International Journal of Water Resources and Arid Environments 8(2): 97-103, 2019
ISSN 2079-7079

Removal of Toxic Hexavalent Chromium from Industrial Wastewater Using Novel Biocarbon – A New Water Treatment Technology

Malairajan Singanan

PG and Research Department of Chemistry, Water and Food Chemistry Research Laboratory, Presidency College (Autonomous), Chennai – 600005, Tamil Nadu, India

Abstract: The water-food-energy-climate nexus are emerging as active issues for the sustainable development of our society. The quality and quantity of fresh water is of vital concern for mankind since it is directly linked with human welfare and settlements.Heavy metals are non-biodegradable and have credible bioaccumulation capacity in nature. Water pollution due to the presence of toxic heavy metal is a dangerous threat human life. Cutting-edge processes for treating industrial wastewater having heavy metals often involve technologies that involve reduction of toxicity in order to meet technology-based treatment standards. In the current research, black pepper (Piper nigrum) plant leaves were used for the production of biocarbon. The maximum adsorption of Cr (VI) took place at pH 5.5. The percentage of the removal of Cr (VI) decreases with the increase in pH. The optimum level of BPL biocarbon required for the effective removal of Cr (VI) was 3.0 g/ 100 mL. It is well noted that the removal rate of 97.60 % Cr (VI) was achieved at the time limit of 180 min.In real sample analysis, the leather industry wastewater is treated. It has greater affinity to remove the metal pollutant particularly.

Key words: Black pepper · Biocarbon · Leather industry wastewater · Chromium · Adsorption

INTRODUCTION

Water pollution due to heavy metals has become one of the most serious environmental problems. Heavy metals, like mercury, lead, chromium, tin, cadmium, selenium and arsenic are introduced into the environment by different industrial and man-made activities and deposit slowly in the surrounding water and soil [1]. The uncontrolled activities and discharge of large volumes of wastewater into aquatic resources cause poisoning of fresh water resources which affects the entire eco-system.

The removal of heavy metals from the environment is of special concern due to their persistence. Because of their high solubility in the aquatic environments, however unlike organic contaminants, they are not biodegradable and tend to accumulate in living organismsand makes adverse effect on aquatic flora and fauna [2, 3]. The heavy metals are very reactive at low concentrations and can accumulate in human body and may also constitute serious public health problems through food chain[4, 5]. Therefore, heavy metals should be prevented from reaching the natural environment [6].

In order to remove the toxic heavy metals from waste water, many conventional technologies have been used such as chemical precipitation, coagulation, ion exchange, solvent extraction, filtration, precipitation, membrane filtration and ion-exchange have been used to remove metal pollutants from water [7, 8, 9, 10].

In fact, many of the conventional treatment techniques not having specificity, resulting in several disadvantages mainly related to low affinity and selectivity and lengthy equilibrium processes: such conditions often produce increased costs. Since much attention is to be focused on innovative and specific water treatment technologies for the removal of inorganic micropollutants are today of great interest in the research world.

Adsorption is one of the best of the technology for the decontamination of water because it is very simple, an operative, economical and eco-friendly treatment technique [11]. It is basically a mass transfer process by which the metal ion is transferred from the solution to the surface of sorbent and becomes bound mainly by physical interactions [12, 13].

Corresponding Author: Malairajan Singanan, PG and Research Department of Chemistry, Water and Food Chemistry Research Laboratory, Presidency College (Autonomous), Chennai - 600005, Tamil Nadu, India.

For the purpose of adsorption process, variety of materials such as granular red mud [14], sugar beet pulp [15], custardapple (Annona Squamosa) peel powder [16], tamarind seeds [17] rice husk [18], *Azardica indica* (Neem leaf powder) [19] and waste maize bran [20] ect., are examples of low-cost materials used in the removal of heavy metals.

In the present investigation, the use of biocarbon produced from the leaves of black pepper (Piper nigrum) was used as an effective andinexpensive material for the removal of Cr (VI) from aqueous solution as model synthetic pollutant for the evolution of adsorption behaviour of the biocarbon and then treatment of leather industry wastewater was described.

MATERIALS AND METHODS

Preparation of Black Pepper Leaves Biocarbon (BPL): The black pepper (Piper nigrum) plant leaves were collected from the agricultural field and cleaned with running tap water for removing the dust and other impurities. Then, the leaves were shade dried for 2-3 days and crushed in ball mill. The produced biomass was subjected to the preparation of biocarbon as per the scheme outlined below. The produced biocarbon was stored in air free glass container for further use.

Preparation of Synthetic Wastewater: In the present research work, Cr (VI) is used as a model metal pollutant for the evaluation of adsorption capacity of the biocarbon. Hence, 1000 mg/L of the stock solution of Cr (VI) is prepared by dissolving 2.835 g of analytical grade $K_2Cr_2O_7$ in double Distilled water and diluted to 1L. Further, working solutions were prepared by appropriate dilutions. The pH of the solutions were adjusted using 0.1N HCl and 0.1N NaOH solutions.

Collection and Analysis of Leather Industry Wastewater: In Northern Tamil Nadu, India several leather industries are working with varying capacities. Some of the industries are using conventional vegetable tanning process and majority of the industries are using the chrome tanning process. All such industries are consuming large volume of fresh water for their industrial operations. It is also releases huge volume of wastewater and associated sludge into the environment. Many of the industries are following conventional water treatment methods. However, the released water into the environment still lacking quality standards. It is well observed that, these type activities are leading to overexploitation of available fresh water resources and cross contamination of ground and surface water systems. It also accelerates the soil pollution in the receiving area.In this context, leather industry wastewater was collected from the combined storage units and analysed for important wastewater quality parameters and the analytical results are presented in the Table 1.

Adsorption Process: The adsorption process of the metal ions on biocarbon was performed in batch mode. The biosorption capacity of the adsorbent was evaluated by optimizing the effect of pH, amount of adsorbent dose, contact time, initial metal ion concentration and influence of temperature. For the purpose of optimization, 50 mL of Cr (VI) solution (100 mg/L) was placed in eight 250 mL capacity Erlenmeyer flask with stopper. In the experimental flask, biocarbon dose of 0.5 to 4.0 g was added and equilibrated at the predetermined speed of 250 rpm for 3 hours (pH = 5.0). At the end of the equilibrium time, the samples were filtered off and the concentration of Cr (VI) was determined using Shimadzu 6200 AAS system. In the similar way, the optimal contact time was established with the interval of 30 min with the initial concentration of 100 mg/L of Cr (VI) solution at the biocarbon dose rate of 3.0 g/100mL. The effect of pH on the removal of Cr (VI) on biocarbon was established by varying the pH of the working solution in the range of 3.0 to 8.0.

The percentage removal of chromium (VI) from aqueous solution was computed from the following equation.

$$\%\ \text{Removal} = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad (1)$$

The metal uptake (q_e) at equilibrium time was calculated from the following equation

$$q_e = \left(\frac{C_o - C_e}{w}\right) \times V \qquad (2)$$

where q_e = amount of dissolved solids adsorbed (mg/g), V = volume of wastewater (L), w = mass of biocarbon (g), C_o = initial dissolved solids concentration (mg/L) and C_e = concentration of dissolved solids at equilibrium (mg/L). Statistical analysis of the data was carried out by IBMSPSS statistics 20.0 software.

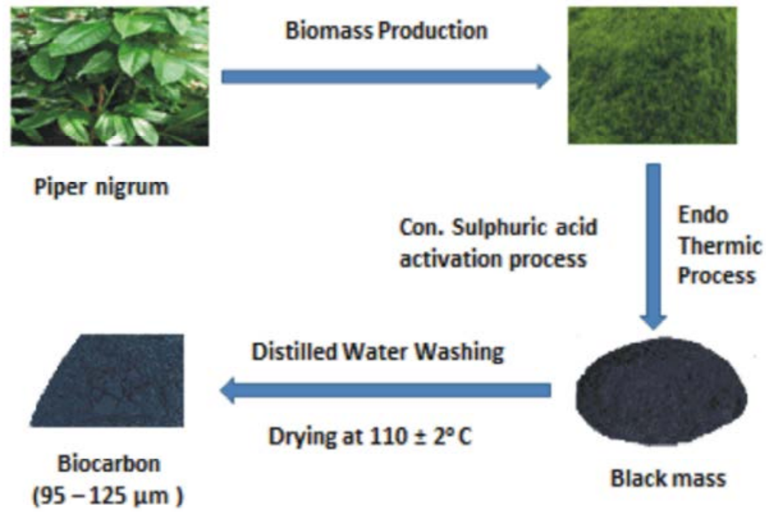

Fig. 1: Process for the preparation of biocarbon

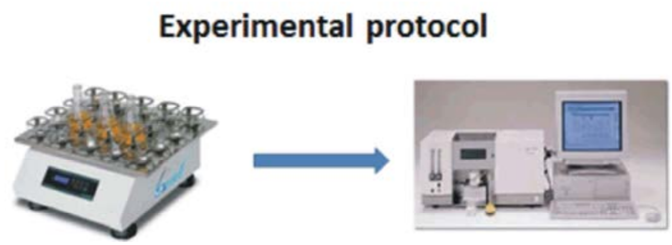

Fig. 2: Batch adsorption process and measurement of Cr (VI) ions by AAS

Table 1: Physico-chemical analysis of leather industry wastewater

Sl.No	Parameters	Value	Sl.No	Parameters	Value
1.	Color	Black green	6.	COD	3255 mg/L
2.	pH	6.85	7.	BOD	1650 mg/L
3.	EC	123920 μmhos/cm	8.	Sulphate	4350 mg/L
4.	TDS	80, 550 mg/L	9.	Chloride	19, 550 mg/L
5.	TSS	35, 450 mg/L	10.	Total Chromium	4850 mg/L

RESULTS AND DISCUSSION

Effect of pH: The pH of the solution is one of the most important parameterthat affects the adsorption process of metal ions. It can influence the surface charge of the adsorbent and the availability of functional groups on the surface of adsorbent [21].The effect of pH on adsorption of metal ion by BPL biocarbon is presented in Figure 3.

It is well observed that, the adsorption process of metal ions on the surface of BPL increases gradually and reaching a maximum value 97.60% at pH of 5.5. This is because less H_3O^+ ions were available at pH values higher than 3.0. Therefore, the competition between H_3O^+ and metal ions was reduced, increasing the electrostatic attraction between metal ions and active site at the adsorbent [22]. Therefore, the adsorption process becomes more favourable. Beyond certain limits (pH>8.0) the adsorption process drastically decreases due the formation of hydroxide precipitates.

Effect of BBL Biocarbon Dose: Influence of amount of adsorbent is very essential parameters that should be considered in designing a good adsorption system [23]. This is because; the amount of adsorbent is directly proportional towards the availability of the active binding sites and the operational cost. The effect of amount of BPL biocarbon was shown in the Figure 4. It is noted that, an increase in BBPbiocarbon dosage was found to increase the metal ions removal. The removal percentage for Cr (VI) increased from 52.6 to 97.6% when the amount of BPL biocarbon was adjusted from 1.5 to 3.0 g. This phenomenon can be explained by the fact that

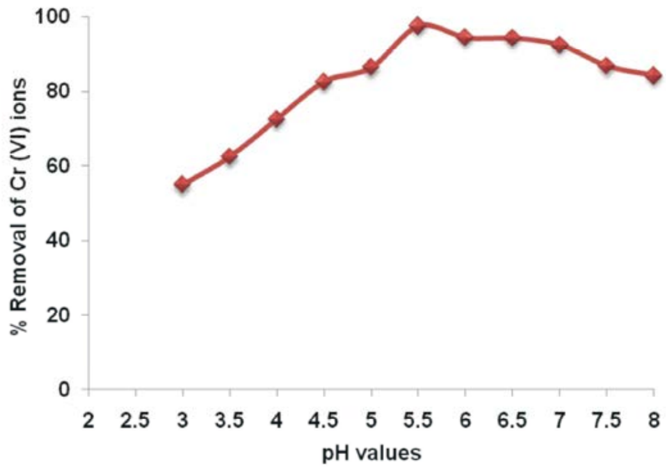

Fig. 3: Effect of pH on Cr (VI) removal

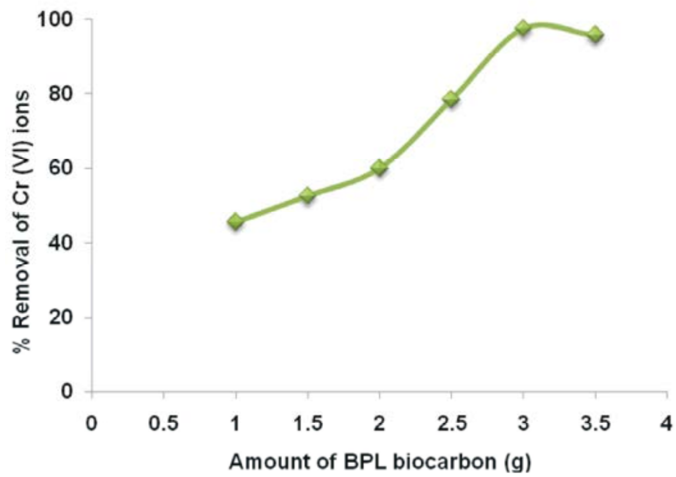

Fig. 4: Effect of amount of BPL biocarbon on Cr (VI) removal

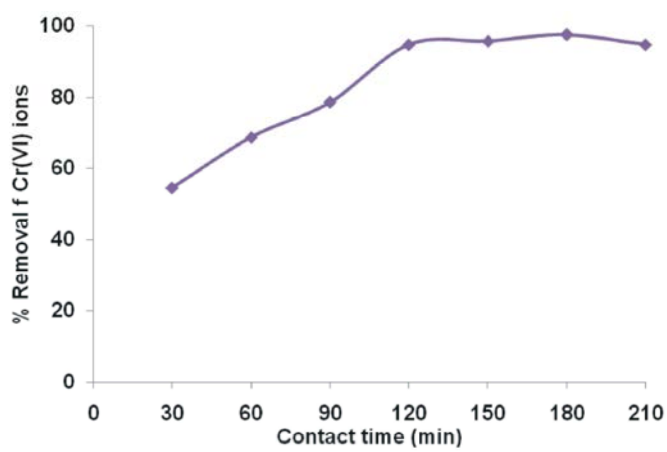

Fig. 5: Effect of contact time on Cr (VI) removal.

more active sites are available for metal ion binding at high dosage andbesides provide high surface area which is favourable for adsorption process [24-26].

Effect of Contact Time: It is very important to establish an appropriate contact time between the adsorbent and metallic ion in solution. The adsorption capacity of Cr (VI)

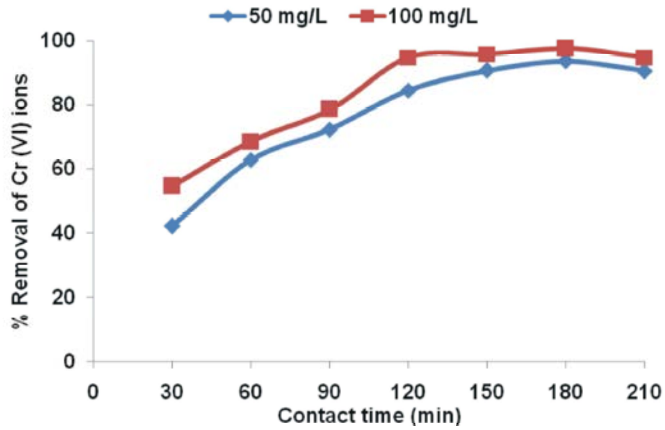

Fig. 6: Effect of initial concentration of on Cr (VI) ions on removal

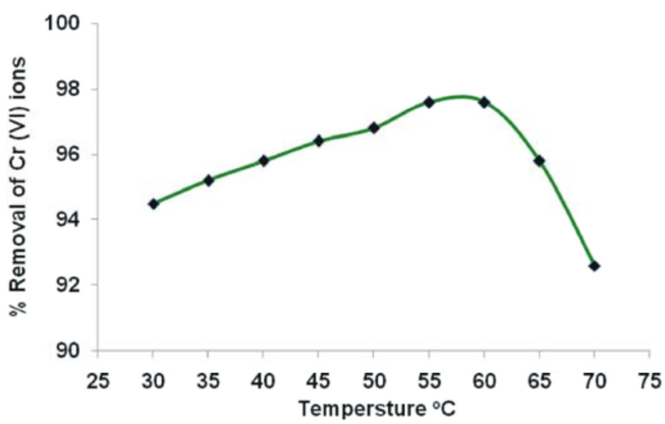

Fig. 7: Effect of temperature on Cr (VI) removal

Table 2: Physico-chemical analysis of leather industry wastewater after treatment process

Sl.No	Parameters	Value	Sl.No	Parameters	Value
1.	Color	Colourless	6.	COD	380 mg/L
2.	pH	5.30	7.	BOD	70 mg/L
3.	EC	2750 μmhos/cm	8.	Sulphate	360 mg/L
4.	TDS	1810 mg/L	9.	Chloride	235 mg/L
5.	TSS	1350 mg/L	10.	Total Chromium	1.80 mg/L

metal ion was measured as a function of contact time (Fig. 5). The plot revealed that the rate of Cr (VI) removal is steadily increasing and reached a maximum value of 97.60% and then decreased. That is probably due to the availability of larger surface area of the BPL biocarbon for the adsorption of metal ions. It is understood that, the uptake rate is mainly controlled by the transfer of metal ions from bulk solution to the interior sites of the adsorbent particles. The effective removal of Cr (VI) was attained at the time limits of 150 – 180 min. Therefore, equilibrium time of 180 min was selected for all further studies. It is also well known and established that; the adsorption is a physical-chemical process that the mass transfers a solute from the fluid phase to the adsorbent surface [27].

Effect of Initial Metal Concentration: The amount of metal ion adsorbed by BPL biocarbon was increased when the initial metal concentration was increased from 50 mg/L to 100 mg/L. This can be explained by the fact that there was a high probability of collision between adsorbent surface and metal ions at high concentrations [28]. Therefore, the rate of diffusion of metal ions towards the BPL biocarbon surface was increased. The influence of initial metal ion concentration on adsorption process on BPL biocarbon is illustrated in Figure 6.

Effect of Temperature: The effect of temperature on the initial Cr (VI) concentration (C_o = 100 mg/L) on BPL biocarbon performance was investigated. The analytical results were presented in the Figure 7. It is confirmed that adsorption of Cr (VI) increases with increase in temperature at the range of 30 – 70°C. This increase in binding could be due to increase in surface activity, utilization of all active sites available for the adsorptionand increased kinetic energy of the Cr (VI) metal ions [29, 30]. When the temperature of the system beyond certain limit, the adsorption process in not progressing well and shows decreasing trend. The decrease in percentage removal can be explained by thefact that all the adsorbents had a limited number of activesites, which would have become saturated.

Treatment of Leather Industry Wastewater: The collected leather industry wastewater is screened through filter cloths and all dirt materials were removed. The wastewater is subjected to batch adoption process with predetermined equilibrium data obtained for the synthetic wastewater system. It is noted that, the load of organic and inorganic pollutants were significantly reduced (Table 2). The results are very much promising for the use of BPL biocarbon for the treatment of leather industry wastewater. It has greater affinity to remove the metal pollutant particularly.

CONCLUSION

The use of biocarbon prepared from black pepper leaves, capable of adsorption of Cr (VI) from aqueous stream, is cost effective and efficient. The maximum adsorption of Cr (VI) took place at pH 5.5. The percentage of the removal of Cr (VI) decreases with the increase in pH. The optimum level of BPL biocarbon required for the effective removal of Cr (VI) was 3.0 g/ 100 mL. It is well noted that the removal rate of 97.60 % Cr (VI) was achieved at the time limit of 180 min. In real ample analysis, a leather industry wastewater was used for the batch adsorption process. The results are very much promising for the use of BPL biocarbon for the treatment of leather industry wastewater. It has greater affinity to remove the metal pollutant particularly. These results demonstrate the great potential for the application of biomaterials would be an effective method for economic treatment of wastewater.

REFERENCES

1. Abdel Salam, O.E, N.A. Reiad and M.M. El-Shafei, 2011. A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. J. Adv. Res., 2: 297–303.
2. Gaur, N., G. Flora, M. Yadav and A. Tiwari, 2014. A review with recent advancements on bioremediation-basedabolition of heavy metals. Environ. Sci. Process. Impacts., 16: 180-193.
3. Dixit, R., D. Malaviya, K. Pandiyan, U.B. Singh, A. Sahu, R. Shukla, B.P. Singh, J.P. Rai, P.K. Sharma and H. Lade, 2015. Bioremediation of heavy metals from soil and aquatic environment: An overview of principles andcriteria of fundamental processes. Sustainability, 7: 2189-2212.
4. Barakat, M.A., 2011. New trends in removing heavy metals from industrial wastewater. Arabian J. Chem., 4: 361-377.
5. Fu, F. and Q. Wang, 2011. Removal of heavy metal ions from wastewaters: A review. J. Env. Manage., 92: 407-418.
6. Hua, M., S. Zhang, B. Pan, W. Zhang, L. Lv and Q. Zhang, 2012. Heavy metal removal from water/wastewater by nanosizedmetal oxides: A review. J. Hazard. Mat., 211: 317-331.
7. Panayotova, M. and B. Velikov, 2003. Influence of zeolite transformation in a homoionic form on the removal of some heavy metal ions from wastewater. J. Environ. Sci. Health. Part A., 38(3): 545-554.
8. Chingombe, P., B. Saha and R. Wakeman, 2005. Surface modification and characterization of a coal-based activated carbon. Carbon., 43: 3132-3143.
9. Gupta, V.K., I. Ali, T.A. Saleh, A. Nayak and S. Agarwal, 2012. Chemical treatment technologies for waste-water recycling: An overview. RSC Adv., 2: 6380-6388.
10. Saleh, T.A. and V.K. Gupta, 2012. Column with CNT/magnesium oxide composite for lead (II) removal from water. Environ. Sci. Pollut. Res., 19: 1224-1228.
11. Abdel-Raouf, M.S. and A.R.M. Abdul-Raheim, 2017. Removal of heavy metals from industrial waste water by biomass-based materials: A review. J. Pollut. Eff. Cont., 5: 180. doi: 10.4172/2375-4397.1000180.
12. Gupta, V. and A. Nayak, 2012. Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe_2O_3 nanoparticles. Chem. Eng. J., 180: 81-90.

13. Gupta, V.K., S. Agarwal and T.A. Saleh, 2011. Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. J. Hazard. Mat., 185: 17-23.
14. Zhu, C., Z. Luan, Y. Wang and X. Shan, 2007. Removal of cadmium from aqueous solutions by adsorption on granular red mud (GRM). Purif. Technol., 57(1): 161.
15. Pehlivan, E., B.H. Yanık, G. Ahmetli and M. Pehlivan, 2008. Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp. Bioresour. Technol., 99(9): 3520.
16. Krishna, D. and R. Padma Sree, 2013. Removal of chromium from aqueous solution by *Custard Apple* (*Annona Squamosa*) peel powder as adsorbent. Int. J. App. Sci. Eng., 11(2): 171-194.
17. Gupta, S. and B.V. Babu, 2009. Utilization of waste product (Tamarind seeds) for the removal of Cr (VI) from aqueous solutions: Equilibrium, kinetics and regeneration studies. J. Env. Manage., 90: 3013-3022.
18. Shafey, E.I., 2005. Behaviour of reduction-sorption of chromium (VI) from an aqueous solution on a modified sorbent from rice husk. Water. Air. Soil. Pollution., 163: 81-102.
19. Sharma, A. and K.G. Bhattacharya, 2004. Adsorption of Pb (II) from aqueous solution by*Azardica indica* (Neem leaf powder). J. Hazard. Mat., 113: 97-109.
20. Hasan, S.H., K.K. Singh, O. Prakash, M. Talat and Y.S. Ho, 2008. Removal of Cr (VI) from aqueous solutions using agricultural waste maize bran. J. Hazard. Mat., 152: 356-365.
21. Hokkanen, S., E. Repo and M. Sillanpää, 2013. Removal of heavy metals from aqueous solutions by succinic anhydride modified mercerized nanocellulos. Chem. Eng. J., 223: 40-47.
22. Yargıç, A.Ş, R.Z.Y. Şahin, N. Özbay and E. Önal, 2015. Assessment of toxic copper (II) biosorption from aqueous solution by chemically-treated tomato waste. J. Clean. Prod., 88: 152-159.
23. Taşar, Ş, F. Kaya and A. Özer, 2014. Biosorption of lead (II) ions from aqueous solution by peanut shells: Equilibrium, thermodynamic and kinetic studies. J. Environ. Chem. Eng., 2: 1018-1026.
24. Gupta, V.K., S. Agarwal, P. Singh and D. Pathania, 2013. Acrylic acid grafted cellulosic Luffa cylindrical fiber for the removal of dye and metal ions. Carbohydr. Polym., 98: 1214-1221.
25. Buasri, A., N. Chaiyut, K. Tapang, S. Jaroensin and S. Panphrom, 2012. Equilibrium and kinetic studies of biosorption of Zn(II) ions from wastewater using modified corn cob. APCBEE Procedia., 3: 60-64.
26. Mahajan, G. and D. Sud, 2013. Application of ligno-cellulosic waste material for heavy metal ions removal from aqueous solution. J.Environ. Chem. Eng., 1: 1020-1027.
27. Werkneh, A.A, N.G. Habtu and H.D. Beyene, 2014. Removal of hexavalent chromium from tannery wastewater using activated carbon primed from sugarcane bagasse: Adsorption/desorption studies. American. J. App. Chem., 2(6): 128-135.
28. Shamsudin, R., H. Abdullah and A. Kamari, 2016. Application of Kenaf Bast fiber to adsorb Cu(II), Pb(II) and Zn(II) in aqueous solution: Single and multi-metal systems. Int. J. Env. Sci. Devel., 7(10): 715-723.
29. Panumati, S., K. Chudecha and P. Vankhaew, 2008. Adsorption of phenol from diluted aqueous solutions by activated carbons obtained from bagasse, oil palm shell and pericarp of rubber fruit. J. Sci. Technol., 30(2): 185-189.
30. Jabari, M., F. Aqra, S. Shahin and A. Khatib, 2009. Monitoring chromium content in tannery waste water. J. Argentine. Chem. Soc., 97(2): 77-87.