Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.1218

71 (2017) 321–326
April

Production of physically and chemically modified biomass of corncob and its applications for the removal of Co(II) ion from its aqueous solution: optimum conditions determination

Raziya Nadeem[a,*], Mahak Naeem[a], Hazafa Zafar[a], Rohama Gill[b], Ghazala Yasmean[c], Qaiser Mehmood Khan[d]

[a]Department of Chemistry, University of Agriculture, Faisalabad 38040, Pakistan, Tel. +92 419200161-3309; Cell: +92 3228669634; Fax: +92 419200764; email: raziyaanalyst@yahoo.com (R. Nadeem); Cell: +923074622130; email: mahak_khalid@yahoo.com (M. Naeem); Cell: +923049498783; email: hazafachemist@yahoo.com (H. Zafar)
[b]Department of Environmental Sciences, Fatima Jinnah Women University, Rawalpindi 46000, Pakistan, Cell: +923028993313; email: rohama_gill@hotmail.com
[c]Institute of Chemical Sciences Bahauddin Zakariya University (BZU), Multan 60800, Pakistan, email: ghazala31pk@yahoo.com
[d]National Institute of Biotechnology and Genetic Engineering (NIBGE), Faisalabad 38040, Pakistan, email: qk_5@yahoo.com

Received 18 June 2014; Accepted 18 July 2016

ABSTRACT

In the present study, the use of agricultural waste product such as corncob (in its native, physically and chemically modified form) has been examined as a potential replacement for the expensive adsorbents for the removal of Co (II) from aqueous solutions. The influence of the parameters such as solution pH, initial metal concentration and time of contact on abatement of Co (II) metal were assessed. The uptake capacity q (mg g^{-1}) of biomass clearly increased with increase in pH up to optimum pH 4 followed by precipitation at higher pH values. Initially, the biosorption rate was very fast followed by slow sorption showing equilibrium was reached at around 60 to 120 min. Equilibrium data were found to explain well by Freundlich isotherm than by Langmuir isotherm with $R^2 = 0.999$ and kinetics was well explained by pseudo-second-order with correlation coefficient values close to unity. Therefore, corncob being abundant and low cost can serve as natural biosorbent for exclusion of Co (II) metal from aqueous solution.

Keywords: Corncob; Heavy metals; Pretreatments; Kinetics; Equilibrium modeling

1. Introduction

Contemporary pattern of the developed and industrialized activities alters the innate flow of materials and initiates several chemicals into the environment. As a result of increased urbanization, effluents are discharged more and more into aquatic environment which is chief concern [1]. Primary sources of the effluents are tanneries, disposal of sludge, pigments, metal plating, mining operations, alloy industries, smelting, chloralkali, paints and radiator manufacturing etc. [2].

The elimination of intractable contaminants like cobalt from contaminated water is necessary as they masquerade a severe environmental hazard and health [3]. Relentless effects of discriminating cobalt poisoning on human beings include several diseases like asthma, vomiting, nausea, damages liver, heart failure, reproductive failures, nervous system failures, formation of tumor and thyroid gland [4]. Cobalt with its highest concentration may also cause mutation of genes in

---

* Corresponding author.

living cells of humans, cancer, neuro toxicological disorders, focusing on awareness of the problems allied with cobalt poisoning [5,6].

Current study focused on the removal of cobalt from the aqueous solution have drawn broad attention and demonstrated that mitigation of cobalt cannot be passably achieved sometimes with the usage of expensive traditional wastewater treatment methods [7]. Wastewater treatment methods include adsorption, ion exchange, membrane separation, electrolysis, chemical precipitation, reverse osmosis and electro-winning etc. [8]. These treatment methods require high levels of expertise, high cost and high energy requirement as these treatment methods are not useful when metal concentration is low particularly in range of 1–100 mgL^{-1} [9]. For these disadvantages, biosorption treatment technique seems to be a promising substitute even when metal concentration is low as 1 mgL^{-1} because of its low cost, cleanliness, effectiveness, eco-friendliness and flexibility [10].

Biosorption is inactive, physicochemical binding of chemical species, utilizes economical dead biomass for the sequestration of toxic heavy metals from contaminated water systems [11]. Biosorption is a progression towards a perspective method [12]. Biosorption process requires appropriate biosorbent as a source to entrap heavy metals from aqueous systems for its success. Several biosorbents such as fungi, algae, bacteria are used for the treatment of contaminated water but they are costly [13]. Therefore, the usage of low cost agricultural waste product such as corncob paying attention for the removal of heavy metals from aqueous solutions [14]. The purpose of the present study was to scrutinize the metal removal potential of physically pretreated (heating, autoclaving and boiling) and chemically pretreated (citric acid, oxalic acid and tartaric acid) biomass of corncob from aqueous solution.

2. Materials and methods

2.1. Reagents

All chemicals used to perform experiments in this research were of standard analytical grade such as cobalt chloride ($CoCl_2.6H_2O$), sodium hydroxide, hydrochloric acid, acetone, deionized distilled water and standard co solutions of atomic absorption spectrophotometer (AAS). For the preparation of stock solution of Co (II) (1,000 mgL^{-1}), 4.039 g of $CoCl_2.6H_2O$ was dissolved in 100 mL of deionized distilled water and further diluted up to 1,000 mL by using deionized distilled water. Stock solutions were stored in air-tight plastic bottle. Working solutions of different concentrations (25, 50, 100, 200 and 400 mgL^{-1}) were prepared by required dilutions of the stock solution by using deionized distilled water.

2.2. Preparation and pretreatment of biomass

Corncob (*zea mays* stalk) used as a biomass for the biosorption of Co (II) metal. Biomass was taken from CPC-Rafhan Faisalabad. The collected biomass was well washed with deionized distilled water for mitigation of surface impurities, particulate matter, dust and debris, then dried at the temperature of 50°C for 72 h by placing it in oven. Then, dried biosorbent was cut, ground and sieved. Grinding was done with food processor (Moulinex, France) and sieving was done with Octagon siever. Sieving was carried out for the abolition of huge sized particles and to obtain biomass of recognized component size (0.25 mm) that was preferred for biosorption study. Physical and chemical modifications are done to analyze enhancement or decrease in adsorption capacity of biomass. For physical modification like, heating (20 g of biosorbent was taken in oven and heated at 60°C for 72 h), boiling (20 g of biosorbent was drenched in deionized distilled water and boiled for 1 h) and autoclaving (20 g of biosorbent was drenched in deionized distilled water to autoclaved at 121°C for 45 min). For chemical modification, 20 g of biomass was pretreated with 0.1 M citric acid, 0.1 M oxalic acid and 0.1 M tartaric acid in orbital shaker at 120 rpm and 30°C for 24 h. Then, pretreated biomass were filtered and washed repeatedly by usage of deionized distilled water till its pH becomes neutral followed by drying.

2.3. Batch biosorption studies

To conduct the experiments, fixed volume of Co (II) solution (100 mL of 100 mgL^{-1}) were taken in each 250 mL conical flasks. Weighed amount (0.1 g) of biosorbent was added to each conical flask and then conical flasks were covered with aluminum foil. After 24 h of shaking filtration of samples were done with filter paper and filtrate were kept in plastic bottles pending AAS analysis. Analyses of Co (II) concentration was determined by using AAS. For each experiment, different conditions were selected.

2.4. Adsorption capacity and % removal

Uptake capacity "q" (mgg^{-1}) is quantity of Co (II) ions sorbed per g (dehydrated weight) of biosorbent. q is the metal uptake capacity and maximum rate of q is recognized as q_{max}. Maximum Co (II) adsorption capacity (q) was examined by the decline in Co (II) concentration in sample solution following addition of special quantity of biosorbent. The Co (II) adsorption capacity (q) was evaluated through concentration difference method. Initial Co (II) concentration was represented by C_i (mgL^{-1}) and equilibrium Co (II) concentration was designated with C_e (mgL^{-1}). The % uptake of biosorbent and metal uptake capacity on equilibrium stage q_e (mgg^{-1}) were examined through Eqs. (1) and (2), respectively:

$$\%\ adsorption = \left(C_i - C_e\right) 100 \ / \ C_i \tag{1}$$

$$q_e = \left(C_i - C_e\right) V \ / \ 1000 \tag{2}$$

in which V is a volume of sample solution (mL) and w is the weight of biosorbent in g.

The efficiency of biosorbent for the removal of Co (II) from aqueous solution was studied by varying the parameters such as initial metal concentration, pH and contact time. On these parameters, a strong dependence of adsorption capacity was observed.

3. Results and discussions

3.1. Effect of pretreatments

Pretreatment methods include generally physical and chemical modifications. With the advancement of pretreatment methods, modified biomass possesses superb potential for the reduction of cost and improved efficiency towards metal exclusion. Physical pretreatments such as heat (Heat-PCC), Autoclave (Auto-PCC) and Boil (Boil-PCC) were implemented in these experiments (PCC stands for pretreated corncob) where autoclaving and boiling engenders more adsorption points on biosorbent surface by omission of mineral matter [15]. As a consequence, pretreatments are accomplished for raising the obscured binding sites and responsible for increasing the adsorption capacity of biomass.

Fig. 1 indicated the metal uptake capacity *q* (mgg^{-1}) for Co (II) as a result of physical and chemical pretreatments. Sorption capacity *q* (mgg^{-1}) of physically pretreated corncob was in the following order:

Auto-PCC (38.4) > Boil-PCC (35.5) > Heat-PCC (32.6) > Nat-CC (25.9)

Chemical pretreatment such as citric (CA-PCC), oxalic (OA-PCC) and tartaric (TA-PCC) acids were implemented in experiments where tartaric and citric acid showed better results because they dissolved polysaccharide components of biosorbent cell wall generating additional binding sites [16].

Effect of organic acids pretreatment on corncob indicated that the metal uptake capacity *q* (mgg^{-1}) value for Co (II) metal was in the following order:

TA-PCC (46.8) > CA-PCC (41.8) > OA-PCC (38.7) > Nat-CC (25.9)

3.2. Effect of pH on Co (II) sorption

In the biosorption process, pH plays most important role. Protonation or deprotonation of the adsorbent is influenced by the pH. In this work, different pH ranges (2–8) were chosen in solubility range of Co (II), while all other operational parameters were kept constant. Fig. 2 showed that sorption capacities (mgg^{-1}) increased with increase pH from low (2) to an optimum value (4) for Co (II) metal. The metal uptake capacity *q* (mgg^{-1}) of adsorbent increased from 19.2 to 27.9, 33.2 to 44.1, 36.2 to 48.5, 31.4 to 40.9, 29.1 to 40.5, 26.1 to 37.5 and 23.1 to 34.5 for Nat-CC, CA-PCC, TA-PCC, OA-PCC, Auto-PCC, Boil-PCC and Heat-PCC, when pH values of the solutions changed from 2 to 4. A slow increase in metal uptake capacity was observed which stabilized till pH 8. This is due to the precipitation of metal ions and not by biosorption. At low pH value, adsorbent surface would be closely associated with (H_3O^+) ions and holds specifically protonation sites, therefore it maintains positive charge on surface and hinders the access of the metal ions to the surface functional group [17].

3.3. Effect of initial metal concentration

The effect of initial metal ion concentration on the elimination of Co (II) metal from aqueous solution by corncob in its native and pretreated form was studied at optimum pH 4 by changing the concentration of the system from 25 to 400 mgL^{-1}. As the Co(II) initial concentration increased from 25 to 400 mgL^{-1} as shown in Fig. 3, metal uptake capacities *q* (mgg^{-1}) increased from 9.9 to 60.5, 13.95 to 137.5, 15.55 to 139.6, 12.3 to 134.2, 11.9 to 127.2, 11.2 to 125.8 and 10.4 to 117.2, while % removal decreased from 39.6 to 15.1, 55.8 to 34.4, 62.2 to 34.9, 49.2 to 33.55, 47.6 to 31.8, 44.8 to 31.45 and 41.6 to 29.3 for Nat-CC, CA-PCC, TA-PCC, OA-PCC, Auto-PCC, Boil-PCC and Heat-PCC as concentration increased from 25 to 400 mgL^{-1}. It can be explained by the fact that at low concentration, adsorption sites were more quickly occupied by metal and at high concentration metal ions diffuse to the surface of biomass [18]. This is obvious that for higher initial concentrations, more efficient utilization of sorption sites is expected due to a greater driving force by a higher concentration gradient.

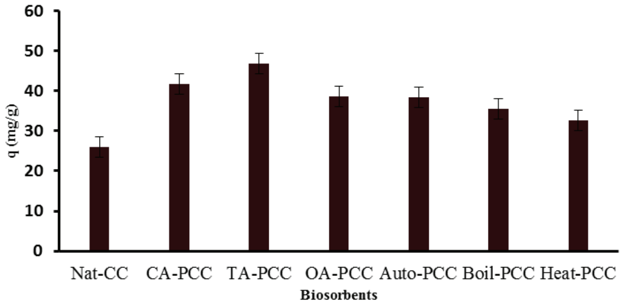

Fig. 1. Effect of pretreatments on biosorption of Co (II).

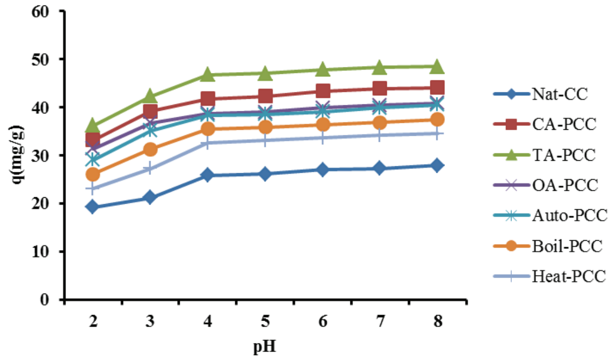

Fig. 2. Effect of pH on biosorption of Co (II).

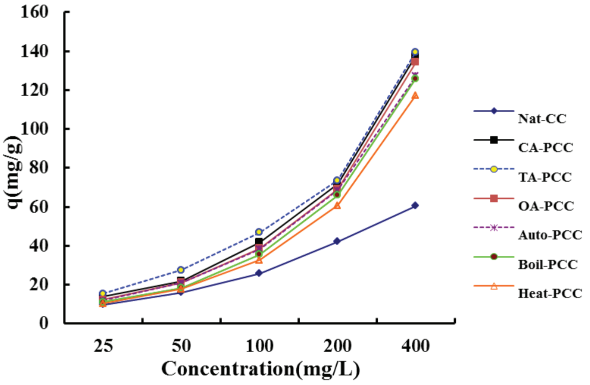

Fig. 3. Effect of initial metal concentration on biosorption of Co (II).

3.4. Equilibrium modeling

Metal ions biosorption can be studied by two types of isotherms such as Langmuir model, in which the amount of metal uptake by biomass reaches equilibrium and the Freundlich model, in which the amount of metal uptake by biomass increases with time [18]. Therefore, by applying the Langmuir and Freundlich isotherms, equilibrium adsorption tests were examined.

3.4.1. Langmuir isotherm

The common type of this isotherm in the form of equation is represented as follows:

$$1/q_e = 1/q_{\max} + 1/\left(b\,q_{\max}\right)C_e \tag{3}$$

In this equation, q_e is the adsorption capacity at equilibrium stage; C_e is concentration at this stage; $1/q_{\max}$ and b are called constants obtained from regression equation, called intercept and slope, respectively. This isotherm supposes that compact surface has a limited amount of equal points which are actively identical. This isotherm elucidated that all adsorbed group interrelate simply with a binding site and they cannot interfere with each other so, the adsorption is restricted to monolayer. As a result, it is stated that when a Co (II) ions engages a point, no additional adsorption can acquire on that point and this is the equilibrium point (Fig. 4).

Linearized outline of the Langmuir isotherm equation can be written as follows:

$$C_e/q_e = 1/X_mK_L + C_e/X_m \tag{4}$$

In this equation, q_e is the amount of Co (II) ions sorbed at the point of equilibrium, C_e (mgL^{-1}) is the equilibrium concentration; X_m and K_L both are the Langmuir constants.

3.4.2. Freundlich isotherm

Freundlich isotherm can be represented in the following equation:

$$q_e = KC_e 1/n \tag{5}$$

This isotherm equation presumes that a monolayer adsorption among a various energetic allocation of active binding sites, come with the interfaces among adsorbed particles. Freundlich equation describes the relation of solute particles that adsorb from solution to the solid surface of biomass. The linearized outline of this model is as follows:

$$\log q_e = \log K_f + \left(1/\mathrm{n}\right)\log C_e \tag{6}$$

in which C_e (mgL^{-1}) is concentration of metal ions at equilibrium point, q_e (mgg^{-1}) is the total amount of Co (II) ions that adsorbed per specific quantity of adsorbent on equilibrium position, K_f (mgg^{-1}) and "1/n" both are named as the constants obtained by regression equation, which is also termed as intercept and slope respectively. The 1/n and K_f values were obtained by plotting the graph between log q_e versus log C_e. K_f and 1/n tells about the adsorption degree and adsorption amount that may be constant or decreased by increasing the adsorbate concentration (Fig. 5). For Freundlich isotherm model, the R^2 values are greater than R^2 values obtained in case of Langmuir model.

3.5. Effect of contact time

Biosorption efficiency is greatly affected by time contact. A considerable change was observed in biosorption rate by changing the contact time at various conditions. The effects of contact time on adsorption were shown in Fig. 6. More than 80% metal ions are adsorbed in first 10 min, and then metal uptake increased with time because of free availability of extra cellular binding sites and attained quasi-equilibrium up to 120 min [19]. After the attainment of equilibrium, further adsorption of Co (II) metal did not vary with increase in time, which leads to saturation of active binding sites of corncob.

3.6. Kinetic modeling

Kinetic mechanism of Co (II) biosorption were analyzed through Lagergren's pseudo-first-order and pseudo-second-order. Kinetic equations evaluated the transfer of Co (II) metal ions on different adsorbents.

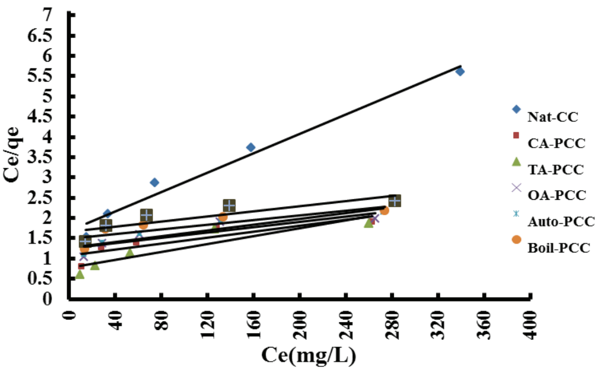

Fig. 4. Langmuir isotherm plot for the biosorption of Co (II).

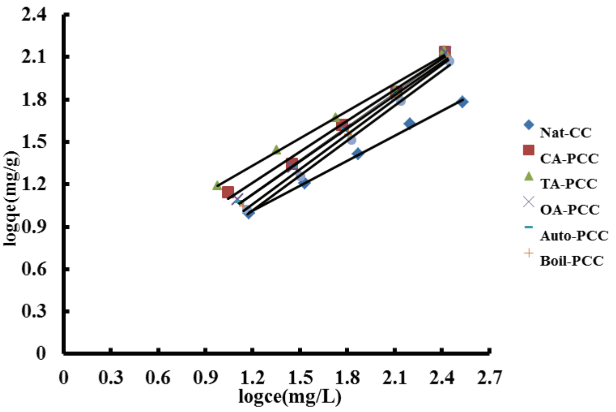

Fig. 5. Freundlich isotherm plot for the biosorption of Co (II).

3.6.1. Pseudo-first-order kinetics

The common shape of pseudo-first-order in solid/liquid system is written as follows:

$$\log\left(q_e - q\right) = \log q_e - k_1 t / 2.303 \tag{7}$$

in which the q_e and q (mgg^{-1}) are the amount of Co (II) adsorbed on the biosorbent at equilibrium position and on time t, in mgg^{-1}, respectively. k_1 (min^{-1}) is called the rate constant of this model. This model is on the statement that the rate of adsorption is proportional to the number of uninhabited points. The rate constant k_1 and equilibrium adsorption capacity q_e evaluated by plotting the graph between the log (q_e – q) versus t. The R^2 values of pseudo-first-order kinetics are lesser when compared with pseudo-second-order as shown in Fig. 7.

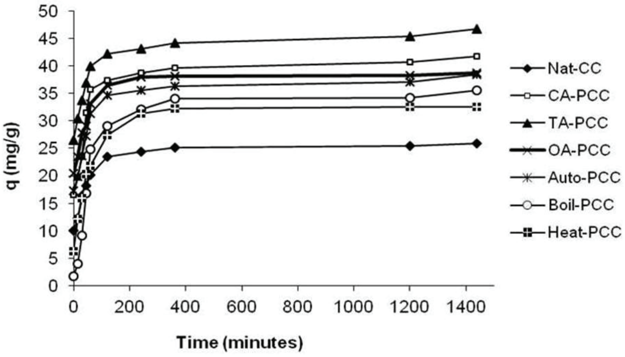

Fig. 6. Effect of contact time on biosorption of Co (II).

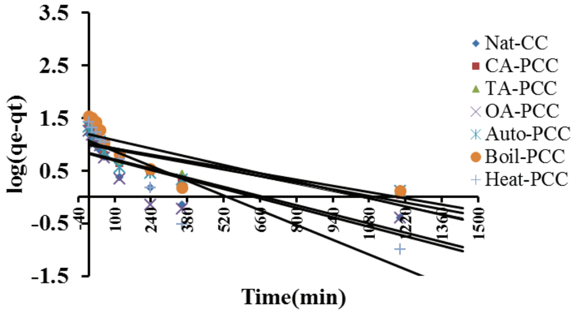

Fig. 7. Pseudo-first-order plot for the biosorption of Co (II).

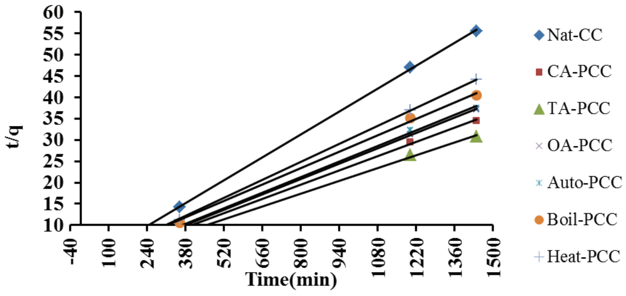

Fig. 8. Pseudo-second-order plot for the biosorption of Co (II).

3.6.2. Pseudo-second-order kinetics

The adsorption kinetics information was more carried out through pseudo-second-order. This kinetic model is supported, which states that adsorption rate is proportional the square of number of uninhabited points. It is represented as follows:

$$T / q = 1 / k_2 q_e^{\,2} + t / q_e \tag{8}$$

In this equation, k_2 is the equilibrium rate constant of pseudo-second-order adsorption (gmg^{-1}min^{-1}). To determine the k_2 and q_e graph is plotted between t / q and t [20,21]. The coefficient of correlation in the second-order-kinetic model was approximately equivalent to one and calculated values of q_e (mgg^{-1}) for Co (II) also approved to the experimental values shown in Fig. 8. These results revealed that the adsorption of Co (II) metal follows the pseudo-second-order efficiently.

4. Conclusion

Biosorption method outperforms when compared with conventional methods because of eco-friendliness and cost effectiveness nature. Corncob after physical and chemical pretreatments was used as a biomass for the removal of Co (II) metal ions from aqueous media in this research work. Adsorption behavior of corncob from aqueous solution was examined by the batch equilibrium technique under different parameters like initial metal concentration, solution pH and time of contact. It was observed that maximum adsorption of Co (II) ions occurred at pH 4. Co (II) ion adsorption on adsorbents improves as the initial Co (II) concentration increase. Analyses of the experiments demonstrated that the uptake capacity of physically and chemically pretreated corncob was considerably elevated when compared with native. The adsorption isotherm was well described by Freundlich model and the pseudo-second-order was well explained the kinetics of the obtained data.

References

[1] M. Akhtar, S. Iqbal, A.M. Kausar, I. Bhangera, M.A. Shaheen, An economically viable method for the removal of selected divalent metal ions from aqueous solutions using activated rice husk, Colloids Surf. B: Biointerfaces, 75 (2010) 149–155.

[2] M.M. Areco, M.S. Afonso, Copper, zinc, cadmium and lead biosorption by *Gymnogongrus torulosus*: thermodynamics and kinetics studies, Colloids Surf. B: 81 (2010) 620–628.

[3] M. Monier, N. Nawar, D.A.A. Latif, Preparation and characterization of chelating fibers based on natural wool for removal of Hg (II), Cu (II) and Co (II) metal ions from aqueous solutions, J. Hazard. Mater, 184 (2010) 118–125.

[4] M. Mohapatra, L. Mohapatra, P. Singh, S. Anand, B.K. Mishra, A comparative study on Pb(II), Cd(II), Cu(II), Co(II), Fe (III) adsorption from single and binary aqueous solutions on additive assisted nano-structured goethite, Int. J. Eng. Sci. Tech., 2 (2010) 89–103.

[5] X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, W. Shao, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel, Colloids Surf. A: Physicochem. Eng. Asp., 317 (2008) 512–521.

[6] M. Horsefall, A.I. Spiff, Equilibrium sorption study of Al^{3+}, Co^{2+} and Ag^{+} in aqueous solution by fluted pumpkin (*Telfairia occidentalis hookf*) waste biomass, Acta Chim. Slov., 52 (2005) 174–181.

[7] Y.S. Negi, S. Kumar, J.S. Upadhaya, Studies on characterization of corncob based nanoparticles, Adv. Mat. Lett., 1 (2010) 246–253.

[8] K. Swayampakula, V.M. Boddu, S.K. Nadavala, K. Abburi, Competitive adsorption of Cu (II), Co (II) and Ni (II) from their binary and tertiary aqueous solutions using chitosan-coated perlite beads as biosorbent, J. Hazard Mater., 170 (2009) 680–689.

[9] M. Tuzen, O.D. Uluozlu, C. Usta, M. Soylak, Biosorption of copper (II), lead (II), iron (III) and cobalt (II) on *Bacillus sphaericus*-loaded Diaion SP-850 resin, Anal. Chim. Acta., 581 (2007) 241–246.

[10] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions, Bioresour. Technol., 99 (2008) 6017–6027.

[11] A. Pal, S. Ghosh, A.K. Paul, Biosorption of cobalt by fungi from serpentine soil of Andaman, Bioresour. Technol., 97 (2006) 1253–1258.

[12] A.I. Adeogun, M.A. Idowu, A.E. Ofudje, S.O. Kareem, S.A. Ahmed, Comparative biosorption of Mn(II) and Pb(II) ions on raw and oxalic acid modified husk: kinetic, thermodynamic and isothermal studies, App. Water Sci., 3 (2013) 167–179.

[13] M. Soylak, M. Tuzen, D. Mendil, I. Turkekul, Biosorption of heavy metals on *Aspergillus fumigatus* immobilized Diaion HP-2MG resin for their atomic absorption spectrometric determinations, Talanta., 70 (2006) 1129–1135.

[14] J.C. Igwe, A.A. Abia, Adsorption kinetics and intraparticulate diffusivities for bioremediation of Co (II), Fe (II) and Cu (II) ions from waste water using modified and unmodified maize cob, Int. J. Physic. Sci., 2 (2007) 119–127.

[15] B. Zhu, T. Fan, D. Zhang, Adsorption of copper ions from aqueous solution by citric acid modified soybean straw, J. Hazard. Mater, 153 (2008) 300–308.

[16] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Biosorption of cobalt (II) and nickel (II) by seaweeds: batch and column studies, Sep. Purif. Sci., 44 (2005) 53–59.

[17] B. Sancey, G. Trunfio, J. Charles, J.M. Francois, S. Gavoille, P.M. Badot, G. Crini, Heavy metal removal from industrial effluents by sorption on cross-linked starch: chemical study and impact on water toxicity, J. Environ. Manag., 92 (2011) 765–772.

[18] H.N. Bhatti, R. Khalid, M.A. Hanif, Dynamic biosorption of Zn (II) and Cu (II) using pretreated *Rosa gruss a teplitz* (red rose) distillation sludge, Chem. Eng. J., 148 (2009) 434–443.

[19] U.K. Garg, M.P. Kaur, V.K. Garg, D. Sud, Removal of hexavalent chromium from aqueous solution by agricultural waste biomass, J. Hazard. Mater, 140 (2007) 60–68.

[20] H. Parab, S. Joshi, N.A. Shenoy, U.S. Sarma, M. Sudersanan, Determination of kinetic and equilibrium parameters of the batch adsorption of Co (II), Cr (III) and Ni (II) onto coir pith, Process Biochem., 41 (2006) 609–615.

[21] H. Zafar, R. Nadeem, R. Saeed, R. Gill, T. Iqbal, K. Akhtar, Exclusion of Zn(II) from aqueous solution using corncob (Zea mays stalk) after chemical modifications with inorganic acids and bases, Desal. Water Treat., 52 (2014) 5605–5610.