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BIOSORPTION OF COPPER (II) ON TO THE WASTE LEAVES OF KAFAL (*Myrica esculenta*)

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ABSTRACT

The commonly used removal processes for heavy metals from contaminated wastewater and cited in the literature are chemical precipitation, electrowinning, carbon adsorption, reverse osmosis, preconcentrations, biosorption, phytoremediation etc. Among these, biosorption is comparatively efficient, low cost, economical and reliable process. Actually, the reliability of the process is depending on the choice of local biosorbents and their abundant availability. The waste plant leaves of Kafal were collected from the region of Kumaun hills of India. The paper explains that the Kafal leaf powder is a good biosorbent for the removal of Cu (II) ions from contaminated wastewater under batch study. The experimental data indicate that high removal efficiency is obtained at optimized conditions viz. higher pH, lower metal ion concentrations, moderate higher temperatures and higher dosage of biosorbents. The biosorption efficiency is recorded 88.98% at pH 6, 48.99% at contact time 70 minutes and 40.01 % at a higher dosage of biosorbent. The regression value is indicating that the order for all used isotherms model is Langmuir> Freundlich > Temkin.

Keywords: Biosorption, Kafal leaves, Batch operation, Optimized conditions, Isotherms

INTRODUCTION

Introduction of heavy metals into the environment, fresh or saline water and waste waters is due to natural and various anthropogenic activities. A worldwide environmental problem due to exposure to heavy metals has been invited over the past two or three decades[1]. The pollution due to heavy metals has become one of the most serious problems, and the presence of these metals even in very low concentrations is toxic and detrimental to living organisms[2,3]. Heavy metals may be defined as the metallic species that has high density and show toxicity to living organisms and natural environment[4,5]. The common heavy metals contaminants are lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), iron (Fe), zinc (Zn), chromium (Cr), chromium (Cr) and arsenic (As). The natural sources of heavy metals are igneous rocks such as augite and olivine, volcanoes, windblown dust, marine aerosol, forest fires, bubble bursting, leaching from leaves and stems, sea sprays and aerosols[6-9]. The heavy metal exposure in water or wastewater or soil is due to anthropogenic activities such as agricultural, mining, burning of fossil fuels, domestic effluents, nuclear power plants and effluents of textile, plastic, paper processing, electronics, wood preservation industries[10-25].

Biologically copper is an essential element for the terrestrial green plants and algae under the concerned limits and involves in photosynthesis, it is a cofactor of oxidase, oxygenase and enzymes such as superoxide dismutase and acrobat oxidase[4]. The overload of copper in human body causes many health problems like anorexia, fatigue, premenstrual syndrome, depression, anxiety, allergies and learning disorders[26-30]. The exposure of copper in the soil, water and wastewater and the atmosphere are due to chemical rock weathering, bubble bursting, animal manure, aerosols, fossil fuel burning and nuclear plants[1,4,6-9]. The conventional methods used for the removal processes of heavy metals from water or wastewater are precipitation, ultrafiltration, ion exchange, reverse osmosis, electrowinning, carbon adsorption, biosorption, phytoremediation etc[31-38]. Among these, biosorption is relatively new, low cost, effective and economical method. The performance and applicability of biosorption on large-scale

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aredepending on the choice of a good and readily available biosorbent. The cheap and easily biological materials cited in the literature are rice husk[39], coconut shell[40], plant barks[41-42], leaves[43], sawdust[44,45], sugarcane bagasse[45], peat moss[47] and algal and fungal biomass[48]. Kafal or *Myrica esculenta* is an angiospermic plant (family Myricaceae) and commonly found in the northern hills Kumaun and Garhwal of India and western Nepal. The waste leaves of the plant were collected from the Kumaun hills of India in the month of April.

EXPERIMENTAL

Biosorbent preparation

The waste and discarded leaves were collected from the hills of Kumaun India in the month of April. After collection, the leaves were washed with double distilled water for removing the water-soluble impurities present on the leaves. Now the leaves are dried in laboratory oven under controlled condition and ground into particle size 63 microns using the sieve MICS 63, BSS 240. Then the powder of leaves was preserved in sealed bottles.

Wastewater preparation

The wastewater containing desired concentration of Cu (II) ions was prepared from the salt copper sulphate ($CuSO_4.5H_2O$) in double distilled water. The amount 3.921 g of $CuSO_4.5H_2O$ was added in 1000 ml of double distilled water for making the solution contain copper 1000 mg/L. The pH of this solution was adjusted 3.5 (Digital pH meter model: MAC 12831) because acidity favors the solubility of metal ions.

Batch operation

Take 100 ml solution containing the desired concentration of Cu (II) ions in a 250 ml of conical flask. Now add 1 g of biosorbent in it at a constant shake 170 rpm. After a certain time, the solution is filtered and the biosorbent was filtered out from the solution. The concentration of copper ions before and after adsorption was determined by atomic absorption spectrophotometer (Model: AAS Vario 6, Analytik Jena). The % biosorption was calculated by using the equation below:

$$\% \text{ Biosorption} = (C_o - C_e/C_o) * 100 \tag{1}$$

Where C_0 and C_e are the initial and final concentrations of copper ions in solution, respectively.

Photo-1: Waste Leaves of Kafal (*Myrica esculenta*) and Prepared Biosorbent

RESULTS AND DISCUSSION

Effect of Contact Time

The minimum contact time is required for the interaction of metal ion and biosorbent and its influence on adsorption capacity. It also offers data of chemical kinetics such as pseudo first order, pseudo-second order, and Elovich model and intraparticle diffusions. The removal of copper (II) ions was studied over a time range 10-70 minutes[49]. The biosorption of metal ion is recorded initially 28.88 % at initial time 10 minutes. After that, it rapidly increased 46.79 % and then reached 48.99 % at contact time 70 minutes (Fig. 1), 4.899 mg copper (II) per gram of biosorbent was removed from the metallic solution at pH 3.5 and rpm 170. The Fig.-1 shows that the removal efficiency of the metal ion is very rapid between the time 30 to 50 minutes, and a large fraction of the total amount of metal ion was removed within a few minutes. This is due to the availability of the active sites and uncovered surface on the adsorbent[50]. After 60 minutes the uptake of metal ion on biosorbent was not rapid and become about constant. It is due to the saturation of available binding sites with the metal ions[51].

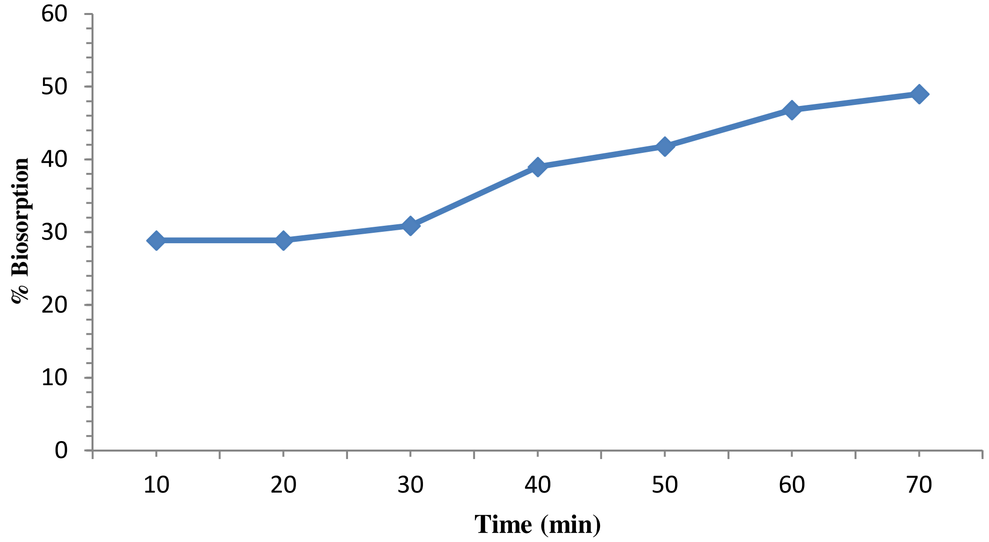

Fig.-1: Effect of Contact time

Effect of Dosage

The biosorption of copper is directly influenced by the amount of biosorbent (Fig.-2). The biosorption process is actually depending on the available surface area of biosorbent and here the surface area of biosorbent increases with the increase in the amount of biosorbent[52,53]. These results increase in the number of binding sites or active groups present on the surface area. The increase in the available surface area helps the conglomeration of the adsorbent[54,55]. The biosorption efficiency is recorded 9.67 % at the initial dose 0.1g and achieved 59.99 % at 1 g of dosage.

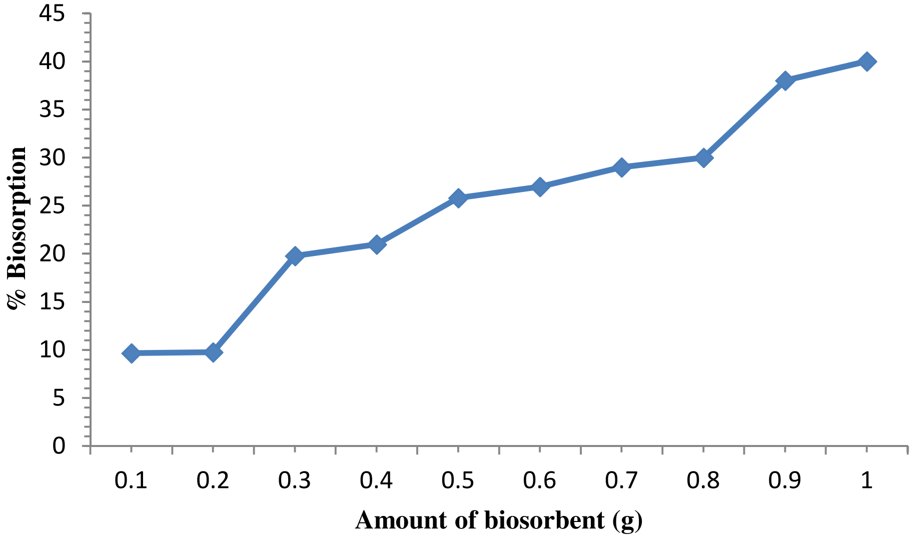

Fig.-2: Effect of dosage

Effect of pH

The pH of the metallic solution is one of the most important parameters to find out maximum biosorption of metal ion on the biosorbents. In order to find out optimum pH for maximum removal, a number of working solutions have been used with different pH[56-65].Experimental data indicate that the biosorption of copper onto Kafal leaves increase very rapidly from the percentage removal 10.98 to 88.98 % under the pH range 1-6. At lower pH, about all active sites or the organic groups present on the surface of biosorbents undergoes protolysis. After that, repulsion occurs between the protonated active sites and metal ions. The removal of metal ions increases with increase in pH; this may be due to the availability of non protonated active sites for metal ions[65]**.**

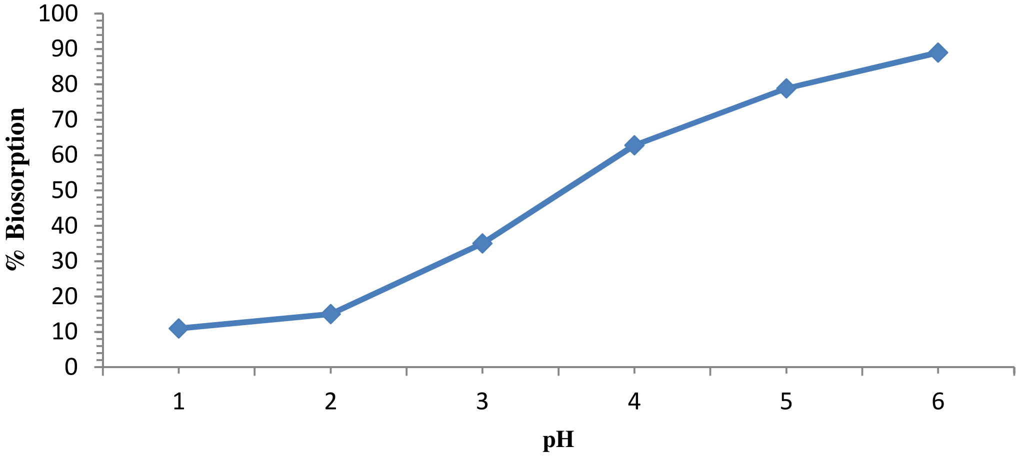

Fig.-3: Effect of pH

Effect of concentration of metallic wastewater

The removal efficiency of metal ions onto the surfaces of biosorbents is decreased with increase in the concentration of metallic species in wastewater. But the metal ion adsorbate per unit mass of adsorbent (mg/g) increases with the concentration of synthetic wastewater. The uptake of metal ion at higher concentrations is due to an increase in the driving force of concentration gradient[66-68]. This is observed from the Fig.-4 that the removal efficiency of copper is recorded30.09 % at the concentration 10 mg/L and then decreases very smoothly to 11.8 % under the concentration 50 mg/L, pH 3.5 and contact time 25 minutes.

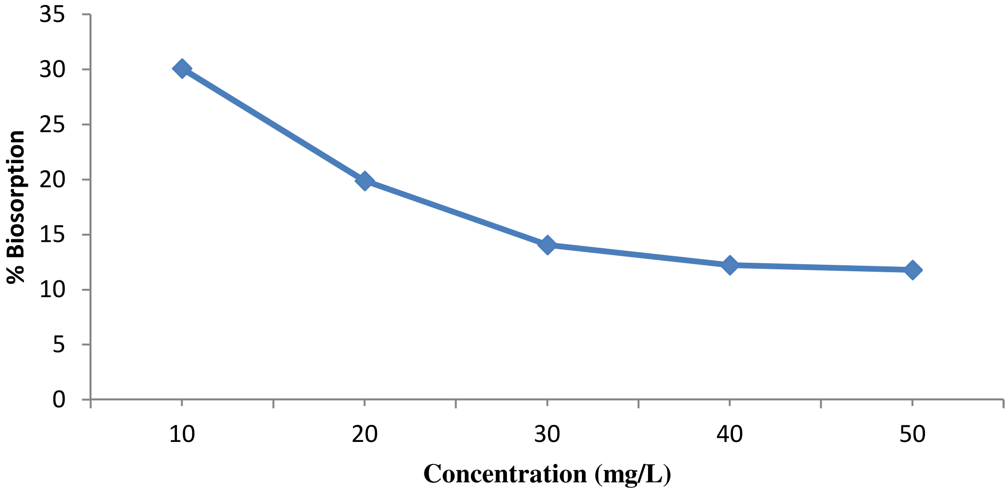

Fig.-4: Effect of the concentrations of metallic solution

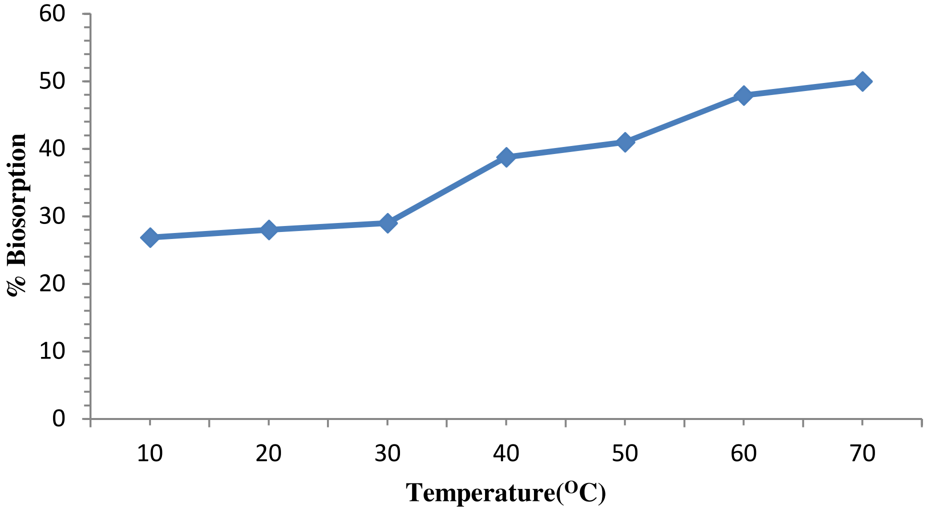

Fig.-5: Effect of temperature

Effect of Temperature

The metal uptake by biodsorbent increases till certain ranges of temperatures. But after a certain temperature the concentration of particular metal ion increases in wastewater. In other words the adsorption rate decrease, it may be attributed to solubility of metal ions from biosorbent in solution[69-72]. Experimental data shows that the biosorption of metal ion increases rapidly from 28.99 to 40.99 % under temperature ranges 30 to 50 ^{0}C (Fig. 5). After that, it is recorded 47.9 % and finally, it becomes 49.9 % at 70 ^{O}C. Finally, it is observed that the higher moderate temperature range 30-50 ^{O}C is suitable for the biosorption rate of copper on to Kafal leaves.

Adsorption Isotherms

The adsorption isotherms assume that the metal uptake by biosorbent from the liquid phase and ability of biosorbents to interact the metal ions. It is necessary to find out the sorption capacity of any biological material and its application in the large-scale operations[73]. It also explains the adsorption phenomenon is either physical or chemical[74].

Langmuir Isotherm

The Langmuir isotherm model is based on the monolayer adsorption of metal adsorbate on to the surface of biosorbents which contain a definite number of binding sites[73,74]. Mathematically, the linear form of Langmuir equation is given as below:

$$C_e/q_e = 1/K_Lb + 1/K_LC_e \quad (2)$$

Where q_e is the amount of metal adsorbed per unit mass of biosorbent (mg/g), K_L and b are the adsorption capacity and rate of adsorption. When C_e/qe was plotted against C_e, a straight line with a slope of $1/K_L$ was obtained (Fig.-6). The value of K_L and b are found to be 6.849 and 4.219. The characteristic of the Langmuir isotherm model is expressed in terms of the dimensionless parameter (R_L). This parameter is mathematically defined as:

$$R_L=1/1+bC_0 \quad (3)$$

Here b is the Langmuir constant and C_O is the initial copper ion concentration in mg/L. The value of R_L indicates the type of isotherm to be either favorable ($0<R_L<1$), unfavorable ($R_L>1$), linear ($R_L=1$) or irreversible ($R_L=0$).The value of R_L was found to be less than one and this confirms that the Langmuir isotherm model is fitted for adsorption of Cu (II) on to Kafal leaf powder. The value of regression (R^2) is found 0.950 and indicating the copper favors the Langmuir isotherm model and monolayer adsorption onto the surface of Kafal leaf powder.

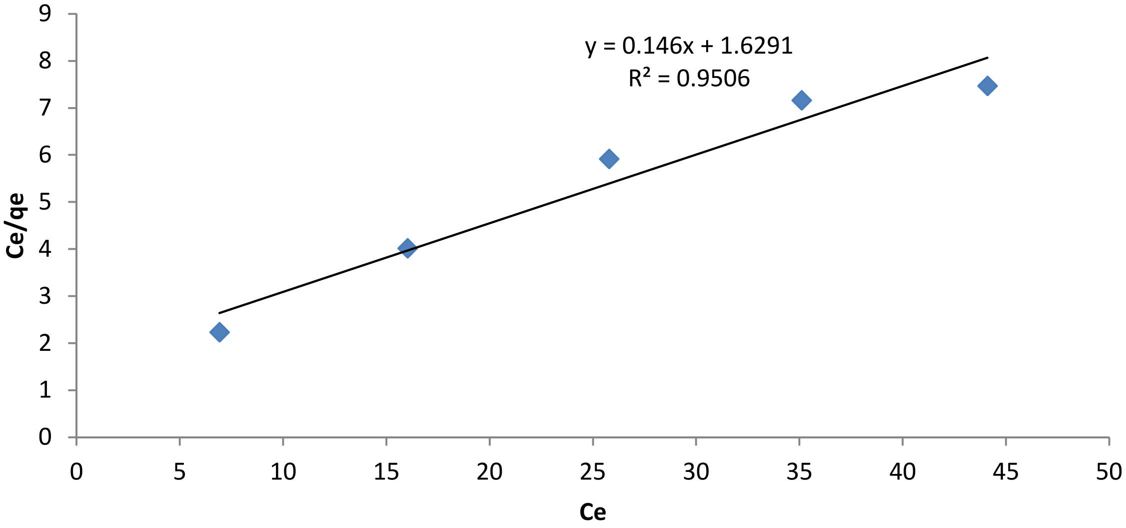

Fig.-6: Langmuir Isotherm Model

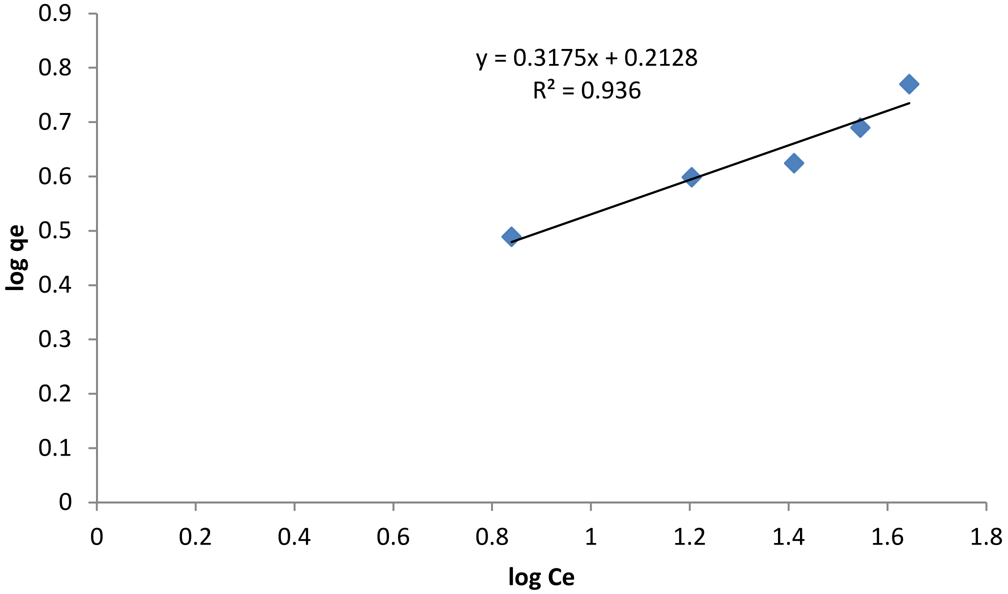

Fig.-7: Freundlich isotherm model

Freundlich Isotherm

Freundlich isotherm[75] is an expression based on the biosorption of metal ions on a nonidentical surface of the biosorbents. The mathematical form of Freundlich equation is given by the following equation:

$$\log q_e = \log K_F + 1/n \log C_e \tag{4}$$

Where, q_e is the number of copper ions adsorbed on the surface of biosorbent in mg/g, C_e is the equilibrium concentration of copper adsorbate in mg/g and K_F and n are the constants relating to the adsorption capacity and intensity of adsorption, respectively. The value of K_F (1.629) and 1/n (0.317) have been found from the slop and intercept of the plot, log q_e vs log C_e (Figure 7).The value of 1/n is less than 1 and $R^2 = 0.931$ for copper which shows favorable adsorption by Kafal leaf powder.

Temkin Isotherm

The Temkin isotherm model explains the influence of metal-metal interaction on the surface of biosorbent. Therefore, the heat of biosorption of metal sorbate on the surface decreases linearly with the occupation due to metal-metal interactions[76]. The linear form of Temkin isotherm model is given by the following expression:

$$q_e = a + b \ln C_e \qquad (5)$$

Where C_e is the equilibrium concentration of copper ions in mg/L, q_e is the amount of copper adsorbed in mg/g, a and b are the isothermal constants related to binding capacity and Temkin constant. The value of a and b can be determined by the plot (Fig.-8) of q_e vs ln C_e. In this pattern, iron shows the adsorption capacity 0.315adsorption intensity 1.340.

CONCLUSION

The performance of biosorption is depended on the choice and abundant availability of the utilized biomaterial. Leaf powder prepared from the waste leaves of Kafal (*Myrica esculenta*) is an efficient and potential biosorbent for the removal of copper (II) from the copper contaminated waste water. The observed optimized conditions of batch operation are higher pH, lower metal ion concentration, higher moderate temperature and high dosage of biosorbent. Such condition can apply to the large-scale removal processes of copper from the water or industrial wastewater. A high regression value of all isotherm models and other parameters indicate the suitability of copper adsorption on to the leaf powder.

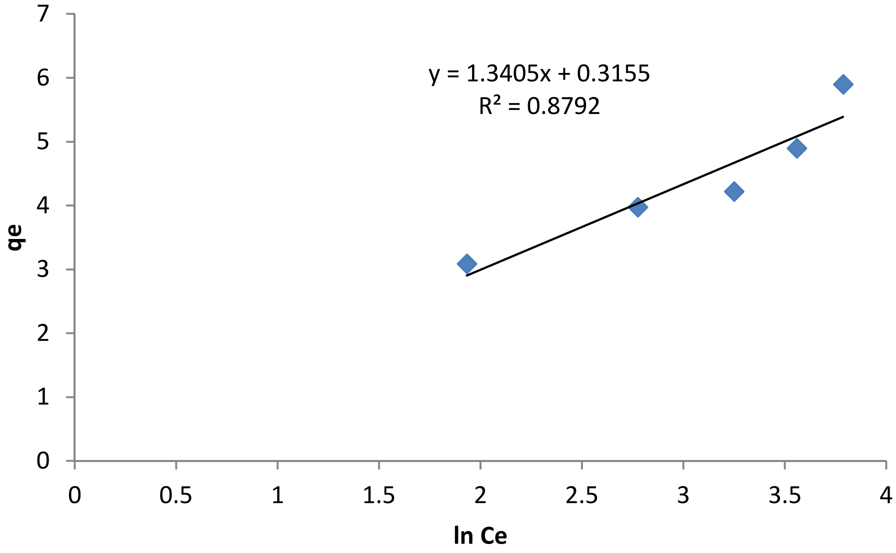

Fig.-8: Temkin isotherm model

Table-1: Parameters of Langmuir, Freundlich and Temkin isotherms

Isotherms	Parameters	Value
Langmuir	K_L	6.849
	b	4.219
	R^2	0.950
Freundlich	K_F	1.629
	1/n	0.317

	R^2	0.936
Temkin	a	0.315
	b	1.340
	R^2	0.879

REFERENCES

1. R. Singh, R. Chadetrik, R. Kumar, K. Bishnoi, D. Bhatia, A. Kumar, N. Singh, *J. Hazard. Mat.*, **174**, 623 (2010).
2. J. Wang, Immobilization Techniques for Biocatalysts and Water Pollution Cont., *Science Press, Beijing,* (2002).
3. N. Salah, A. Anees, *J. Ind. Chem.*, **6,**119 (2015).
4. P. C. Nagajyoti, K. D. Lee, T. V. M. Sreekanth, *Envir. Chem. Let.*, **8**, 199 (2010).
5. Lentech water treatment, http:/www.excelwater.com/thp/filters/water-purification.htm. (2004).
6. J. M. Pacyna, Toxic Metals in the Atmosphere, Chap.2, Wiley New York.
7. S.M. Ross, Toxic metals in soil plant systems, Wiley, Chichester, p 469.
8. Scope, Saharan Duct Scientific common problems of the environ, Wiley, New York (1974).
9. M. R. D. Seaward, D. H. C. Richardson, CRP Press, Boca Raton, 75 (1990).
10. Q. Khan, Y. M. Cao, Y. Z Zheng, Huang,Y.G. Zhu, *Env. Pollution*, **152**,686 (2008).
11. M. K. Zhang, Z. Y. Liu, H. Wang, *Com. in Soil Sci. and Plant Analysis*,**41**, 820 (2010).
12. A. Kabata-Pendias,H. Pendias Trace Metals in Soils and Plants, CRC Press, Boca Raton, Fla, USA, 2nd edition, (2001).
13. G. M. Pierzynski, J. T. Sims, G.F. Vance, Soils and Env. Qual., CRC Press, London, UK, 2nd edition (2000).
14. J. J. D. Amore, S. R. Al-Abed, K. G. Scheckel, J. A. Ryan, *J. of Env. Qual.*, **34**, 1707 (2005).
15. G. Sposito, A. L. Page, "Cycling of metal ions in the soil environment," Metal Ions in Biological Systems, H. Sigel, Ed., Vol. 18 of Circulation of Metals in the Environment, Marcel Dekker, Inc., New York, NY, USA, pp. 287–332 (1984).
16. N. T. Basta, J. A. Ryan, R. L. Chaney, *J Env. Quality*, **34**,49 (2005).
17. A. Scragg, Env. Biotech., Oxford University Press, Oxford, UK, 2nd edition (2006).
18. L. H. P. Jones, S. C. Jarvis, "The fate of heavy metals," in The Chemistry of Soil Processes, D. J. Green and M. H. B. Hayes, Eds., p. 593, John Wiley & Sons, New York, NY, USA (1981).
19. M. E. Sumner, *Communications in Soil Science and Plant Analysis*, **31**, 1701 (2000).
20. R. L. Chaney, D. P. Oliver, "Sources, potential adverse effects and remediation of agricultural soil contaminants," in Contaminants and the Soil Environments in the Australia-Pacific Region, R. Naidu, Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands (1996).
21. USEPA, "A Plain English Guide to The EPA Part 503 Biosolids Rule," USEPA Rep. 832/R-93/003, USEPA, Washington, DC, USA (1994)
22. M. L. A. Silveira, L. R. F. Alleoni,L. R. G. Guilherme, *Scientia Agricola*, **60**, 64 (2003).
23. S. C. Reed, R. W. Crites, E. J. Middlebrooks, Natural Systems for Waste Management and Treatment, McGraw-Hill, New York, NY, USA, 2nd edition, (1995).
24. P. S. DeVolder, S. L. Brown, D. Hesterberg, K. Pandya, *J Env. Qual.*, **32**, 851(2003).
25. N. T. Basta, R. Gradwohl, *Better Crops*, **82**, 29 (1998).
26. C. A. Flemming, J.T. Trevers, *Water air and soil pollution*, **49,** 1(1989).
27. G. J. Brewer, *J. Am. Coll Nutr*, **28**, 238 (2009).
28. Toxicological profile for copper, U S Department of health and human services, https:/www.atsdr.cdc.gov/toxprofiles/tp132.pdf
29. Web of science, www.southerwestsalmon.org/wp-content/10/copper-ljt-Rev-2-Dec-2013-CAW.pdf
30. The response of plants to metal toxicity, http://citeseerx.ist.psu.edu/viewdoc/download, doi 10.1.1198.5537
31. K. Trivunac, S. Stevanoic, *Chemosphere*, **073**,11 (2005).
32. T. Marrow, C. Erwe, C Blochor, H. Chamiel, *Desalination,* **157,** 97 (2003).

33. M.A. Barakot, E. Schmidt, *Desalination,* **256**, 90 (2010).
34. A. Groffman, S. Peterson, D. Brookens,*Water Environ Techonol*,**4**, 54 (1992).
35. G. Blonchord, M. Maunaye, G. Martin, *Water Research*,**18**, 1501 (1984).
36. H. A. Qduissa, H. Maussa, *Desalination*,**164**, 105 (2004).
37. J. B. C KershawElectro metallurgy, Bibilobazaar, LIC, ISBN 0559681895(2008).
38. P. E. Flathman, G. R. Lanza, *J. of Soil Cont.*,**7,** 415 (1998).
39. M. C. Manique, C. S. Faccinics, B. Onorevolli, E. V. Benvenutti, E. B. Caramao, *Fuel*, **92**, 56 (2012).
40. M. A Acheampong, K. Pakshirajan, A. P. Annachhatre, P. N. L. Lens, *J. Indust. and Engg. Chemistry*, **19**, 841 (2013).
41. D. H. K. Reddy, K. Seshaiah, A.V. Reddy, M. M. Rao, M. C.Wang, *Desalination*, **268**,150 (2010).
42. D. H. K. Reddy, K. Seshaiah, A. V. R. Reddy, *Chem. Engg. J.*, **162**,626 (2010).
43. D. H. K. Reddy, K. Seshaiah, A. V. R. Reddy, S. M. Lee, *Carb.Poly.*,**88**, 1077(2012).
44. W. A. Krowiak, *Europ. J. of Wood and Wood products*, **71**, 227 (2013).
45. W. A. Krowiak, *A. Chem. Engg. J.*, **171**, 976 (2011).
46. E. Khoramzadeh, B. Nasernejad, R. Halladj, *J. Taiwan Inst. Chem. Eng*, **44**, 226 (2013).
47. W. Ma, J. M. Tobin, *Water Res.*, **37**, 3967 (2003).
48. L. P. Deng, Y. Y. Su, H. Su, X. T. Wang, X. B. Zhu, *J. Haza. Mat.*, **143**, 220 (2007).
49. J. L. G.Torresday, G. D. Rosa, J. R. Peralta Videa, *Pure App. Chem*, **76**, 801(2004).
50. A. Nasrullah, H. Khan, A. Khan, Z. Manz, N. Muhammad, M. Khan, N. A. E. Salam, *Sci. World J.*, (2015) (Article ID562693, 11 pages).
51. S. Tasar, F. Kaya, A. Ozer, *J. Env. Chem. Engg.*, **2**, 1018 (2014).
52. G. Mckay, Y. S. Ho, **5**, 217(1999).
53. K. C. Lakshminarayan, K. Rao, A. Krishna, *Indian J. Chem. Tech.*, **1**, 13(1994).
54. G. Annadurai, M. Chellapandian, M.RV. Krishnan, *Ind. J. Env. Prot.*, **17**, 95(1997).
55. U. Danis, A. Gurses, Cauplot, *Fres. Env. Bull.*, **8**, 358(1999).
56. Z. Asku, S. Tezer, *Process Biochemistry*, **36**, 431 (2006).
57. P. Janos, J. Sypecka, P. Mlckovska, P. Kuran, V. Pilarova, *Sep. Purif. Techn.* **53**, 322(2007).
58. P .M. Devaprasth , J.S. Solomon, B.V. Thomas, *J. App. Sci. Env. San.,***2**, 77(2007).
59. A. G. Devi Prasad, M. B. S. Abdullah, *J. App. Sci in Env. San.*, **4** , 273(2009).
60. G. Karthikeyan, N. M. Andal, K. Anbalgan, *J. Ind. Chem. Soc.*, **82**, 21(2005)
61. M. Y. Arica, Y. Kacar, O. Genc, *Biores. Techonol.*, **80**, 121 (2011).
62. C. C. V. Cruz, A. C. A. Casta, C. A. D., Henriques, A. S. Luna, *Bio. Tech.*,**91,** 249 (2004).
63. E. Fourest, B. Volesky, *Biochem. Biotechnol.*, **67**, 215(1997).
64. A. Esposito, F. Pagnanelli, A. Lodi, C. Solisio, F. Veligo, *Hydromet.*, **60**, 129(2001).
65. A. Ozer, *J. Hazad. Mat.*, **141**, 753 (2007).
66. R. Ayyapan, A.C. Sophia, K. Swaminathan, *Pro. Bioch.,***40**, 1293 (2005).
67. A. M. Kumar, K. Kadirvelu, G. K. Mishra, C. Rajagopal, P. N. Nagar, *J. Hazard. Mater.,* **150,** 604 (2008).
68. N. Lokeshwari, K. Joshi, *Global Journal of Environmental Research,***3**,29(2009).
69. J. E. Ramiro, R. Martins, A. R. Pardo, B. Rui, *Water Research,* **38**, 693 (2004).
70. Z. Asku, S. Tezer, *Process Biochemistry,***36***,* 431(2000).
71. Z. Asku, *Process Biochemistry,* **38,** 89(2007).
72. S. S. Tahir, N. Rauf, *Journal of Environmental Management*, **73**, 285(2004).
73. R. Sivaraj, C. Namasivayam, K. Kadirvelu, *Wast. Mgmt.*, **21**, 105(2001).
74. M. A. Rehab, A. H. Hamad, M. M. Hussain, G. F. Malash, *Eco. Engg.*, **91**, 317(2016).
75. H. Freundlich, Colloid and capillary chemistry, Methuen, London UK (1926).
76. M. Alam, M. Aslam, S. Rais, *Rasayan J. Chem.,***2**, 791 (2009).

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