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Factors and Kinetics Involved in Adsorption of Copper from Aqueous and Waste Water onto *Pongamia Pinnata*

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Abstract: Presence of copper in the water used for various activities affects living beings in its own way depending on its concentration. Considering the effects of high dose of copper concentration on humans and animals, it is important to remove this metal ion from industrial effluent before discharge to environmental stream. In this regard Pongamia pinnata tree bark is proven to be an effective and promising adsorbent. Removal of copper ion from aqueous and industrial waste water depends on pH, concentration of metal ion, concentration of adsorbent, contact time and agitation. Equilibrium adsorption data was tested for the Langmuir, Freundlich and Tempkin equations. Adsorption isotherm studies indicated that Langmuir model fits better for the present case. Adsorption kinetics data were modeled using the pseudo-first, pseudo-second order, Elovich and intra particle diffusion models. Adsorption data was best suited by second order model. Hence, this adsorbent has a potential to be used in the industries emitting copper ions in its effluent.

Keywords: Adsorption, copper ion, *Pongamia pinnata* tree bark, adsorption isotherms, kinetic models

I. INTRODUCTION

Growth in the industrial sector in the last few decades has led to a number of environmental related issues. Extensive use of metals, chemicals, natural and artificial materials in manufacturing sector with ineffective treatment of effluent has led to generation of various levels of toxic heavy metals such as Lead, Copper, Zinc, Iron, Nickel, Arsenic, Cobalt, Mercury, Cadmium, Chromium etc., into the environment. [1-5] Worldwide research to remove heavy metals from effluents up to permissible limits before discharge into environment is in continuous progress. Electroplating, painting, metallurgical, mining, textile, municipal incineration and chemical manufacturing industries all generate toxic heavy metals of various levels. [6, 7] Stringent regulations have been made by different countries for safe discharge standards of these effluents. [8, 9]

Copper ions and other heavy metal ions enter into water and soil from different waste water sources and thus pollute the water streams and soil. A number of crops and aquatic plants take up these heavy metals and accumulate within them. When humans consume food and water with copper concentration exceeding the permissible limits then problems like nausea, gastrointestinal disturbance, vomiting, liver or kidney damage etc is likely to be caused. [10,11] Researchers worldwide have developed a number of methods such as chemical precipitation, oxidation or reduction, ion exchange, filtration, membrane separations, electrochemical treatment, reverse osmosis, evaporation recovery, coagulation etc., for removing the heavy metals from industrial effluents before discharging into aquatic streams. [12-16] The conventional treatments produce toxic chemical sludge and in turn disposal or treatment becomes costly and not ecofriendly.

Adsorption is considered as one of the effective and economical technology compared to others for removal of heavy metals from effluents. A variety of materials like polymers,[17] newspaper pulp,[18] amino starch,[19] tamarind fruit shell,[20] Agricultural waste materials,[21] shells of lentil, wheat, rice,[22] cassava peel,[23] *Eichhornia crassipes*,[24] orange peel,[25] unye clay,[26] rose waste biomass,[27] collagen tannin resin,[28] bagasse,[29] barley straw,[30] rice straw,[31] chestnut shell, grape seed activated carbon,[32] pine,[33] peanut hull,[34]*Fucus serratus*,[35] Bacillus Sp.,[36] polysaccharide based materials,[37] sericite,[38] Indian barks,[39] plant biomass,[40] are used for the process. Activated carbon is widely used in many industries as an effective adsorbent for heavy metal removal. The cost of activated carbon is high and hence in some industries the process is not economical.[41] Usually industries strive for low cost methods for waste water treatment and hence may opt for low cost adsorbents. In the present context, a large number of low cost adsorbents prepared from different sources have made their way for heavy metal removal. Though research reported shows varieties of low cost adsorbents, all adsorbents are not available easily throughout the world. Hence, considering the availability of materials in particular region, the adsorbents may be suitably selected to cater the needs of that region.

Pongamia pinnata trees are widely grown in Asia and also in other parts of the world. All parts of this tree have application in medicinal and other areas including the most important one the production of biofuel from *Pongamia pinnata* seeds. Hence, large number of trees are grown at farms and availability of the tree bark is more.[42] Based on the spectroscopic data interpretation of *Pongamia pinnata* tree bark, eight compounds were determined by Haoyin et al.,[43]

The present study shows the feasibility of using adsorbent prepared from *Pongamia pinnata* tree bark for removal of copper ions from aqueous and industrial waste water with parameters as pH, concentration of adsorbent, concentration of metal ion and contact time.

II. EXPERIMENTAL

A. Adsorbent

Pongamia pinnata tree bark popularly known as Karanja was collected in the study area, Davangere, Karnataka, India. It was sundried for 3 days. Then the bark was dried in hot air oven for 80^0C and pulverized into powder to get 225 µm size particles. This powder was washed several times with double distilled water to remove soluble, coloring matter, oven dried for 8 hours at 60^0C and stored in air tight containers.

B. Stock solution

Analytical grade copper sulphate (Nice Chemicals) of required quantity was dissolved in double distilled water to prepare stock solution. 0.1N HCl and 0.1N NaOH were used to adjust the pH of the solutions. Stock solution was diluted with double distilled water to obtain solutions of various concentrations. Industrial waste water (before treatment) collected from a local industry was used for adsorption studies.

C. Batch mode adsorption studies

Effect of several parameters such as pH, concentration of metal ion, concentration of adsorbent and contact time on adsorption of copper on powdered raw *Pongamia pinnata* tree bark was studied by batch technique. All experiments were carried out at room temperature so as to avoid the heating of effluent in case this study would be applied for the pilot scale at the industry. Batch experiments were carried out at an agitation of 200 rpm, samples at predetermined time intervals were collected, filtered by whatman no.42 filter paper and remaining copper was analyzed by UV-VIS Spectrophotometer (Shimadzu) as per standard methods. All experiments were carried out at pH values ranging from 2 to 8, the initial concentration of metal ion from 10 to100 mgL^{-1}, 2 to 10 gL^{-1} of adsorbent of particle size 225µm. The contact time was selected based on equilibrium conditions. Equilibrium was established in 2 hours and no further uptake was observed. Results were used to get optimum conditions for maximum copper removal from aqueous and industrial effluent. All experiments were carried out in duplicate and mean values are presented. The maximum deviation was 5.0 %. The percentage removal of heavy metal from the solution was calculated using the equation,

$$\%\,Removal = \frac{C_0 - C_i}{C_0} X 100 \quad (1)$$

Where C_0 is initial concentration of heavy metal, C_i is final concentration of heavy metal. The adsorption capacity q_e (mgg^{-1}) after reaching equilibrium was calculated using the equation.

$$q_e = (C_0 - C_e)\frac{V}{W} \quad (2)$$

Where V is the volume (L) of solution and W is the mass (g) of adsorbate used.

III. RESULTS AND DISCUSSION

A. Characteristics of Pongamia pinnata adsorbent

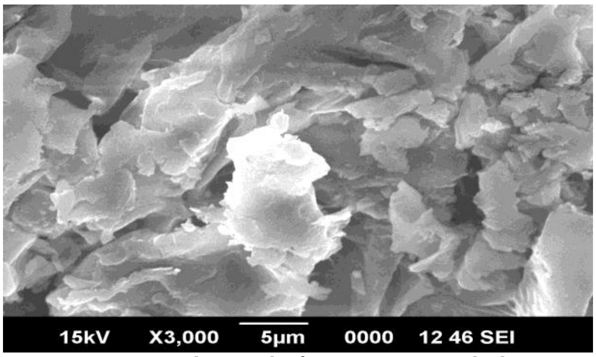

Fig.1 SEM photograph of *Pongamia pinnata* bark

The elemental composition of powdered *Pongamia pinnata* tree bark shows the presence of carbon 38.98%, hydrogen 4.63%, nitrogen 2.76% and sulphur 0.68%. A scanning electron microscope was used to examine the surface of the bark. Figure 1 shows the SEM photograph of the bark and the changes on the surface of the particles. SEM of bark revealed surface physical morphology, its complex porous surface texture and porosity. Pores and internal surface are requisite for an efficient adsorbent.

B. Effect of pH

In order to establish the effect of pH on adsorption of copper ions a function of hydrogen ion concentration was determined and batch experiments were carried out at pH values below the onset of metal hydrolysis and precipitation, determined as pH>6.5 for copper ions. The pH of the solution determines the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate. Copper adsorption was very low at pH<2 and at pH>8.0, metal removal was due to precipitation caused when OH^- ions formed complex with copper. Hence all experiments were carried out in the pH range 2 to 8. Figure 2 shows that the maximum percent removal of copper ions on adsorbent was observed at pH 5.8 and significantly decreased by reducing the pH values and slightly decreased at higher pH values. At higher H+ concentration the adsorbent surface becomes more positively charged hence reduces the attraction between metal ions and adsorbent.

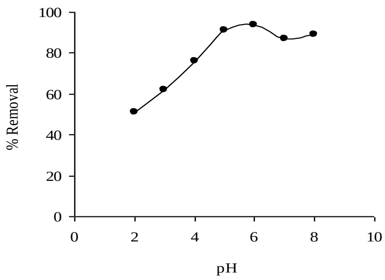

Fig. 2 Effect of pH on adsorption onto *Pongamia pinnata* bark.

C. Effect of initial concentration of copper ions

The adsorption of copper ion on adsorbent depends on initial concentration. Copper ions have smaller hydrated radii (8.38 Å) and hence can enter into smaller pores on the surface of the adsorbent. Copper has high electro negativity (1.9) and standard reduction potential (0.341) which shows a trend with sorption capacity [44]. At low concentrations, metal ions are easily adsorbed on vacant sites. As the metal ion concentration increases, the vacant sites are filled up and no further adsorption occurs due to saturation of vacant sites of adsorbent. Figure 3 shows the effect of metal ion concentration on percent removal of copper. As the metal ion concentration decreases, the percent removal increases.

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Vol. 2, Issue 4, April 2013

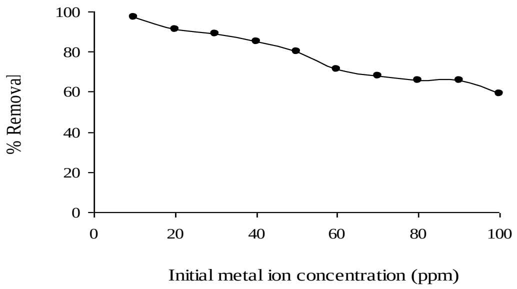

Fig.3 Effect of Initial metal ion concentration on adsorption onto *Pongamia pinnata* bark.

D. Effect of amount of adsorbent

As the amount of adsorbent was increased for copper ion removal, the available number of vacant sites for adsorption also increased. Hence adsorption of metal ion significantly increased with an increase in amount of adsorbent. Figure 4 shows the effect of amount of adsorbent on adsorption of copper ions. The maximum amount of adsorbent used was $10gL^{-1}$.

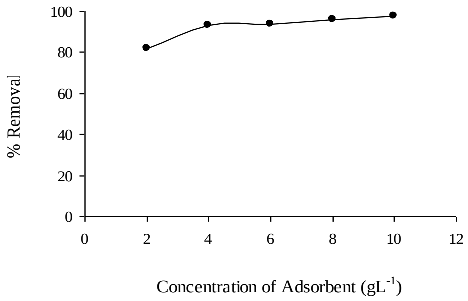

Fig.4 Effect of concentration of adsorbent on adsorption onto *Pongamia pinnata* bark.

E. Effect of contact time

The metal ions adsorbed on to the vacant sites of adsorbent as soon as it came in contact with it. In the beginning, large numbers of active sites were available for adsorption so the removal of copper ions increased. As time passed the sites were filled up and they attained saturation in about 2 hours. The removal of metal ion is rapid, but then gradually decreased with time till it reaches equilibrium. The mechanism of adsorption follows a rapid followed by slow adsorption. Figure 5 shows that the percent removal of copper ions is fast during first 40 min of adsorption and then almost remains constant till it reaches equilibrium.

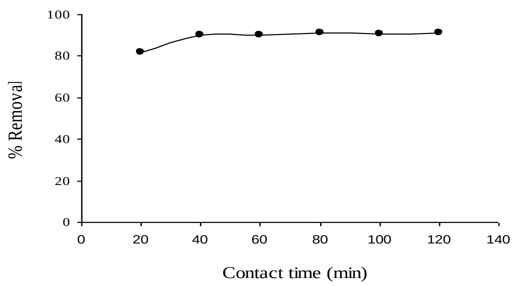

Fig.5 Effect of contact time on adsorption onto *Pongamia pinnata* bark.

F. Adsorption isotherms

To understand the effect of various factors on adsorption, different adsorption isotherms are available in literature. The distribution of metal ion between the liquid phase and sorbent is a measure of the position of equilibrium in the adsorption process and can generally be expressed by one or more series of isotherms. The shape of an isotherm can usually predict to know whether the adsorption is favourable or unfavourable. [45] For the present study, three isotherms were tested to fit the experimental data. The Langmuir adsorption isotherm was used to describe the observed sorption of copper ions and is as shown by the following equation.

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International Journal of Innovative Research in Science, Engineering and Technology
Vol. 2, Issue 4, April 2013

$$\frac{C_e}{q_e} = \frac{1}{b\theta} + \frac{C_e}{\theta} \quad (3)$$

Where, θ is the measure of adsorption capacity (mgg^{-1}) under the experimental conditions and b is a constant related to the energy of adsorption. Figure 6 shows the Langmuir isotherm for copper adsorption.

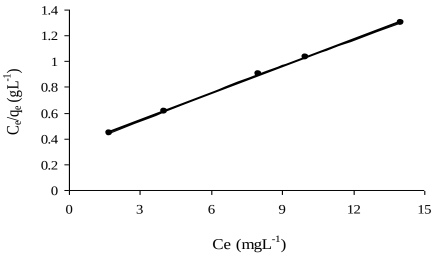

Fig.6 Langmuir adsorption isotherm for adsorption of copper ion onto *Pongamia pinnata* bark

Freundlich model is an empirical model used to describe the adsorption in aqueous systems and to explain the adsorption of copper ions on to adsorbent. The Freundlich isotherm is shown by the following equation.

$$\ln q_e = \ln K + \frac{1}{n}\ln C_e \quad (4)$$

Where, n is the bond energy between metal ion and adsorbent. K is related to the bond strength. Freundlich adsorption isotherm for copper adsorption is as shown in Figure 7.

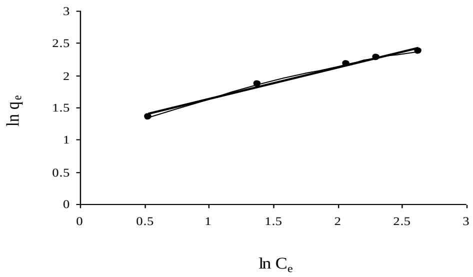

Fig.7 Freundlich adsorption isotherm for adsorption of copper ion onto *Pongamia pinnata* bark

Tempkin adsorption isotherm was also chosen to evaluate the adsorption potentials of adsorbate and adsorbent. The heat of sorption of molecules in layer decreases linearly with coverage due to sorbate and sorbent interactions. Tempkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithm. Tempkin isotherm is as shown by the following equation.

$$q_e = \frac{RT}{b_T}\ln K_T + \frac{RT}{b_T}\ln C_e \quad (5)$$

Where K_T is Tempkin adsorption potential (m^{3}g^{-1}) and b_T is heat of adsorption (kJmol^{-1}). Further equation may be reduced for constant temperature as

$$q_e = a + b\ln C_e \quad (6)$$

Where a and b values depend on K_T and b_T.
Tempkin adsorption isotherm for copper adsorption is as shown in Figure 8.

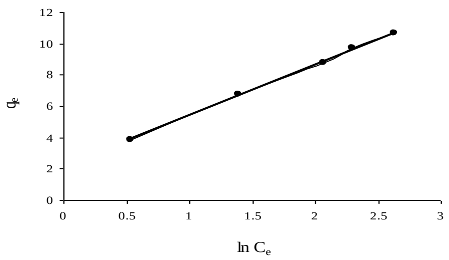

Fig. 8 Tempkin adsorption isotherm for adsorption of copper ion onto *Pongamia pinnata* bark

ISSN: 2319-8753
International Journal of Innovative Research in Science, Engineering and Technology
Vol. 2, Issue 4, April 2013

The estimated model parameters with correlation coefficient (R^2) for different models are as shown in Table 1. The values of R^2 are used to select the best adsorption isotherm model.

Table-I
Correlation coefficient (R^2) for adsorption isotherms

Model	**R^2**
Langmuir	0.9994
Tempkin	0.9986
Freundlich	0.9863

For the present study based on R^2 values the following order is suitable, Langmuir>Tempkin>Freundlich. The essential feature of the Langmuir equation can be given in terms of a dimensionless separation parameter R_L.[46] The values of constants indicate favourable conditions for adsorption. Langmuir type model presupposes homogeneity of the adsorbing surface and no interactions, involving uniform energies of adsorption on the surface and no transmigration of metal ion in the plane of the surface. R_L is given as

$$R_L = \frac{1}{1+bC_0} \quad (7)$$

Where, b is the Langmuir constant, C_0 is the initial concentration. R_L indicates the shape of the isotherm ($R_L>1$, unfavourable, $R_L=1$ linear, $0<R_L<1$, favourable, $R_L<0$ irreversible). For the present study the value of R_L is 0.044 which indicates that adsorption is favourable.

G. Adsorption kinetics

The kinetics involved in the adsorption of copper ions on to *Pongamia pinnata* were studied based on three models namely, the pseudo first, pseudo second order and Elovich model. For the adsorption of solute from liquid solutions, pseudo first order model is most widely used. This model is as below,

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (8)$$

Where q_e is the mass of metal ion adsorbed at equilibrium (mgg^{-1}), q_t is the mass of metal adsorbed at time t (mgg^{-1}), K_1 is the first order reaction rate constant (min^{-1}). A plot of $\ln(q_e-q_t)$ vs. t indicates the application of the first-order kinetic model and is shown in Figure 9.

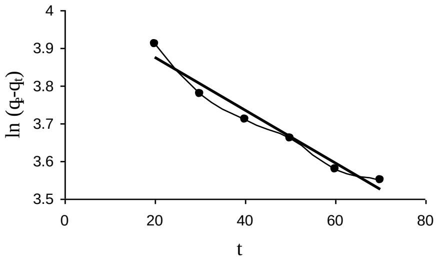

Fig.9 Pseudo First order kinetic model for copper ion adsorption onto *Pongamia pinnata* bark

Based on equilibrium adsorption capacity pseudo second order model is as shown in the form

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

Where K_2 is the second order reaction rate constant ($mgg^{-1}min^{-1}$). A plot of t/q_t against t is a linear relation for the second order kinetics to be applicable to that model as shown in Figure 10.

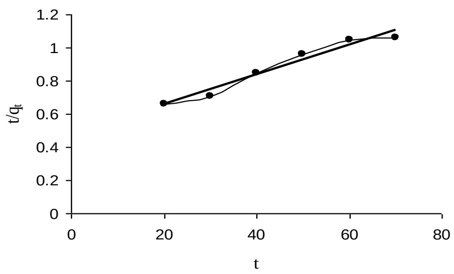

Fig.1: Pseudo second order kinetic model for copper ion adsorption onto *Pongamia pinnata* bark

Elovich model for the adsorption is expressed as

$$q_t = \alpha + \beta \ln t \qquad (10)$$

A plot of q_t against ln t should give a linear relationship for the applicability of the simple Elovich kinetic model as shown in Figure 11. Comparing all the above models the parameters are reported in Table 2.

Table-II
Correlation coefficient (R^2) for kinetic models

Model	**R^2**
Pseudo First order	0.9626
Pseudo Second Order	0.9594
Elovich Model	0.9937

Based on linear regression (R^2>0.99) values, the kinetics of copper ion adsorption on *Pongamia pinnata* can be described well by Elovich Model.

H. Removal of copper from industrial effluent

Industrial effluent was collected from a local wire drawing industry and filtered using Whatman No 42 filter paper. 100 ml of effluent was taken with 5 gL^{-1} of powdered *Pongamia pinnata* tree bark and was agitated at 200 rpm. The effect of pH on percentage removal was studied by varying the pH of effluent from 3 to 7. It was observed that at pH 5.0 the percentage removal of copper ion was more. Compared to synthetic waste water in industrial effluent percentage removal was decreased. This was due to the interference of other metal ions such as iron, zinc, lead and nickel in the effluent as the effluent also consists of these heavy metals. There was every chance the other heavy metals also compete for vacant site and adsorb on adsorbent. To reduce the interference of other metal ions, at industries, effluent has to be treated with the bark at various lines of the source of individual metal ions.

IV. CONCLUSION

The present study demonstrates that *Pongamia pinnata* tree bark can be used as an effective and economical adsorbent for removal of copper ions from aqueous and industrial effluents. In recent years availability of *Pongamia pinnata* tree bark is more and also at low cost. The adsorption process using this adsorbent can reduce the levels of toxic heavy metal ions from industrial effluents. Activation of the bark is not required hence, only drying and size reduction costs are considered. The percentage removal of copper from synthetic solution is more compared to that in industrial effluent as there were interfering metal ions in effluent. The optimum parameters were pH of 5.8 with adsorbent dose 10gL^{-1}, contact time of 2h. The adsorption data for copper ion removal from synthetic solution was better fitted by Langmuir model than Freundlich and Tempkin isotherms. Adsorption kinetics follows Elovich model. Finally to increase the efficiency in removing heavy metals from Industrial effluents, this adsorption process can be used in line wherever an individual metal ion is generated in the waste water.

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REFERENCES

[1] Aradhi, K.Krishna., Satyanarayanan, M., and Pradip, K. Govil., "Assessment of heavy metal pollution in water using multivariable statistical techniques in an industrial area: A Case study from Patancheru, Medak District, Andra Pradesh, India". J. Hazard. Mater., 167, (1-3), pp. 366-373, 2009.

[2] Kaushik, A., Ankur, Kansal., Santosh., Meena., Shivkumari., and Kaushik, C. P., "Heavy metal contamination of river Yamuna, Haryana, India: Assessment by metal enrichment factor of the sediments". J. Hazard. Mater., 164, (1), pp. 265-270, 2009.

[3] Edvardo, Moreno-Jimenez., Jesus, M. Penalosa., Rebeca, Manzano., Ramon, O. Carbena-Ruiz., Roberto, Gamarra., and Elvira, Esteban., "Heavy metal distribution in solids surrounding and abandoned mine in NW Madrid (Spain) and their transference to wild flora". J. Hazard. Mater., 162, 2(3), pp. 854-859, 2009.

[4] Vijayanand, C., Rajaguru, P., Kalaiselvi, K., Paneer, K. Selvam., and Palanivel, M., "Assessment of heavy metal contents in the ambient air of the Coimbatore city, Tamil Nadu, India". J. Hazard Mater., 160, (3), pp. 548-553,2008.

[5] Jaime, Pizarro., Pablo, M. Vergara., Jose, A. Rodriguez., and Alejandra, M. Valenzula., "Heavy metals in northern Chilean rivers: Spatial variation and temporal trends". J. Hazard. Mater., 181, 1(3), pp. 747-754, 2010.

[6] Davydova, S., "Heavy metal as toxicants in big cities". Microchem. J., 1(2), pp. 133-136, 2005.

[7] Peng, Xia., Xianwei, Meng., Ping, Yin., Zhimin, Cao., and Xiangquin, Wang., "Eighty year sedimentary record of heavy metal inputs in the intertidal sediments from the Nanliu river estuary, Beibu Gulf of South China sea".,Environ. Pollut. 159 (1), pp. 92-99, 2011.

[8] IS, " Drinking water specifications", IS 10500. 1991.
[9] ISI, "Tolerance limits for industrial effluents: ISI 2490". Part I. Indian Standard Institutions. 1982.
[10] Grytsyuk, N., Arapis, G., Perepelyatnikova, L., Ivanova, T. and Vynograds'ka, V., "Heavy metals effects on forage crops yields and estimation of elements accumulation in plants as affected by soil". Sci. Total Environ., 354, 2(3), pp. 224-231, 2006.
[11] Sawidis, T., Chettri, M. K., Zachariadis, G. A., and Stratis, J. A., "Heavy metals in aquatic plants and sediments from water systems in Macedonia, Greece". Ecotoxicology and Environmental safety, 32 (1), pp. 73-80, 1995.
[12] Dabrowski, A., Hubicki, Z., Podkoscielny, P., and Robens, E., "Selective removal of the heavy metal ions from waters and industrial waste waters by ion exchange method". Chemosphere., 56, pp. 91-106, 2004.
[13]Matlock, M. M., Howerton, B. S., and Atwood, D. A., "Chemical precipitation of lead from lead battery recycling plant wastewater", Ind. Eng. Chem. Res., 41, pp. 1579-1582, 2002.
[14] Paaez, Hernaandez, M. E., Aguirar, Arrteaga, K., Gallan, Vidal, C. A., and Palomar, Pardavea, M., "Mercury ions removal from aqueous solution using an activated composite membrane". Environ. Sci. Technol., 39, pp. 7667-7670, 2005.
[15] Benito, Y., and Ruiz, M. L., "Reverse osmosis applied to metal finishing wastewater". Desalination, 142, pp. 229-234, 2002.
[16] Yurlova, L., and Kryvoruchko, A., "Removal of Ni(II) ions from waste water by micellar enhanced ultrafiltration", Desalination, 144, pp. 255-260, 2002.
[17] Jong, Hun, Choi., Shin, Dong, Kim., Yoon, Jung, Kwon, and Wha, Jung, Kim., "Adsorption behaviors of ETS-10 and its variant, ETAS-10 on removal of heavy metals, Cu^{2+}, Co^{2+}, Mn^{2+} and Zn^{2+} from a waste water". Micropor. Mesopor. Mat., 96, pp. 157-167, 2006.
[18] Chakravarthy, S., Pimple, S., Hema, T. Chaturvedi., Singh, S., and Gupta, K. K., "Removal of Copper from aqueous solution using newspaper pulp as an adsorbent". J. Hazard. Mater., 159, 2(3), pp. 396-403, 2008.
[19] Aiquin, Dong., Jie, Xie., Wenmin, Wang., Liping, Yu., Qian, Liu., and Yeping, Yin., "A novel method for amino starch preparation and its adsorption for Cu(II) and Cr(VI)". J. Hazard. Mater., 181, 1(3), pp. 448-454, 2010.
[20] Anirudhan, T. S., and Radhakrishnan, P. G., "Thermodynamics and kinetics of adsorption of Cu(II) from aqueous solutions onto a new cation exchanger derived from tamarind fruit shell". J Chem. Thermodyn., 40 (4), pp. 702-709, 2008.
[21] Henrik, K, Hansen., Fernanda, Arancibia., and Claudia, Gutierrez., "Adsorption of copper onto agriculture waste materials". J. Hazard. Mater., 180, 1(3), pp. 442-448, 2010.
[22] Haluk, Aydin., Yasemin, Bulut., and Cigdem, Yerlika., "Removal of copper (II) from aqueous solution by adsorption onto low cost adsorbents". J. Environ. Manage., 87(1), pp. 37-45, 2008.
[23] Aline, Natasia, Kosasih., Jonathan, Febrianto., Jaka, Sunarso., Yi-Hsuju., Nani, Indraswati., and Suryadi, Ismadji., "Sequestering of Cu(II) from aqueous solution using cassava peel (*Manihot esculenta*)". J.Hazard.Mater., 1(3), pp. 366-374, 2010.
[24] Aparecido, N, Modenes., Fernando, R, Espinoza- Quinones., Daniela, E. G. Trigueros., Fabio, L. Lavarda., Andreia, Colombo., Nora, D. Mora., "Kinetic and equilibrium adsorption of Cu(II) and Cd(II) ions on *Eichhornia crassipes* in single and binary systems". Chem Eng J., 168, pp. 44-51, 2011.
[25] Feng, N., Guo, X., and Liang, S., "Kinetic and thermodynamic studies of the biosorption of Cu(II) by chemically modified orange peel, Trans. Non ferrous". Met. Soc. China., 19, pp. 1365-1370, 2009.
[26] Erdal, Eren., "Removal of Copper ions by modified unye clay, Turkey". J. Hazard. Mater., 159, 2(3), pp. 235-244, 2008.
[27]Abdur, Rauf, Iftikar., Haq, Nawaz, bhatti., Muhammad, Asif, Hanif., and Raziya, Nadeem., "Kinetic and thermodynamic aspects of Cu(II) and Cr(III) removal from aqueous solution using rose water biomass". J. Hazard. Mater., 161, 2(3), pp. 941-947, 2009.
[28] Xia, Sun., Xin, Huang., Xue, Pin, Liao., and Bishi., "Adsorptive removal of Cu(II) from aqueous solutions using collagen-tannin resin". J. Hazard. Mater., 186, 2(3), pp. 1058-1063, 2011.
[29] Hao, Pang., and Bing, Liao., "Removal of Copper (II) ions from aqueous solution by modified bagasse". J. Hazard. Mater., 164, 1, pp. 1-9, 2009.
[30] Erol, Pehlivan., Turkan, Altun., and Serife, Parlayici., "Utilization of barley straws as biosorbents for Cu^{2+} and Pb^{2+} ions", J. Hazard. Mater., 164, 2-3, 982-986, 2009.
[31] Crystian, Goncalves, Rocha., Dimas, Augusto., Morozin, Zaia., Reni, Ventura, Da, Silva, Alfaya., and Antonio, Alberto, Da, Silva, Alfaya., J. Hazard. Mater., 166, 1, pp. 383-388, 2009.
[32] Didem, Ozcimen., and Aysegul, Ersoy, Mericboyu., "Removal of Copper from aqueous solutions by adsorption onto chestnut shell and grape seed activated carbons". J. Hazard. Mater., 168, 2-3, pp. 1118-1125, 2009.
[33] Ofamaja, A. E., Naidoo, E. B., Modise, S. J., "Removal of Copper (II) from aqueous solution by pine and base modified pine cone powder as biosorbent". J. Hazard. Mater., 168, 2-3, pp. 909-917, 2009.
[34] Chun, Shui, Zhu., Li, Ping, Wang., and Wen, Bin, Chem., "Removal of Cu (II) from aqueous solution by agricultural by product: peanut hull". J. Hazard. Mater., 168, 2-3, 739-746, 2009.
[35] Salman, Ahmady, Asbehin., Yves, Andres., Claire, Gerente., and Pierre, Le, Cloirec., "Biosorption of Cu(II) from aqueous solution by Fucus Serratus: Surface Characterization and Sorption Mechanisms". Bioresource Technology, 99, pp. 6150-6155, 2008.
[36] Nurbas, M. Nourbakhsh., Kilicarslan, S., Ilhan, S., and Ozdag, H., "Biosorption of Cr^{6+}, Pb^{2+} and Cu^{2+} ions in industrial waste water on *Bacillus Sp*." Chem. Eng. J., 85, pp. 351-355, 2002.
[37] Gregario, Crini., "Recent developments in Polysaccharide- based materials used as adsorbents in waste water treatment". Prog. Polym. Sci., (30), pp. 38-70, 2005.
[38] Diwakar, Tiwari., Hyoug-Uk, Kim., and Seung-Mok, Lee., "Removal behavior of sericite for Cu (II) and Pb (II) from aqueous solutions: Batch and Column studies". Sep. Purif. Technol., 57, pp. 11-16, 2007.
[39] Reddy, B. R., Mirghaffari, N., and Gaballah, I., "Removal and recycling of copper from aqueous solutions using treated Indian barks". Resour. Conserv. Recy., 21, pp. 227-245, 1997.
[40] Chandra, Sekhar, K., Kamala, C, T., Chary, N, S., and Anjaneyalu, Y., "Removal of heavy metals using a plant biomass with reference to environmental control". Int. J. Miner. Process., 68, 37-45, 2003.
[41] Joana, M. Dias., Maria, C, M., Aluim-Ferroz., Manuel, F. Almeida., Jose, Rivera, Utrilla., and Manuel, Sanchez-Polo., Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. J. of Environ. Manage. 85 (4), pp. 833-846. 2007
[42] Chopade, V. V., Tankar, A. N., Pande, V. V., Tekade, A. R., Gowekar, N. M., Bhandari, S. R., and Khandake, S. N., "*Pongamia pinnata*: phytochemical constituents, traditional uses and pharmacological properties: A review". Int. J. green pharm., 2, pp. 72-75, 2008.
[43] Haoyin., Si, Zhang., Jun, Wu., and Haihan, Nan., "Dihydropyranoflavones from *Pongamia pinnata"*. J. Braz. Chem. Soc. , 17, pp. 1432-1435, 2006.
[44] Dinesh, Mohan., Charles, U. Pittman., Jr. Philip, H. Steele., "Single, binary and multicomponent adsorption of copper and cadmium from aqueous solutions on kraft lignin- a biosorbent". J. Colloid. Interf. Sci., 297, pp. 489-504, 2006.
[45] Shukla, A., Zhang, Y, H., Dubey, P., Margrave, J. L., Shukla, S. S., "The role of HA in the removal of unwanted materials from water". J. Hazard. Mater., 95, pp. 137-152, 2002.
[46] Weber, T. W., Chakraborty, R. K., "Pore and solid diffusion models for fixed bed adsorbents". J.Am.Inst. Chem.Eng., 20, pp. 228-238, 1974.