

## Utilization of three low cost bio adsorbents in their native as well as carbonized forms for the removal of cobalt(II) from aqueous solutions

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Groundnut seed cake powder (GNSCP), sesame seed cake powder (SSCP) and coconut cake powders (CCP) were used in the bio-sorption of cobalt(II) from aqueous solutions. These powders in their native as well as carbonized forms were used for the removal of cobalt(II). Effect of pH, contact time adsorbent dosage, temperature and initial metal concentration on the uptake of the metal ions were investigated. Kinetic studies for the bio-sorption of cobalt(II) showed that the process followed a pseudo-second order kinetics for both the forms of the adsorbents. Isothermal studies indicated that Langmuir isotherm fits for the adsorptive removal of cobalt(II). With a maximum adsorption capacity of 5.0 mg/g using both the forms of the adsorbents showed an effective and efficient removal 99.8% of cobalt(II) from aqueous solutions. The three adsorbents chosen for the present study, have not been used so far in the removal of cobalt(II).

Keywords: Bio-sorption, cobalt(II), pseudo-second order kinetics, Langmuir isotherms, Temkin isotherm, Freundlich isotherm.

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### Introduction

Heavy metals enter the environment through anthropogenic activities, direct atmosphere deposition, geologic weathering or through the discharge of agricultural, municipal, residential or industrial waste products<sup>1</sup>. Metal species and their concentration, pH, sludge concentration, wastewater pollution load<sup>2,3</sup> and solubility of the metal ions<sup>4</sup> are the significant factors that influence the presence of toxic metals. As<sup>III</sup>, Co<sup>II</sup>, Cr<sup>III</sup>, Cd<sup>II</sup> and Zn<sup>II</sup> are some of the toxic metals whose treatment from industrial waste waters and acid drainage is a serious environmental concern<sup>5-9</sup>. Heavy metals are used as inhibitors in nitrification processes and are another reason for the occurrence of heavy metals in the environment<sup>10,11</sup>.

Cobalt is one among the toxic metals found in various industrial effluents from metal plating, mining, fertilizers, tanneries, batteries, paper, pesticides, electronics and petrochemical and textile industries. It is also released in to the environment from burning coal and oil, exhaust of automobiles. The metal is extensively used in nuclear medicine, semiconductors, and paint and varnish industries and as catalyst in organic reactions. Environmental contamination through toxic metals is a serious concern in developed coun-

tries. Bio accumulation, carcinogenicity and non-degradable nature of these toxic metals enhance the seriousness of the problem<sup>12,13</sup>. Toxic metals enter the water bodies either by direct or indirect means<sup>14</sup>. In India, the maximum tolerable limit of cobalt(II) concentration in water is 0.01 mg/L in drinking water in 0.05 mg/L in inland surface water (Central Pollution Control Board, India).

Various physical, chemical and biological treatment technologies exist to metal contaminated wastewater. Among the methods, adsorption is a highly efficient and feasible cost effective and widely employed for heavy metal removal<sup>15</sup>, natural adsorbents including agro-wastes, forestry residues, etc. elicit the scope of adopting adsorption due to its wider availability, physicochemical stability, high adsorption capacity and desirable regeneration potential<sup>16</sup>.

Adsorption seemed to be a good treatment option, because of its efficiency and efficiency<sup>17-22</sup>. Several natural adsorbents have been reported to effectively remove cationic metal ions from aqueous solution in their native or modified form. Few of them includes, Citrus maxima peel<sup>23</sup>, litchi cinensis seeds<sup>24</sup>, tea waste<sup>25</sup>, sunflower biomass<sup>26</sup>, sesame straw<sup>27</sup>, teak waste<sup>28</sup>, chrysanthemum indicum flower<sup>29,30</sup>, and rice straw<sup>31</sup>. Different studies in adsorption removal of

cobalt(II) with different varieties of adsorption have been earlier tried and the yield reported. Plant material tried as adsorption was locker japonica<sup>32,33</sup> and rose waste biomass<sup>34</sup>. Some tried leaf powder-of cocosnucifera<sup>35</sup>, acacia nilotica<sup>36</sup>, erythrina variegata orientalis<sup>37</sup> and ficus religiosa<sup>38</sup>. Fruit waste such as blighiasapida pod<sup>39</sup>, banana and orange<sup>40</sup>, lemon<sup>41</sup>, everniaprunastri<sup>42</sup> and black carrot residue<sup>43</sup> has also been reported. Hazelnut shell<sup>44</sup>, shells of crab<sup>45</sup> and of crab and area shell<sup>46</sup> were also studied. The present paper is aimed at the removal of cobalt(II) from aqueous solutions using three low cost adsorbents in their native form as well as carbonized form.

*Materials and methods:*

All the chemicals used were of analytical grade. Double distilled water was used throughout the experiment. XRD analysis was carried out by using Bruker advanced D8 PXRD instrument. FTIR analysis was carried out by ATSON II FTIR instrument. Perkin-Elmer high sensitivity AAS was used to determine the concentration of metal ions.

*Preparation of adsorbents:*

Groundnut seed cake, sesame seed cake and coconut seed cake were obtained from the local market. These are the substances remained after the extraction of oil from the respective seeds. This raw material was found to be a hard mass. Hence the substance was first crushed and then ground into a fine powder using laboratory mill. The resulting powder was sieved to get a powder of homogenous particle size. The material was tested for the absence of any residual oil. Such powder samples were washed thoroughly with distilled water and dried at room temperature and made moisture free. Such samples were stored for further experimentation.

The three raw materials were placed in three different crucibles and heated until all the mass is completely carbonized. These carbonized powders stored in air tight containers to avoid any further contamination.

*Characterization of adsorbents:*

The surface area of groundnut seed cake, sesame seed cake and coconut seed cake was found to be 470, 456 and 480 m<sup>2</sup> g<sup>-1</sup>. The same for the carbonized powders were found to be 485, 492 and 496 m<sup>2</sup> g<sup>-1</sup>. These values are higher on comparison with other carbons. The adsorption capacity of carbon is influenced by the chemical structure of its surface, which are of carbon-oxygen functional groups. Most often

the functional groups responsible for surface activity are carboxyl groups, phenolic groups, hydroxyl groups, carbonyl groups and lactones groups. FTIR spectrum of the adsorbents confirms the same. The bulk chemical composition of the same was studied using XRD. X-Ray diffraction studies were carried out for the adsorbents prior and after adsorption (Figures are incorporated as supplementary data). The FTIR spectra of the three adsorbents showed similar bands. Some important bands observed are at 3270.8 cm<sup>-1</sup> for N-H stretching in amines, 2921 cm<sup>-1</sup> for -OH stretching in -COOH, 1743.2 cm<sup>-1</sup> for C=O stretching in amides or aldehydes or ketones. From these data it is found that the adsorbent materials contain lignin, protein, amines and carboxylic acid groups in them. XRD patterns of the adsorbents before and after adsorption process clearly depicts the presence of metal ion in the adsorbent after experimentation.

*Preparation of Co<sup>II</sup> solution:*

Stock solution of cobaltous chloride was prepared by dissolving an adequate amount of the substance in distilled water to result solution of concentration 100 mg L<sup>-1</sup> and standardized. Various concentrated solutions were obtained by diluting the stock solution.

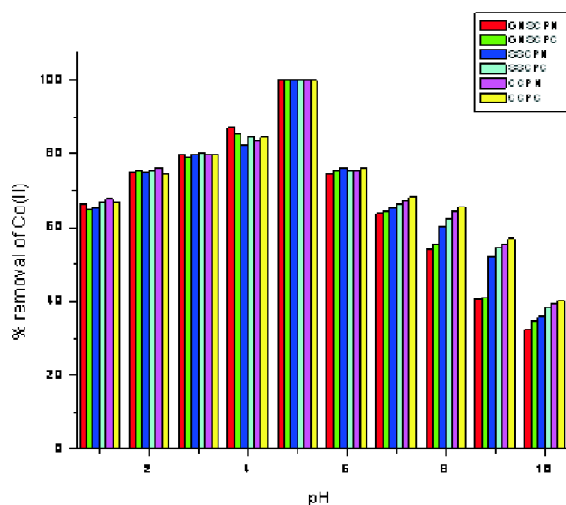
*Methodology:*

By agitating a series of bottles containing various amounts of the different adsorbents with the adsorbate (heavy metal ion). Batch experimentation was carried out at optimum pH. The adsorbents were mixed with 50 ml of stock solution of the metal ions. The pH of the solution was adjusted by using 0.1 N HCl and 0.1 N NaOH until the pH was stabilized. Then the resulting solution was agitated at room temperature for a period of time until equilibrium was attained. After the equilibration period the adsorbent was separated from the suspension through Whatman No. 1 filter paper. The residual concentration of cobalt(II) was determined by AAS.

**Results and discussion**

*Effect of pH:*

A significant influence of pH on the uptake of heavy metals was observed, since pH determines the surface charge of the adsorbent, degree of ionization and speciation of adsorbate. The results obtained were shown in Fig. 1. It depicts the effect of pH on the removal of cobalt(II) from aqueous solution on to the three adsorbents in their native as well as carbonized forms. At a higher initial pH (> 8) precipitation

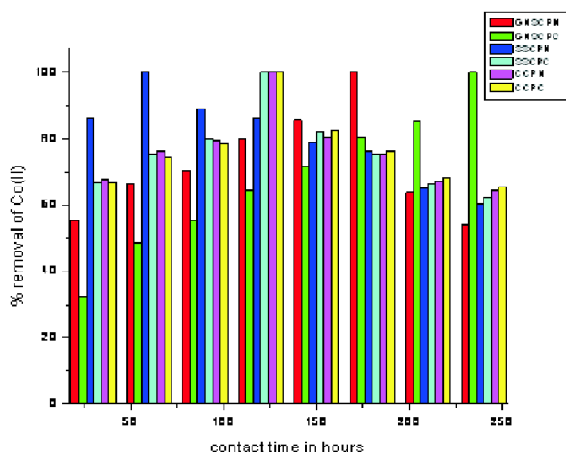


**Fig. 1.** Effect of pH on the removal of cobalt(II) using the chosen adsorbents.

of cobalt ions was found. From the results it was clear that the adsorption of the metal ions is found to be effective at a pH value of 5 with the selected adsorbents and hence pH of 5 was fixed as optimum pH for the present study.

*Effect of contact time:*

Series of experimentation was carried out to investigate the effect of contact time on the adsorption capacity of the chosen adsorbents. The results were shown in Fig. 2. From such series of experiments equilibrium time for the effective removal of cobalt ions using the adsorbents was established. By fixing the adsorbent dosage batch experiments were carried out at varying time intervals. From the results obtained

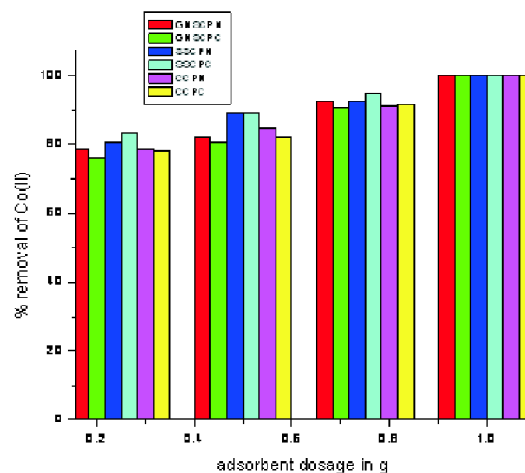


**Fig. 2.** Effect of contact time on the removal of cobalt(II) using the adsorbents.

99.8% of removal of cobalt ions was found at a time of 3 h for native GNDCP; 4 h for carbonized GNDCP; 2 h for both native and carbonized forms of CCP; 1 h for SSCP in the native form and 2 h carbonized form of SSCP.

*Effect of adsorbent dosage:*

A series of experiments were carried out to ascertain the adsorbent dosage for the efficient removal of cobalt(II) by the three different adsorbents in both the forms. The experimentation was carried out by taking 0.25, 0.5, 0.75, 1.0, 1.5 and 2.0 g of the adsorbents for batch studies. The results obtained were shown in Fig. 3. From the results it was found that removal of cobalt ions from aqueous solution was effective for 1.0 g for all the selected adsorbents and the same was fixed as optimum adsorbent dosage.



**Fig. 3.** Effect of adsorbent dosage on the removal of cobalt(II).

*Effect of initial metal ion concentration:*

By fixing adsorbent dosage, pH and contact time a study was carried out to fix the initial metal ion concentration. A series of cobalt(II) solutions of concentration 10, 20, 30, 40, 50, 60, 70, 80, 90 mg L<sup>-1</sup> were mixed in separate flasks with 1.0 g of the adsorbents. These mixtures were agitated for the optimum/equilibrium time period at a pH of 5. After the equilibration time concentration of cobalt(II) in the filtrate was determined. The results obtained were shown in Fig. 4. Due to the absence of sorption sites in the chosen adsorbents the efficiency of metal ion uptake by the adsorbent decreases as the concentration of the metal ion increases. The maximum removal of cobalt using the adsorbents was found at a metal concentration of 20 mg L<sup>-1</sup>.

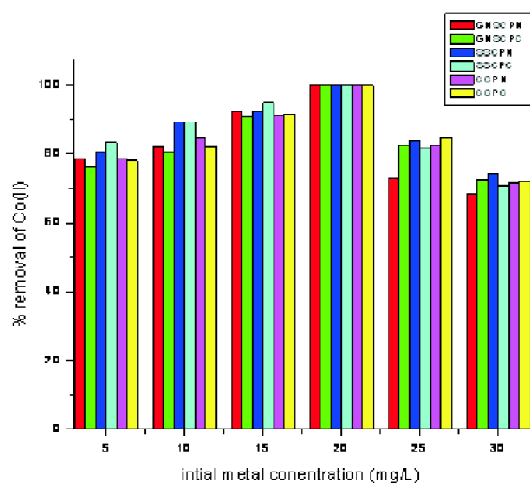


Fig. 4. Effect of initial metal concentration on the removal of cobalt(II).

*Effect of temperature:*

Experimentation was conducted to establish the effect of temperature on the adsorption capacity of the selected adsorbents. The results were shown in Fig. 5. A series of experiments were carried out to establish the equilibrium temperature for the effective removal of cobalt ions using the adsorbents. By fixing the adsorbent dosage, contact time, pH and initial metal concentration batch experiments were carried out at varying temperatures. From the results obtained 99.8% of removal of cobalt ions was found at a temperature of 40°C.

*Kinetic models of the present study:*

In understanding the mechanism of uptake of heavy metals by adsorbents and to evaluate the performance of

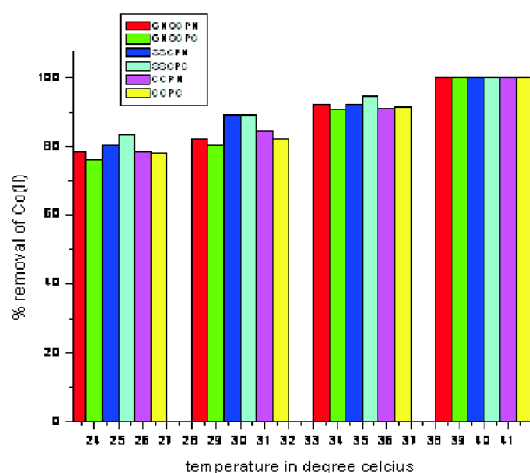


Fig. 5. Effect of temperature on the removal of cobalt(II).

various adsorbents for the removal of metals kinetic models are extremely helpful. Lagargren's pseudo-first order kinetics and pseudo-second order models are the widely used models among the many kinetic models developed. The sorption kinetics of pseudo-first order was

$$\log (q_e - q) = \log q_e - k_f/2.303$$

where  $q_e$  is the amount of solute adsorbed at equilibrium per unit weight of adsorbent,  $q$  is the amount of solute adsorbed at any time and  $k$  is adsorption constant.

The pseudo-second order kinetic model is described by the following equation:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

where  $q_t$  and  $q_e$  are the sorption quantity at time  $t$  and equilibrium respectively,  $k$  is the rate constant. Thus a plot of  $t/q_t$  vs  $t$  gives the pseudo-second order adsorption. Pseudo-second order rate constant was determined from the respective plots.

It is inferred from the results that the sorption of cobalt(II) using the chosen adsorbents followed pseudo-second order kinetics the same was presented in Fig. 6. Correlation coefficient ( $R^2$ ) for the process was found greater than 0.97 indicating the fitness of the model for the present process.

*Adsorption isotherms:*

Among the many adsorption isotherms available Langmuir, Freundlich and Temkin adsorption isotherms were used in the present study. The mathematical expressions for

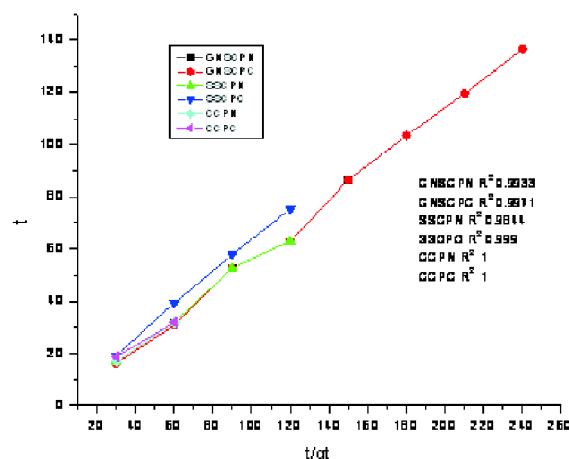


Fig. 6. Pseudo-second order kinetic plot for the removal of cobalt(II) using the adsorbents.

these three adsorption isotherms are as follows:

Langmuir adsorption isotherm:

$$q_e = \frac{q_m K C_e}{1 + K C_e}$$

(or)

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Freundlich adsorption isotherm:

$$q_e = K_F C_e^{1/n}$$

And in linearized form

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Temkin isotherm model can be represented as

$$Q_e = \left(\frac{RT}{b}\right) \ln(K_T C_e)$$

This equation can also be represented as

$$Q_e = \left(\frac{RT}{b}\right) \ln K_T + \left(\frac{RT}{b}\right) \ln C_e$$

The results of isothermal analysis showed that adsorption of cobalt(II) from aqueous solution fit to Langmuir adsorption

isotherm. Various terms involved in the isotherm are  $q_m$  and  $K$  are Langmuir constants related to the sorption capacity and sorption energy respectively.  $C_e$  is the equilibrium concentration in  $\text{mg L}^{-1}$  and  $Q_e$  is the amount of adsorbate adsorbed per unit weight of adsorbent. A plot of  $C_e/Q_e$  against  $C_e$  was drawn and correlation coefficient from the graph was found to be 0.9843. This substantiates the fitness of the isotherm for the present study.  $Q_{\text{max}}$  obtained for the removal of cobalt(II) using various adsorbents was compared with that of the present study and presented in Table 2. The adsorbents used were found to be superior with respect to  $Q_{\text{max}}$  obtained on comparison with other adsorbents.

*Thermodynamic parameters:*

Standard Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) for the adsorptive removal of  $\text{Co}^{II}$  from aqueous solutions using the three chosen adsorbents were computed. From the result analysis data it was found that,  $\Delta G$  for the present study was found to be negative indicating that the reaction is spontaneous. A negative value of  $\Delta H$  was found from the results indicating the exothermic nature of the reaction. A positive value for  $\Delta S$  was the result. It indicated that the randomness increased on increase in temperature. Similar trends were observed for each of the adsorbent used. Hence it is concluded that the reaction under study is spontaneous, exothermic and randomness is increased.

**Table 1.** Results of adsorption characteristic parameters

Sr. No.	Parameter	GNSCP		CCP		SSCP	
		Native form	Carbonized form	Native form	Carbonized form	Native form	Carbonized form
1.	pH	5	5	5	5	5	5
2.	Temperature (°C)	40	40	40	40	40	40
3.	Dosage (g)	1	1	1	1	1	1
4.	Contact time (h)	3	4	2	2	1	2
5.	Initial metal concentration (ppm)	20	20	20	20	20	20
6.	Percentage removal	99.8	99.8	99.8	99.8	99.8	99.8

**Table 2.** Results of pseudo-second order kinetics parameters

Sr. No.	Adsorbent	Pseudo-first order kinetics			Pseudo-second order kinetics		
		$q_e$	$K_1$	$R^2$	$q_e$	$K_2$	$R^2$
1.	GNSCP	0.000014	26.51	0.165	0.00099	$4.91 \times 10^{-7}$	0.9933
2.	SSCP	0.0000119	25.512	0.16	0.001	$4.913 \times 10^{-7}$	0.9844
3.	CCP	0.0000118	25.512	0.156	0.001	$4.923 \times 10^{-7}$	1
4.	GNSCP	0.000019	26.32	0.16	0.00098	$5.02 \times 10^{-7}$	0.9971
5.	SSCP	0.000015	25.18	0.162	0.001	$5.12 \times 10^{-7}$	0.999
6.	CCP	0.000016	26.35	0.164	0.001	$5.08 \times 10^{-7}$	1

**Table 3.** Comparative study for various adsorbents in the removal of cobalt (II) with the adsorbents chosen for the present study

Sr. No.	Name of the adsorbent	Q <sub>max</sub> (mg/g)	Ref.
1.	Mangosteen shell	0.34	46
2.	South African coal fly ash	0.401	46
3.	Ficus benghalensis leaf powder	5.65	45
4.	Kaolinite	0.909	47
5.	GNSCP,CCP,SSCP(Both in native form and carbonised form)	5.00	Present study

Based on the results of the present study, it was found that, sesame seed cake powder in its native form (SSCPN) suits the best for the adsorptive removal of cobalt(II) from aqueous solutions. It is clear from the results of optimization parameters that, the time required for the removal of the metal using SSCPN was found to be lesser on comparison with other adsorbents used. Hence SSCPN fits the best for the study.

### Conclusions

Adsorption of Co<sup>II</sup> using groundnut seed cake powder, sesame seed cake powder and coconut cake powder in their native form as well as carbonized form was carried out. Adsorption of cobalt using the chosen bio-adsorbents was optimized at a pH of 5, temperature of 40°C, initial metal concentration of 20 mg/L, contact time of 2 h for CCP (both native and carbonized), 1 h for SSCP in native form and 2 h for SSCP in carbonized form, 3 h for native GNSCP and 4 h for carbonized GNSCP, adsorbent dosage 1.0 g for each of the adsorbents. From the results of kinetic studies it was concluded that the adsorption process followed pseudo-second order kinetics. Langmuir adsorption isotherm fit perfect for the adsorption of cobalt(II) using the three adsorbents. Using these adsorbents 99.8% of the metal ion were effectively removed from aqueous solutions.

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### References

- M. Dawson and E. J. Macklin, *Environmental Geochemistry and Health*, 1998, **20**, 67.
- A. Braam and F. Klapwijk, *Water Res.*, 1981, **15**, 1093.
- K. O. Warra, *Water Res.*, 1992, **26**, 355.
- Dilek and F. B. Yetis, *Water Sci. Technol.*, 1992, **26**, 80.
- E. F. Imai and A. Glyona, *Water Res.*, 1990, **24**, 1143.
- J. H. Surittononta and S. Sherrad, *Control Fed.*, **53**, 1314.
- F. U. Fu and Q. Wang, *Journal of Environmental Managements*, 2011, **92**, 407.
- M. A. Barakat, *Arabic Journal of Chemistry*, 2011, **4**, 361.
- H. Dumurul, A. N. Kursunlu, O. Kocyigit, E. Guler and S. Ertul, *Desalination*, 2011, **271**, 92.
- J. L. Aguirre, V. Pongranz and E. R. L. Keiski, *Desalination*, 2009, **24**, 262.
- G. Annadurai, R. S. Juang and D. J. Lee, *Water Sci. Technol.*, 2003, **47**, 185.
- A. Bhatnagar, K. Minocha and M. Sillanpa, *J. Biochem. Eng.*, 2010, **48**, 181.
- Demirbas, *Adsorb. Sci. Technol.*, 2003, **21**, 951.
- A. G. El-Samrani, B. S. Laartges and F. Villieras, *Water Res.*, 2008, **42**, 951.
- N. F. Gray, "Water Technology: An introduction for environmental scientists and engineers", 2nd ed., Elsevier Sci. and Technol. Books, Ireland, 2005.
- F. Gujel, H. Yakut and G. Topal, *J. Hazard. Mater.*, 2000, **153**, 1275.
- M. A. Shahalam, A. Al-Harthy and A. Al-Zawhry, *Desalination*, 2002, **150(3)**, 235.
- D. Sudhir, R. M. Tripathi and A. G. Hegde, *Bioresour. Technol.*, 2008, **99**, 179.
- P. Thilagavath and T. Santhi, *Chin. J. Chem. Eng.*, 2014.
- G. Vijayalakshmi, N. Chittibabu, P. V. Ravi Kumar, D. Subba Rao and P. Venkateswarlu, *Chem. Eng. Comm.*, 2009, **196**, 463.
- K. Vijayaraghavan, K. Palanivelu and M. Velan, *Bioresour. Technol.*, 2006, **97**, 1411.
- S. Vilvanathan and S. Shanthakumar, *Proce. Safe. and Environ. Protect.*, 2015, **96**, 98.
- D. Hymavathi and G. Prabhakar, *Chem. Eng. Comm.*, 2017.
- D. Hymavathi and G. Prabhakar, *Austin Chem. Eng.*, 2017, **4(1)**, 1.
- D. Hymavathi and G. Prabhakar, *J. Pharma Bio. Sci.*, 2017, **8(2)**, (B) 107.
- M. A. Javed, H. N. Bhatti, M. A. Hanf and R. Nadeem, *Sci. and Technol.*, 2011, **42**, 3641.
- T. O. Jimoh, A. T. Buoro and M. Murjana, *J. Environ. Chem. and Exotoxi.*, 2012, 178.
- B. Krishna and P. Venkateswarlu, *Indian J. Chem. Technol.*, 2011, **18**, 381.
- M. Pipsika, M. Hornik, L. Vrtoch, J. Augustin and J. Lency, *Chem. and Ecol.*, 2008, **24**, 181.
- L. L. Prassana, J. K. Yang, Y. Y. Chang, K. J. Reddy, Hy-

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- drometallurgy*, 2015.
31. M. Sadrzadeha, T. Mohammadi, J. Ivakpour and N. Kasiri, *J. Chem. Eng. Pro.*, 2009, **48**, 1371.
  32. D. Kratochvil and B. Volesky, *Trends in Biotechnology*, 1998, **16**, 291.
  33. R. Apiratikul and P. Pavasant, *Bioresource Technology*, 2000, **99**, 2766.
  34. H. P. Chao, C. C. Chang and Neiva, *Journal of Industrial and Engineering Chemistry*, 2014, **20**, 3408.
  35. J. G. Flores-Garnica, L. Morales-Barrera, G. Pineda-Camacho and E. Cristiani-Urbina, *Bioresource Technology*, 2013, **136**, 635.
  36. M. K. Mondal, *Journal of Environment Management Safety*, 2009, **99**, 54.
  37. J. H. Park, Y. S. Ok, S. H. Kim, J. S. Cho, J. S. Heo and R. D. Delaune, *Chemosphere*, 2015, **142**, 77.
  38. S. Vilvanathan and S. Shanthakumar, *Desalination Water Treatment*, 2014, **57**, 3995.
  39. S. Vilvanathan and S. Shanthakumar, *International Journal of Phytoremediation*, 2015, **18**, 1046.
  40. R. Sharma and B. Singh, *Bioresource Technology*, 2013, **146**, 519.
  41. H. Dumurul, A. N. Kursunlu, O. Kocyigit and E. Guler, *Desalination*, 2014, **271**, 92.
  42. M. Kazemipour, M. Ansari, S. Tajrobehkar, M. K. Majdzadeh and H. H. R. Kermani, *J. Hazard. Mater.*, 2008, **150**, 322.
  43. A. N. Kurnsulu, E. Guler, H. Dumurul, O. Kocyigit and I. H. Gubbuk, *Appl. Surf. Sci.*, 2009, **225**, 8798.
  44. E. T. Musapatika, M. S. Onyango and O. Aoyi, *Afr. J. Sci.*, 2010, **106(9/10)**, 167.
  45. D. Hymavathi and G. Prabhakar, *Chemical Engineering Communications*, 2017.
  46. Stela Nhandeyara do Carmo Ramos, AmáliaLuísa Pedrosa Xavier, Filipe Simões Teodoro, Laurent Frédéric Gil and Leandro Vinícius Alves Gurgel, *Industrial Crops and Products*, 2016, **79**, 116.
  47. O. Yauz, Y. Altunkaynak and F. Guzel, *Water Res.*, 2003, **37**, 948.
  48. E. Erdem, N. Karapinar and R. Donat, *J. Colloid Interface Sci.*, 2004, **280**, 309.

