 1991. 1996;156-166.

7. Osaigbovo AE, Orhue ER. Influence of pharmaceutical effluent on some soil chemical properties and early growth of maize (*Zea mays* Leaf). African Journal of Biotechnology. 2006;5:18.

8. Steinhauser G, Bichler M. Adsorption of ions onto high silica volcanic glass. Applied Radiation Isotopes. 2008;66:1-8.

9. Vinodhini V, Das N. Relevant approach to assess the performance of saw dust as adsorbent of chromium VI ions from aqueous solution. International Journal of Science Technology. 2010;7:85-92.

10. Malakootian M, Nouri J, Hossaini H. Removal of heavy metal from paint industry's wastewater using Leca as an available adsorbent. International Journal of Environmental Science and Technology. 2009;6(2):183-190.

11. Rahman A, Saad B, Shaidan S, Rizai S. Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical thermal process. Bioresources Technology. 2005;90(14):1578- 1583.

12. Odebunmi E, Okeola F. Preparation and characterization of activated carbon from waste material. Journal of Chemical Society of Nigeria. 2001;26(2):149-155.

13. Turoti M, Gimba C, Ocholi O, Nok A. Effect of different activated methods on the adsorption characteristics of activated carbon from *Kyaya senegalensis* fruits and *Delonix regia* pods. Chemical Journals. 2007;1:107-112.

14. Vaughan T, Seo WE, Marshell T. Removal of selected metal ions from aqueous solution using modified corn cobs. Bioresources and Technology. 2001;79:135-139.

15. Ademoroti CMA. Standard method for water and effluent analysis. Ibadan. 1996;97-145.

16. Ahmedna M, Marshall WE, Rao RM. Surface properties of granular activated carbons from agricultural by-products and their effects on raw sugar decolorization. Bioresource Technology. 2000;71:103–112.

17. Ioannidou O, Zabaniotou A. Agricultural pre-cursors for activated carbon production. Renewable and Sustainable Energy Review. 2006;11(1):1966-2005.

18. Apipreeya K, Phussadee P, Prasert P. Removal of metal ion from synthetic waste water by activated carbon from *Eucalyptus camaldulensis* Denn bark. The 2nd joint International Conference on Sustainable Energy and Environment (SSE). 2006;041:1-9.

19. Okiemen FE, Ojokoh FL, Okiemen CD, Wuana RA. Preparation and evaluation of activated carbon from rice husk and rubber seed shell. Chemical Journal. 2004;191-196.

20. AOAC. Official Method of Analysis, Washinton Dc. Association of Official Analytical Chemistry 14th Edition: 140-147; 1990.

21. Hameed BH, Mahmoud DK, Ahmed AL. Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low cost adsorbent coconut (*cocos mucifera*) bunch waste. Journal of Hazardous Materials. 2008;158:65-72.

22. Kobya M, Demirbas, Senturk E, Ince M. Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Bioresource Technology. 2005;96:1518-1521.

23. Shukl SR, Pai RS. Removal of Pb II from aqueous solution using cellulose containing materials. Journal of Chem. Technology Biotechnology. 2005;80:176-183.

24. Lawal OS, Sanni AR, Ajayi IA, Rabiu OO. Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of *Calophyllum inophyllum*. J. Hazard. Mater. 2010;177:829-835.

25. Mustapha S, Dauda BEN, Ndamitso MM, Mathew TJ, Bassey U, Muhammed SS. Biosorption of copper from aqueous solutions by raw and activated spines of *Bombax buonopozense*: Equilibrium, kinetics and thermodynamic studies. International Research Journal of Pure & Applied Chemistry. 2014;4(6): 887-903.

26. Pehlivan E, Arslan G. Removal of metal ions using lignite in aqueous solution in low cost bisorbents. Fuel Process Technol. 2007;88:99–106.

27. Asrari E, Tavallali H, Hagshenas M. Removal of Zn(II) and Pb(II) ions using rice husk in food industrial wastewater. Journal of Applied Science and Environment Manage. 2010;14(4):159-162.

28. Khazaii I, Aliabadi M, Hamed Mosavian HT. Use of agricultural waste for the removal of Cr(VI) from aqueous solution. Iranian Journal of Chemical Engineering. 2011;8(4):11-23.

29. Abia G, Osuguo B. Adsorption of chromium VI from water using agricultural waste barley husk. Environmental Science and Technology. 2006;28:29-33.

30. Oboh OI, Aluyor EO. The removal of heavy metal ions from aqueous solutions using sour sop geeds as biosorbent. African Journal of Biotechnology. 2008;7(24): 4508-4511.

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