International Journal of Ethics in Engineering & Management Education
Website: www.ijeee.in (ISSN: 2348-4748, Volume 1, Issue 2, February 2014)

A Review on Isotherms and Kinetics of Heavy Metal Removal

Sunil Kulkarni
Datta Meghe College of Engineering, Airoli, Navi Mumbai
Maharashtra, India,
suniljayantkulkarni@gmail.com

Sonali Dhokpande
Datta Meghe College of Engineering, Airoli, Navi Mumbai
Maharashtra, India,
srdhokpande@gmail.com

Dr. Jayant Kaware
College of Engineering and Technology,Akola, Maharashtra, India.
jayantpkaware@gmail.com

***Abstract*—The heavy metal removal from effluent is very important area of research. Various methods, both, biological and non biological, have been tried for heavy metal removal. Many methods involve the sorption of heavy metals on the sorbents. To study the effectiveness of removal, capacity of adsorbent, it is very important to have detailed research on isotherms and kinetics. Many researchers have concentrated their research on this area. Present paper is review on the isotherms and kinetic findings for heavy metal removal by various researchers.**

***Index Terms*—heavy metal, sorption, isotherm, kinetics**

I. INTRODUCTION

Water pollution because of heavy metals is very important area of research. Various heavy metals, like cadmium, nickel, arsenic cause various diseases like nausea, vomiting, diarrhea, pulmonary fibrosis, renal edema, and skin dermatitis. Varios methods used for nickel removal includes Adsorption, Ion Exchange ,Biological Methods, Electro coagulations ,Electrodialysis,Floatation, Coagulation and Flocculation Membrane Seperation. Present review paper is aimed and studying the research carried out in order to investigate the mechnism of removal, in terms of kinetics of metal uptake and the isotherms.

II. KINETICS OF HEAVY METAL REMOVAL

A series of ion-exchange equilibrium tests of Cu^{2+}/H^{+}, Zn^{2+}/H^{+}, and Cd^{2+}/H^{+} systems using Amberlite IR-120 were performed by Lee et al[1]. They used Amberlite IR-120 (Rohm Haas Corp., USA), a strong cationic ion-exchange resin with effective particle size from 0.43 to 0.55 mm and 44 to 48% moisture content. The heavy metal solutions were prepared by copper nitrate, zinc nitrate, and cadmium nitrate with purity greater than 95.0%They put different amounts of the conditioned resin in H-form in Poly ethylene bottles , filled with 500 ml heavy metal solution with desired concentrations, shaken for 24 h at desired temperature. The samples were analyzed after filtration.They analyzed the removal of copper, zinc, and cadmium by using the Langmuir and Freundlich isotherms. The batch experiments were carried out at 350 rpm as this speed was found optimum. It was observed that the Langmuir adsorption isotherm provided a better fit to the experimental data of copper, zinc, and cadmium isotherm than the Freundlich approach.The effect of the resin to solution ratio on the heavy metal ion exchange kinetics was studied by performing a series of experiments with different amount of resins and same intial concentration. The final equilibrium copper in the resin phase decreases with increasing resin used, as shown in fig 1.

Tyagi and Du developed Neural network based models for the cases of both unacclimatized and acclimatized microorganisms and they performed studies on kinetic model for the effects of heavy metals on activated sludge process using neural networks[2]. The models were presented for unacclimatized sludge based on toxic effects of Pb, Cr, Zn, Ni and their mixture on the microbial growth of batch operation and for both unacclimatized and acclimatized cases correspond to the observations concerning the effects of Ni, Cr and substrate concentration (COD) on the batch growth. It was observed that complex kinetics patterns for waste water treatment processes can be described with substantial accuracy and robustness.

Kinetics and isotherm studies on the nickel removal by using the activated carbon prepared from Rosa Canina L were carried out by Ghasemi et.al[3]. They obtained Rosa canina L (RC) from Arak-Iran. After washing and drying, it was impregnated with hydrochloric acid and activated at 150^{0}C. Then washed and soaked in sodium hypochloride, again washed and then sieved.The batch studies indicated that both, Langmuir and Freundlich isotherm suited well for the solute uptake. The kinetics of solute removal showed psedo first order kinetics. Pseudo second order gave better R2 values confirming chemisorptions onto the surface. Rosa canina L (RC) was observed to be environmentally friendly and promising material. It can be used successfully for separation of Ni(II) from aqueous solution.

International Journal of Ethics in Engineering & Management Education

Website: www.ijeee.in (ISSN: 2348-4748, Volume 1, Issue 2, February 2014)

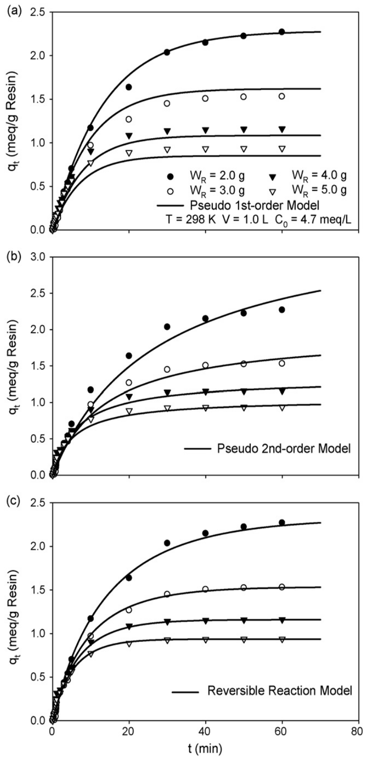

Fig.1

Thermodynamic and kinetic study by using modified fly ash for cadmium and nickel removal from wastewater was carried out by Vişa and Duță[4].They modified the Fly ash surface at room temperature with alkaline solutions of NaOH,with different concentrations. It was observed that that moderate NaOH concentrations (2N) were enough for developing a substrate that, in optimized conditions, insures adsorption efficiencies above 97%, for cadmium and nickel ions in a large concentration range. Carbon contributed only in a limited amount to adsorption and the oxide components are the preferential adsorption sites on the modified flyash.

In the last few years the use of dead, dried aquatic plants, for metal removal from water from industrial activities is important research area. Similar work has been carried out Miretzky et.al.[5]. Their studies were aimed at the investigation of the mechanism of the simultaneous removal of metals derived from industrial activities (electroplating, metal finishing,textile, storage batteries, lead smelting, mining,plating, ceramic and glass industries) by dead freshwater macrophytes. Kinetic studies were carried out by suspending dead S. intermedia, L. minor and P. stratiotes. It was observed that L. minor biomass presented the highest mean removal percentage and P. stratiotes the lowest for all metals tested. The metal removal was more based on percentage removal for individual metal solutions than with multi-metal solution. Metal adsorption data (Pb^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+}) fitted Freundlich isotherm (heterogeneous surfaces) and followed first order kinetics.

The studies on the possible use of Cassia siamea to remove Cd (II) ions from aqueous solutions were carried out by John et.al.[6]. They carried out batch equilibrium studies a function of pH, initial metal concentration and contact time to determine the efficiency of biosorbent. The biosorption kinetic studies were carried out to study the metal uptake mechanism.

$$dq/dt = k1(qe - q0) \qquad (1)$$

Where qe (mg/g) and q are the amounts of adsorbed t = o to t = t and q = o to q = q gives metal ions on the biosorbent at the equilibrium and at any time t, respectively; k1 is the langergren rate constant of the first order biosorption (h 1)

The liberalized form of this equation is

$$\log(qe - q) = \log qe - \frac{k1\,t}{2.303} \qquad (2)$$

It was observed that the psedo first order model was not suitable for the cadmium ions. Psedo second order model was applied for the metal uptake.The model is expressed as

$$dq/dt = k_2 qe - q)^2 \qquad (3)$$

Integrated pseudo-second order rate law, for the boundary conditions, t = o to t = t and q = o to q = q gives,

$$t/q_t = 1/k_2 q_e{}^2 + 1/_{1/q_t}\, t \qquad (4)$$

Where k_2(g/mg h) is the rate constant of second-order adsorption. If second-order kinetics is applicable, the plot of *t* /*q* versus *t* should show a linear relationship.It was observed that kinetics of cadmium biosorption by Cassia siamea biomass is better described by pseudo second order kinetic model.

Freunlich isotherm was tried, the equation for the same is

$$X/M = b\, C^{*m} \qquad (5)$$

$$\log X/M = \log b + m \log C^{*} \qquad (6)$$

X is the amount of adsorbate adsorbed and M is the amount of adsorbent. X/M is the catalyst loading, C* is the equilibrium concentration of organic matter, b and m are constants. From the figure, the adsorption phenomenon follows Freundlich isotherms.In case of adsorption isotherms, they observed that adsorption process follows Freundlich isotherm model, which expresses that monolayer adsorption exist under the experimental conditions employed.

Igwe and Abida carried out the research to remove the heavy metals from wastewater by using various biosorbents[7].The isotherm and kinetics studies were carried out to study the process of metal uptake. Freundlich isotherm parameters for Cd(II), Pd (II) and Zn (II) sorption on maize cob and husk. Were estimated for various particle sizes. For cob and husk, values of constant b varied from 4.9×10^{-7} to 9.46×10^{-20} for various particle sizes ranging from 450 µm to 850 µm. The values of m, were found to have their values between 2 to 6. For, lead the values of these constant were observed to be 7.12×10^{-8} to 4.30×10^{-2} and 3 to 1 respectively.

International Journal of Ethics in Engineering & Management Education

Website: www.ijeee.in (ISSN: 2348-4748, Volume 1, Issue 2, February 2014)

For zinc the values of these constants were still lower ranging 0.95 to 1.6 and 0.95 to 1.3 respectively.

Padmapriya and Murugesan studied the Phytoremediation of various heavy metals (Cu, Pb and Hg) from aqueous solution using water hyacinth and its toxicity on plants [8]. In their study, study, various toxic heavy metals (Cu, Pb and Hg) were removed from the aqueous solution using water hyacinth (*Eichhornia crassipes*) plants at various environmental conditions (retention time, initial concentration of heavy metals,organic loading rate and pH). It was observed that the The biosorption capacity sharply increases with increase in time and attains steady state at15th day. They calculated the Langmuir constants (qm and *kd*) along with correlation coefficients (R_2) .

$$qe = \frac{qobCe}{(1 + bCe)} \quad (7)$$

It was observed that The order of maximum capacity (q_0) for the biosorbents of metal removal was roots > shoots of water hyacinth. Here q_e, is the sorption capacity for equilibrium concentration Ce. The Freundlich constants were observed to be , 0.19, 0.18 and 0.17 for biosorption of Cu, Pb and Hg ions respectively and the absorption capacity of the biosorbents with slope m, 7.4, 6.7 and 4.4 for the biosorption of Cu, Pb and Hg ions respectively.

The kinetics of copper ion adsorption was studied by Ho and Ofomaja[9]. They used palm kernel fibre as an adsorbent for the purpose. They carried out batch experiments based on assumption of the pseudo-second-order kinetic model, which was developed to predict the rate constant of adsorption, the equilibrium adsorption capacity and initial adsorption rate with the effect of initial copper concentration and reaction temperature. It was observed that palm kernel fibre has fairly high capacity for the removal of copper ions from solution. The interaction between adsorbent and adsorbate was observed to be endothermic reaction with an activation energy higher than 22kJ/mol. It also indicated that the interaction was of chemical nature. The kinetics fitted well for pseudo first order rate equation.

Pongamia pinnata Tree Bark was used for removal of lead from industrial effluent by Mamatha et. al.[10]. They carried out studies on kinetics and mechanism for adsorption of lead in Aqueous and Industrial Effluent. They carried out Adsorption kinetics using lead Sulphate solutions of 5 to 50 ppm, pH in the range 2 to 9, 2.5 to 10g/L adsorbent of average particle size 225µm, a contact time up to 60 min, constant agitation of 200 rpm and temperature of 300C. The data fitted well with the Langmuir isotherm with R^2 value of 0.9967. The metal uptake agreed fairly well with the Freundlich equation also. The studies also revealed that the pseudo first order kinetics fitted well for the metal uptake.

Torab-Mostaedi et. al. used expended perlite for the removal of heavy metals[11].They investigated the adsorption characteristics of cadmium and nickel onto expanded perlite from aqueous solution. The Langmuir isotherm fitted well for the cadmium and nickel removal. The adsorption results obtained are best described by the Freundlich isotherm models. Pseudo first kinetics desrided the metal uptake with reasonable accuracy. Shrivastava et.al. studied the Competitive adsorption of nickel and cadmium onto bagasse flyash[12]. It was observed that Freundlich and Redlich–Peterson (R–P) isotherm models reasonably described the metal uptake. The Freundlich isotherm fitted better for the competitive adsorption.The The sorption of cadmium ions on the nano zerovalent iron particles was tried by Boparai et.al.[13]. They also studied thermodynamic and kinetic aspects of this process. The studies were conducted in the concentration range of 25-480 mg/l. It was observed that the adsorption in this case increases with the increase in temperature as with endothermic reactions. In this case the Freundlich and Temkin isotherms fitted the adsorption process and kinetics was second order. The research on nickel and cadmium removal by using nettle ash as an adsorbent was carried out by Mousavi and Seyedi[14]. The experimental data well fitted in the Langmuir isotherm equation with the monolayer adsorption capacity of 142.8 mg/g. The adsorption kinetics was found to follow pseudo second order kinetics..Maleki et al. tried Adsorption of cadmium on Barley Hull and Barley Hull Ash[15].The adsorption followed Freundich adsorption isotherm, indicating chemisorptions.

The investigation on thermodynamics and kinetics of cadmium adsorption on rice husk wasc carried out by Kumar et. al [16]. They studied the adsorption behavior of rice husk for cadmium ions from aqueous solutions as a function of appropriate equilibrium time, adsorbent dose, temperature, adsorbate concentrations and pH in a batch system. It was observed that the adsorption preocess was spontaneous in nature and exothermic as well. the adorption process was pseudo first order in its nature hence chemisorptions was predominant.Gouda et.al focused on coconut leaves as an alternative adsorbent for the removal of Ni(II) from wastewater[17]. The batch experiments conducted at at room temperature 270C showed that the adsorption process is affected by various parameters such as contact time, solution pH, adsorbent dose and initial concentration. The data was tested for the Langmuir and Freundlich equations. The data fitted well to both Langmuir and Freundlich isotherms.

III.CONCLUSION

The removal of heavy metal by using sorbent is very attractive alternative. Though the research has been carried out by using various sorbents, there is still scope for the research in this field, with new possibilities in terms of improving the removal efficiency and availability of adsorbents. The kinetic study indicated either first or second order kinetics depending on the sorbent used. The sorption process followed Langmuir and Freundlich isotherms in most of the cases. This indicates monolayer sorption and multilayer sorption, both are important. The values of Freudlich constant and the rate constant depends on the sorbent used.

International Journal of Ethics in Engineering & Management Education
Website: www.ijeee.in (ISSN: 2348-4748, Volume 1, Issue 2, February 2014)

REFERENCES

[1] I-Hsien Lee, Yu-Chung Kuan, Jia-Ming Chern, "Equilibrium and kinetics of heavy metal ion exchange", Journal of the Chinese Institute of Chemical Engineers, Vol. 38, pp.71–84,2007.

[2] R.D. Tyagi, Y.G. Du, "Kinetic model for the effects of heavy metals on activated sludge process using neural networks", Environmental Technology, Vol. 09,pp.883-890.1992

[3] N. Ghasemi, M. Ghasemi , S. Mashhadi and M.H. Tarraf , "Kinetics and Isotherms Studies for The Removal of Ni(Ii) From Aqueous Solutions Using Rosa Canina L", International Congress on Informatics, Environment, Energy and Applications-IEEA 2012, vol.38, IACSIT Press, Singapore.

[4] Maria Visa, Anca Duta, "Cadmium And Nickel Removal From Wastewater Using Modified Fly Ash:Thermodynamic And Kinetic Study", Scientific Study & Research , Vol.9 (1)pp.73-77, 2008.

[5] Patricia Miretzky, Andrea Saralegui, Alicia Ferna ´ndez Cirelli,"Simultaneous heavy metal removal mechanism by dead macrophytes", Chemosphere 62,pp. 247–254,2006.

[6] Ajaelu Chijioke John, Ibironke, Oluwafunke Lara, Adedeji, Victor and Olafisoye Oladunni, "Equilibrium and Kinetic Studies of the Biosorption of Heavy Metal (Cadmium) on Cassia siamea Bark", American-Eurasian Journal of Scientific Research, vol.6,pp.123-130, 2011.

[7] Igwe, J. C. and Abia A.A., "A bioseparation process for removing heavy metals from waste water using biosorbents", African Journal of Biotechnology Vol. 5 (12), pp. 1167-1179, 16 June 2006.

[8] G.Padmapriya and A.G. Murugesan, "Phytoremediation of various heavy metals (Cu, Pb and Hg) from aqueous solution using water hyacinth and its toxicity on plants", International Journal of Environmental Biology, Vol.2, pp.97-103,2012.

[9] Yuh-Shan Hoa, Augustine E. Ofomaja, "Kinetic studies of copper ion adsorption on palm kernel fibre", Journal of Hazardous Materials B137,pp. 1796–1802,2006.

[10] M.Mamatha, H.B.Aravinda, S.Manjappa, E.T.Puttaiah, "Kinetics and Mechanism for Adsorption of Lead in Aqueous and Industrial Effluent from Pongamia pinnata Tree Bark", Journal Of Environmental Science, Toxicology And Food Technology", Volume 2, Issue 3,pP 01-09, Dec.2012.

[11]M.Torab-Mostaedi, H. Ghassabzadeh, M. Ghannadi-Maragheh,S. J. Ahmadi and H. Taheri, "Removal Of Cadmium And Nickel From Aqueous Solution Using Expanded Perlite", Brazilian Journal of Chemical Engineering, Vol. 27, No. 02, pp. 299 - 308, April - June, 2010.

[12] Srivastava V.C., Mall I.D., Mishra I.M., "Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash", Chemical Engineering Journal,Vol.117, p.79–91,2006.

[13] Boparai H.K., Meera J.,Carroll D.O."Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles",J Hazardous Mater, vol.15, p..1-8,2010.

[14] H. Zavvar Mousavi; S. R. Seyedi, "international Journal of Environment Science and Technology" VOL. 8, PP. 195-202,2011.

[15] Maleki A., Mahvi A.H., Zazouli M.A.,, Hassan I., And Barati A.H.,"Aqueous Cadmium Removal by Adsorption on Barley Hull and Barley Hull Ash", Asian J of Chemistry; Vol. 23, p.1373-1376,2011.

[16] Kumar U, Bandyopadhyay M "Sorption of cadmium from aqueous solution using pretreated rice husk", Bioresour Technol. ,Vol.97,pp.104-9,2006.

[17] Rudre Gowda, A.G.Nataraj and N.Manamohan Rao, "Coconut leaves as a low cost adsorbent for the removal of Nickel from Electroplating effluents" International Journal of Scientific & EngineeringResearch,Vol.2,pp.1-5,2012.