



Adsorption of Cu^{2+} ions onto Polyvinyl alcohol-Alginate bound Nano Magnetite Microspheres: A Kinetic and Thermodynamic Study

Alka Tiwari* and Prerna Kathane

Department of Chemistry, Government Vishwanath Yadav Tamskar Post Graduate Autonomous College, Durg, CG, 491001, INDIA

Available online at: www.isca.in, www.isca.me

Received 15th October 2014, revised 17th January 2015, accepted 22nd February 2015

Abstract

The sorption efficiency of elimination of copper (II) ions by adsorption onto polyvinyl alcohol-alginate bound nano magnetite microspheres [PVA-ANM] from water has been investigated. The effect of agitation time, mass of adsorbent, temperature, adsorbate strength, and initial pH was studied by batch mode. The microspheres were magnetized in-situ and the phase identification, morphology and size of magnetite nanoparticles were analyzed using FTIR, XRD, and TEM respectively. Mechanics values like constants for rate, capacities of equilibrium sorption, and coefficients of connected correlation for every kinetic rate model were evaluated and described by using equations of reversible rate model of first order, rate model of pseudo first order, rate model of second order and rate model of pseudo second order equation respectively. Thermodynamic study showed negative values of ΔG , ΔH^0 and ΔS^0 which indicated the surface assimilation of copper (II) ions were physically controlled, exoergic and spontaneous. The prepared adsorbent PVA-ANM microspheres was obtained an efficient sorbent for removal of Cu^{2+} ions from water and wastewater and might be regenerated and reused several times without any detectable losses.

Keywords: Sorption, Cu^{2+} ions, kinetic, nano magnetite, polyvinyl alcohol-alginate.

Introduction

The modern industrial pattern converts the natural flow of materials and brought contamination in their effluents, which contain cytotoxic substances particularly heavy metal ions like arsenic, lead, copper, iron, cadmium and zinc¹. Heavy metal ions are non-biodegradable, accumulated through the food chain and therefore persistent. Contamination of biological environment by heavy metal ions is now became global issue. The ions of Cd^{2+} , Pb^{2+} and Cu^{2+} are extremely toxic ions even at relatively low concentrations. Copper and its compounds are wide employed in metal finishing, electroplating, electronics, paper, textile, chemicals, dyeing and petroleum is of concern to the public, industry and government alike. Copper is an important nutrient for all living beings within a particular range but it could be harmful when exceeds from allowable limits^{2,4}. According to Water Quality Act 1974, the allowable concentration was 0.05mg L^{-1} for copper ions discharged in effluents. More than 1.0 mg L^{-1} intake of copper get starts accumulation within liver of living beings leading to poor hepatocyte regeneration and fibrosis. Epidemiological evidences like Wilson's disease, Indian Childhood Cirrhosis (ICC) that produces psychiatric problems and neurological disorder⁵. Cancer among coppersmiths proves a primary carcinogenic effect and malignant neoplastic diseases is evidence of carcinogenic nature of copper⁶. Thus the elimination of such hazardous metal ions from effluent has now become the topic of significant interest owing to a lot of very strict legislations brought to regulate water pollution. Conventional technologies like chemical precipitation, electro-osmosis, ion-exchange,

reverse diffusion, adsorption, degradation and membrane separation have been applied to remove such type of harmful metal ions. Most of these technologies are expensive, inefficient and also produce secondary sludge that couldn't be reused and regenerated⁷. Among numerous techniques, adsorption being standard, it is a very important separation method and was used widely in the field of environmental remediation, due to cost effectiveness, easy handling, high efficiency, ease of separation and reusability⁸. Many biological, natural and synthetic polymeric materials like sour sop seeds⁹, sawdust¹⁰, chitosan¹¹, cellulose¹², yeast¹³, chitosan-alginate¹⁴, pectin-alginate¹⁵, carboxy methyl cellulose-alginate¹⁶ was reported as adsorbent to adsorb copper (II) ions from water and wastewater.

Advancement in nano science and nano engineering counsel that several of this issues related to water quality improvement by applying nano-materials. Currently nanotechnology is considered as the foremost necessary advancements in field of science and technology was expounded to the manipulation of constants at the nanometer scale for exhibits new properties for novel advantages¹⁷. At the end of 20th century, advancement of nanotechnology has widened the variability of adsorbents. Many literature were reported the sorption of heavy metals with nanocrystalline titanium dioxide, nanoscale zero valent iron and modified form of zero valent iron nanoparticles etc, thus the employment of magnetic nanoparticles for separation and pre-concentration in environmental chemistry is gap a brand new technology which is faster, easier and extra precise than those used traditionally. The best application of this methodology is so desired materials are separated from liquid solution by an

easy and compact method where as minimum secondary wastes are created. Alternative benefits are big active area for given weight of particles and thus ability to technique resolution which contains suspended solids¹⁸. Some carbon based nano materials, nanoparticles of metals and oxides of metals and polymer supported nano sorbent based materials like iron ore, coated materials of iron oxide and granular hydroxide of iron (GHF) etc are according as associated adsorbent to adsorbed metal ions from wastewater¹⁹⁻²⁰. Iron oxide nanoparticles with natural and synthetic polymers were also used for removal of heavy metals²¹⁻²³. These reported methods are not very efficient, thus requirement for additional economical and more effective ways that recovery of valuable heavy metals from effluents has resulted within the development of other treatment technologies. So in present investigation the combine techniques of sorption and magnetic separation applied for uptake of Cu²⁺ ions from waste water and recovery of metal ions are very advantageous and provoking. In this paper a novel adsorbent prepared by using sodium alginate (natural polymer) and polyvinyl alcohol (synthetic polymer) bound nano particles of iron oxide microspheres having high active surface energy and surface area, with high adsorption capacity with relevance to inorganic and organic matter. The current study aimed to analyze the role and the effectiveness of new synthesized polyvinyl alcohol-alginate bound nano magnetite microspheres [PVA-ANM] as adsorbent for sorption of Cu²⁺ ions from wastewater. Magnetic nanoparticles were first synthesized in-situ and then applied for copper uptake in batch mode, mechanics, thermodynamic yet as regeneration studies of PVA-ANM were investigated. The goal of this study was to gauge the applicability of the PVA-ANM towards the sorption of Cu²⁺ ions from industrial sewer water and regeneration of adsorbent for further use and also for recovery of valuable metal ions. The preparation, characterization and batch adsorption study has already been described in our previous study²⁴.

Methodology, Result and Discussion

Adsorption Kinetic modeling: To determine the progress of Cu²⁺ ions removal by PVA-ANM microspheres, several studies were carried out by taking pH 4, adsorbent mass 0.2 gram, 20 milliliter of known concentration of Cu (II) ions as adsorbate at 200 rpm with completely different time intervals starting from 10 to 240 minutes. It was obtained that removal of Cu²⁺ ions was redoubled with time and attains equilibrium in 120 min., after that a decrease within the adsorbed quantity of Cu²⁺ ions was noticed, which may be due to saturation of all binding sites on adsorbent.

First order reversible Kinetic model: For correlate the rates of removal of Cu²⁺ ions between solid and liquid states, a general first-order reversible kinetic model used. It was considered as a rate of reversible reaction may associate with equilibrium states, the overall rate k'', equilibrium constant K_c, forward rate constant k₁ and backward rate constant k₂ were evaluated by applying following equations:

$$\ln[1 - U_t] = -k'' t \tag{1}$$

$$k'' = k_1 + (1 + 1/K_c) = k_1 + k_2 \tag{2}$$

$$K_c = k_1 / k_2 = C_A / C_e \tag{3}$$

Where: U_t is connected with fractional attainment of adsorbate at equilibrium. Plot between ln[1-U_t] versus agitation time (minute) provided a line (figure-1). Various rate constants for a given concentration of Cu (II) ions were calculated by the slope of the straight line by using equation 2 and 3, values given in table-1. Values depicted that the backward rate constant for the sorption of Cu (II) ions is less than the forward rate constant²⁵. Removal of Cu²⁺ ions onto PVA-ANM microspheres has been reversible and therefore has sensible potential to the recovery of valuable Cu²⁺ ions from sewer water bodies.

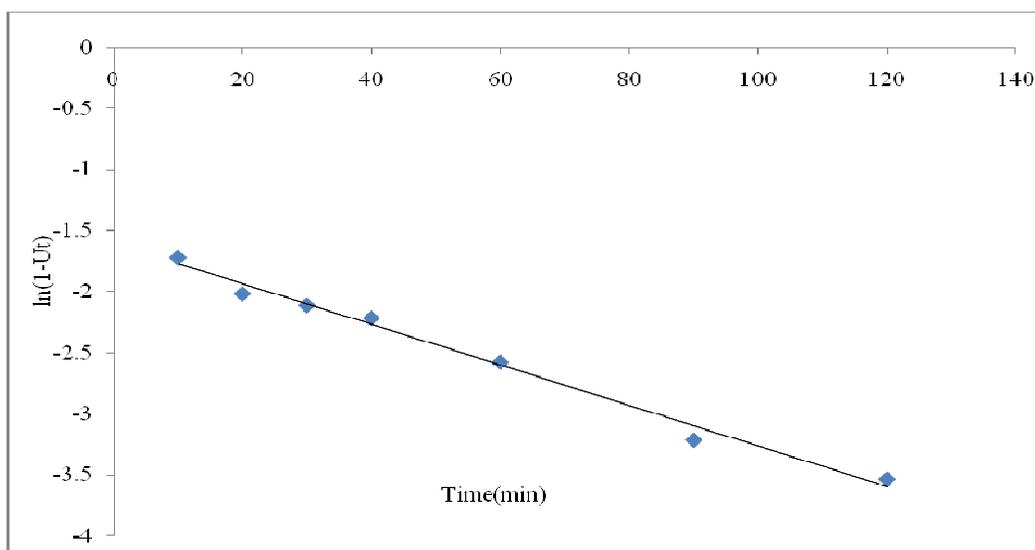


Figure-1
 Linear fit of experimental data obtained using first order reversible model

Second-order kinetic rate model: The proposed kinetic scheme for second-order rate model was given as follows:

$$1 / C_e = K_2 \cdot t / C_i + 1 / C_i \quad (4)$$

The second-order rate constant for sorption K_2 was calculated by plot between $1 / C_e$ versus time and value calculated by using equation-4, where the Cu^{2+} ions concentrations in solution C_e at any given time t and initial concentration C_i at zero time.

Pseudo-first order kinetic rate model: To determine the controlling mechanics of the sorption method like transfer of mass and changes in chemical structure, the pseudo-first order and pseudo-second order rate models were applied. Lagergren projected equation to calculate pseudo-first order kinetic rate constant K_{ad} , given as follows:

$$\log (a_s - a) = \log a_s - (K_{ad} / 2.303)t \quad (5)$$

Where: Sorption capacity a ($mg\ g^{-1}$) at time t and a_s sorption capacity, which were evaluated from the linear plot between $\log(a_s - a)$ and time, values depicted in table-1.

Pseudo-second order kinetic rate model: Sorption dynamics might be represented by Ho's pseudo-second order kinetic

model. Linear integral form of the equation is:-

$$t/a = 1 / (k_2' a^2) + (1 / a_s) t \quad (6)$$

Where: $k_2' a^2 = h$ ($mg\ g^{-1}\ min^{-1}$) is considered as the initial sorption rate ones $t \rightarrow 0$ and k_2' ($g\ mg^{-1}\ min^{-1}$) is that the rate constant of the pseudo-second order equation. The plot between t/a and time gave a line with very high correlation coefficient ($R^2 = 0.999$). The coefficient of correlation for the pseudo 1st order kinetic model is lower than pseudo 2nd order kinetic model. Moreover, an oversize distinction observed between the calculated and experimental worth of equilibrium sorption capability a_s , indicating a poor pseudo-first order suited to the experimental data. If pseudo-second order dynamics is applicable, then a_s , k_2' and h are typically determined from the slope and intercept of the strait line, severally. The evaluated a_s value also agrees with the experimental data within the case of pseudo-second order mechanics, as depicted in table-2. This implies that the sorption data are well described by pseudo-second order mechanics and supports the idea that the rate-regulating step of Cu^{2+} ions sorption on adsorbent might be a physical sorption or chemical sorption, although the metal ions attach with the adsorbent surface by forming a covalent bond in chemisorption and have a tendency to seek out sites that maximize their coordination range with the surface²⁶.

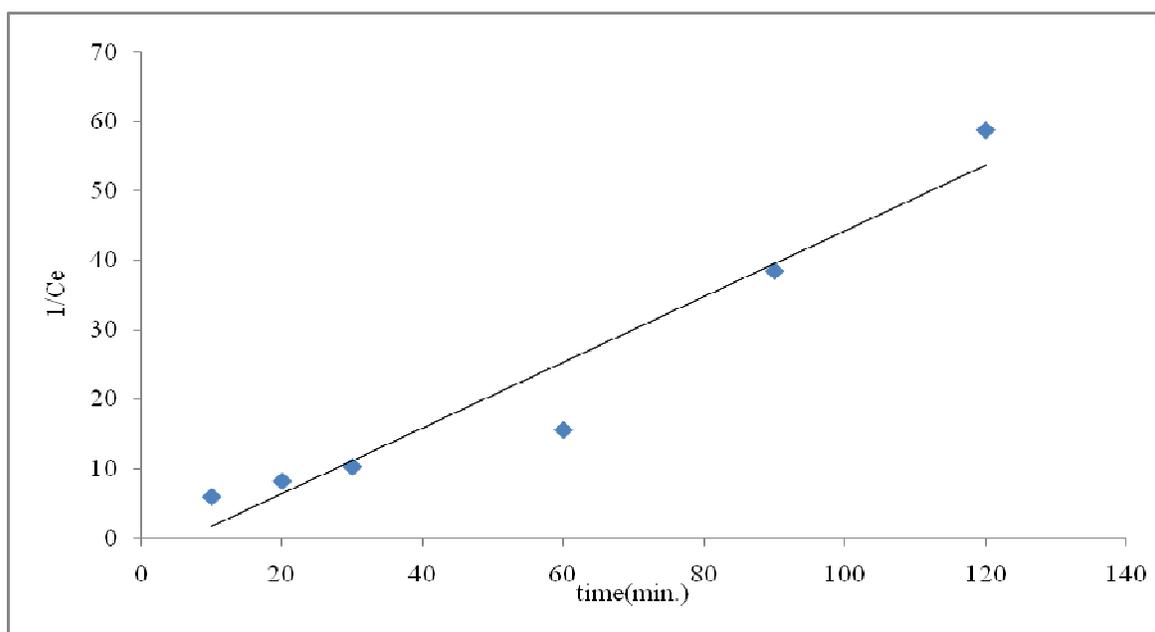


Figure-2
 Linear fit of experimental data obtained using second order reversible model

Table-1
 Values of rate constants for reversible first order model, second-order model and intra particle diffusion of Cu^{2+} ions sorption onto PVA-ANM microspheres

Copper ions concentration ($mg\ dm^{-3}$)	Rate model of the first order reversible					Rate model of the second-order		Rate constant for Intra particle diffusion
	k''	K_c	k_1	k_2	R^2	K_2	R^2	K_p ($mg^{-1}\ min^{-0.5}$)
1	0.0431	38.38	0.0265	0.0166	0.989	0.474	0.935	0.077

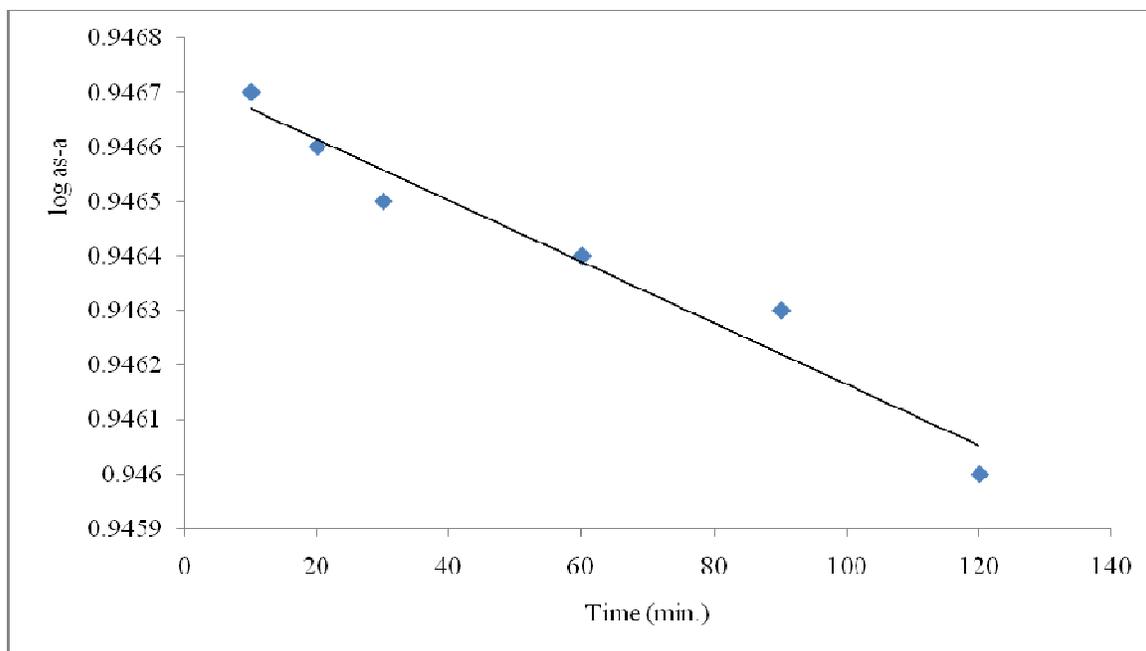


Figure-3
 Plot for Pseudo-first order kinetic model of Cu²⁺ ions sorption onto PVA-ANM microspheres

Table-2
 Values of rate constants for pseudo-first order model and the pseudo-second order model of Cu²⁺ ions sorption onto PVA-ANM microspheres

Copper ions concentration (mg dm ⁻³)	Rate model of the pseudo-first order reversible			Rate model of the pseudo-second order			
	K _{ad} (min ⁻¹)	a _s (mg g ⁻¹)	R ²	K ₂ ' (g mg ⁻¹ min ⁻¹)	A (mg g ⁻¹)	R ²	H (mg g ⁻¹ min ⁻¹)
1	2.179	0.9465	0.956	3.4124	0.0993	0.999	0.0291

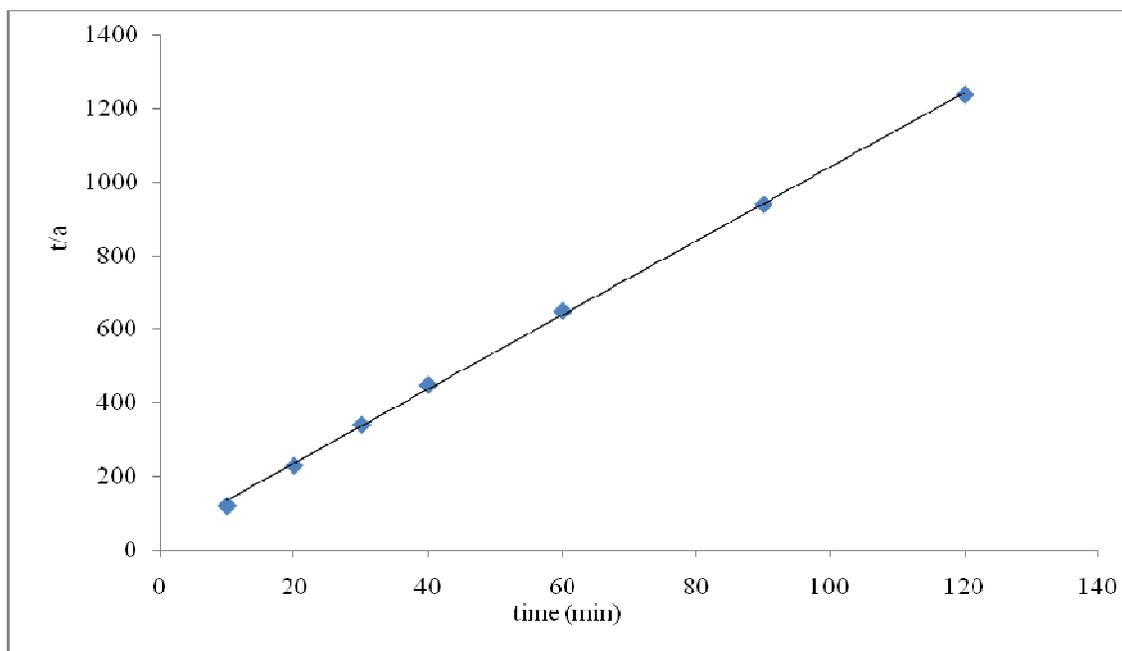


Figure-4
 Linear fit of experimental data obtained using pseudo-second order model

Intraparticle Diffusion: To study the change in the concentration of adsorbate onto composite adsorbent PVA-ANM microspheres with shaking time, the rate constant for intraparticle diffusion K_p ($\text{mg}^{-1} \text{min}^{-0.5}$) was determined by ‘Morris Web’ equation as given below:

$$a = K_p t^{1/2} \tag{7}$$

The sorption mechanics follows the intraparticle diffusion method. Thus as to judge the rate regulating step a plot was drawn between adsorbed amount of copper on adsorbent in g mg^{-1} and square root of time in minute (a versus $t^{1/2}$). The value of K_p was evaluated from the slope of the curve, the values depicted in table-3. It was observed that the plot was non linear over the full time interval proves that the sorption process quite affected by single factor²⁷.

Thermodynamic study of Adsorption: Thermodynamic values, change in Gibbs free energy (ΔG^0), change in enthalpy (ΔH^0) and change in entropy (ΔS^0) may be obtained by using the equilibrium constant K_c that depends on temperature. K_c ,

which is ratio between the equilibrium concentration of Cu^{2+} ions in adsorbate (mg dm^{-3}) and the Cu^{2+} ions concentration on the adsorbent at equilibrium (mg dm^{-3}). Free energy change in sorption ΔG^0 (kJ mol^{-1}) could be calculated by using following equations:

$$K_c = C_a / C_e \tag{8}$$

$$\Delta G^0 = - RT \ln K_c \tag{9}$$

$$\ln K_c = \Delta S^0 / R - \Delta H^0 / RT \tag{10}$$

Where: T is temperature in Kelvin, R is Ridberg’s constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and the K_c can be presented in terms of ΔH^0 ($\text{kJ}^1 \text{mol}^{-1}$) and ΔS^0 ($\text{J mol}^{-1} \text{K}^{-1}$) as a function of temperature. The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot between $\ln K_c$ and $1/T$, severally by using equation (10). Sorption of Cu (II) ions onto adsorbent get decrease with the increase in temperature ranging from 298 to 328 K. Hence the nature of method was exoergic. The enthalpy change (ΔH^0) was found $-54.16 \text{ k J mol}^{-1}$ and the entropy change (ΔS^0) was found $-6.876 \text{ J mol}^{-1} \text{K}^{-1}$.

Table-3
 Values for thermodynamic parameters of Cu^{2+} ions sorption onto PVA-ANM microspheres

Copper ions concentration (mg dm^{-3})	Enthalpy change $\Delta H^0(\text{KJmol}^{-1})$	Entropy change $\Delta S^0(\text{Jmol}^{-1}\text{K}^{-1})$	Gibbs free energy change $\Delta G^0 (\text{Jmol}^{-1}\text{K}^{-1})$				Activation energy $E_a (\text{K Jmol}^{-1})$	Arrhenius factor A
			298K	308K	318K	328K		
1	-54.16	-6.876	-10.91	-7.29	-6.74	-5.77	13.09	7.7102

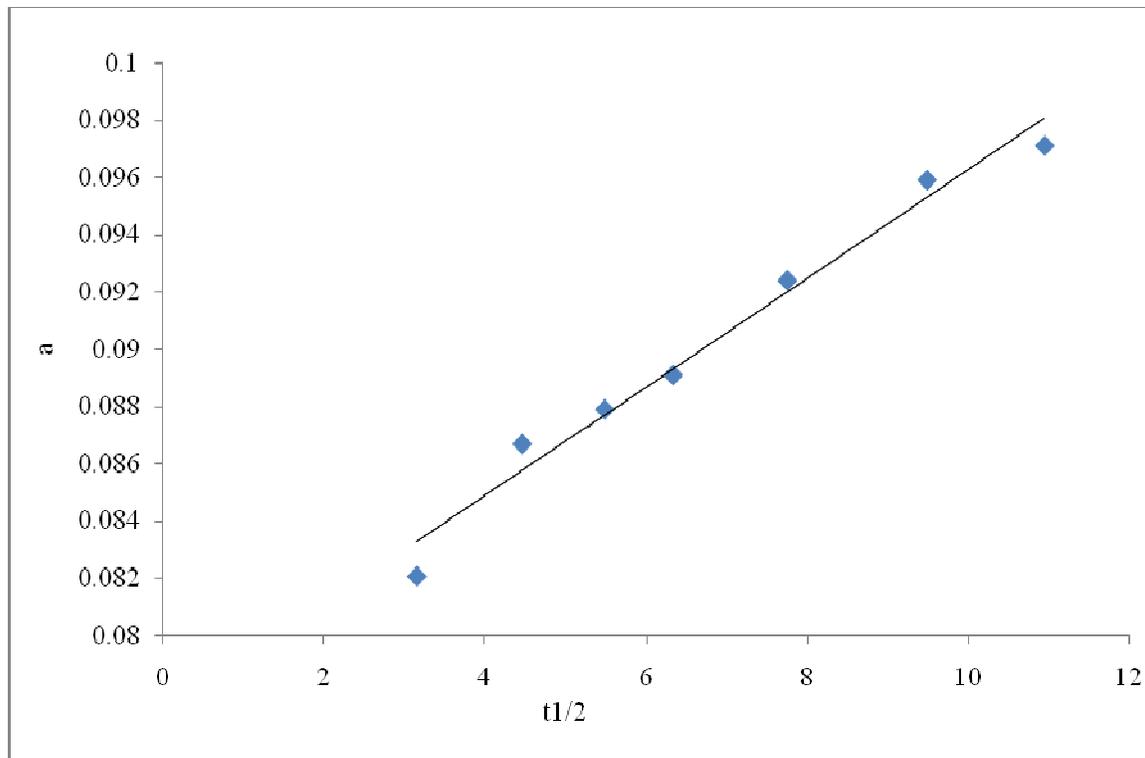


Figure-5
 Plot of intraparticle diffusion of Cu^{2+} ions sorption onto PVA-ANM microspheres

These negative values of ΔG^0 and ΔH^0 showed that the nature of sorption of Cu (II) ions onto PVA-ANM was feasible, spontaneous and exoergic. The entropy change ΔS^0 value is negative, proves a decrease within the randomness at the solid/liquid interface with some configurationally changes in the adsorbent and adsorbate during the sorption process. It was stated that ΔG^0 values higher than -20 kJ mol^{-1} are related with electrostatic interaction between sorption sites and metal ions (physio-sorption), while ΔG^0 values more negative than -40 kJ mol^{-1} related with charge sharing or transfer from the adsorbent to the metal ion to form a chemical bond (chemi-sorption)^{28,29}. The calculated values of ΔG^0 for Cu^{2+} ions were higher than -10 kJ mol^{-1} , which proves that physical sorption is the predominant kinetics in the present sorption method.

The Arrhenius factor A was found 7.7102. The Arrhenius

activation energy of sorption (E_a) was found $13.09 \text{ kJ mol}^{-1}$, positive values proves the feasibility of the sorption method. Low value of E_a indicated that the rate determining step of Cu (II) ions sorption might be physically regulated. Physical sorption occurs usually at low temperatures and as fast compared to chemical sorption³⁰. The activation energy of sorption was determined using Arrhenius equation, given as below:-

$$\ln k_2'' = \ln A - E_a/RT \tag{11}$$

Where: k_2'' ($\text{g mg}^{-1}\text{h}^{-1}$) is the constant of rate calculated from the pseudo-second order mechanics, E_a (kJ mol^{-1}) and A are known as the Arrhenius activation energy and Arrhenius factor of sorption, respectively and can be calculated by the slope of plot between $\ln k_2''$ and $1/T$ (K^{-1}).

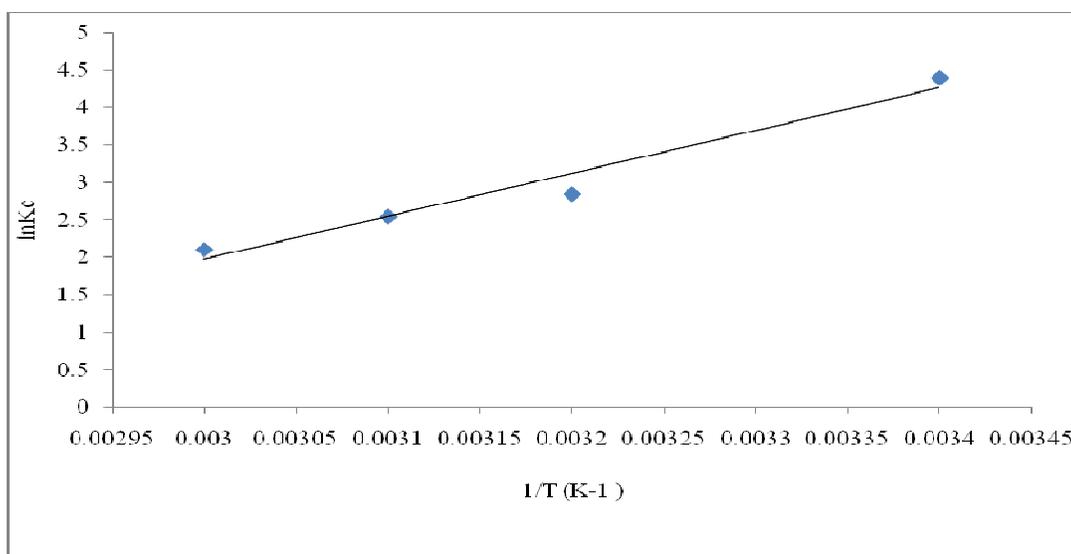


Figure-6

A linear graph between $\ln K_c$ versus $1/T$ of Cu^{2+} ions sorption onto PVA-ANM microspheres

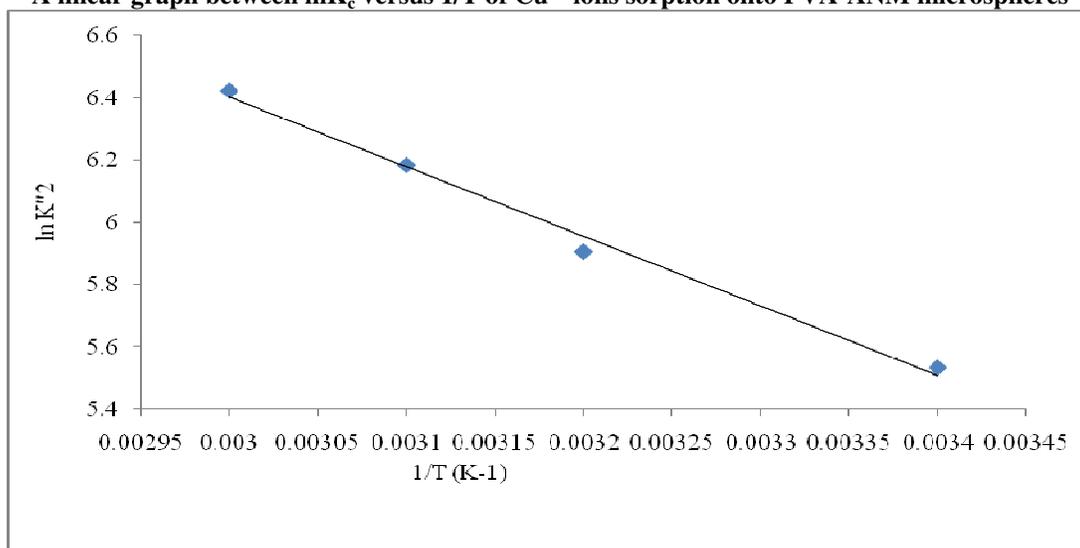


Figure-7

A plot of $\ln K_2''$ versus $1/T$ for Cu^{2+} ions sorption onto PVA-ANM microspheres

Regeneration and Recovery: To determine the suitable eluant and its applicable concentration, batch desorption studies with five different desorbing solutions via, 0.1M HCl, 0.1M HNO₃, 0.1M CH₃COOH, 0.1M H₂SO₄ and 0.1M NaCl was examined. Desorption efficiency of various desorbing agents are shown in figure-8. The nitric acid has shows a better desorption efficiency than others. So nitric acid was selected the desirable eluant for the studies. To determine optimum concentrations of desorbing agent HNO₃ acid for practical applications, the concentration of acid solution should be as low as possible. Hence for the detection of maximum desorption efficiency desorption studies were carried out in different concentration of HNO₃ acid with 1.0g PVA-ANM for 100 ml of 1 mg dm⁻³ of Cu²⁺ ions solution

for sorption and 100 ml solution for desorption in Erlenmeyer flasks. The flask was agitated at 200 rpm, at initial pH 4 and 27°C (±2) temperature for 120 minute to achieving sorption/ desorption equilibrium (Figure-9) depicts the desorption studies of Cu²⁺ ions, which were eliminated from the surface of the sorbent containing 0.0991 mg g⁻¹ of Cu (II) using 0.01, 0.02, 0.04, 0.06, 0.08, 0.1 and 0.2 N HNO₃ strength severally at room temperature (27°C,± 2). Complete desorption of Cu²⁺ ions from the sorbent took place by 0.06 N HNO₃, the percentage recoveries of copper found 98.75%, thus 0.06 N HNO₃ used as the eluant in the subsequent studies. It was stated that the protons compete with Cu²⁺ ions in acidic medium and displace the huge amount of adsorbed Cu²⁺ ions.

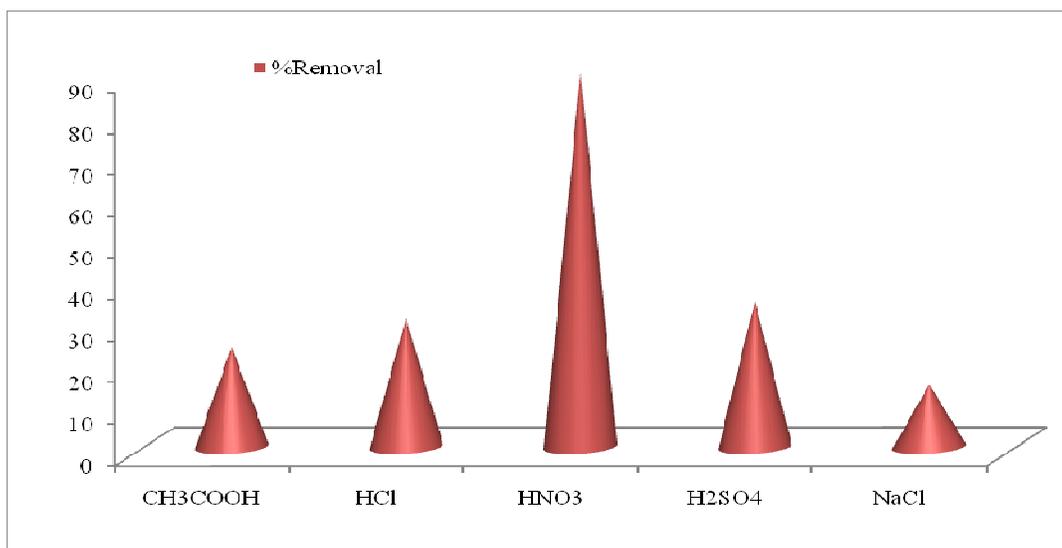


Figure-8
 Desorption studies using various desorbents with Cu²⁺ ions loaded PVA- ANM Microspheres

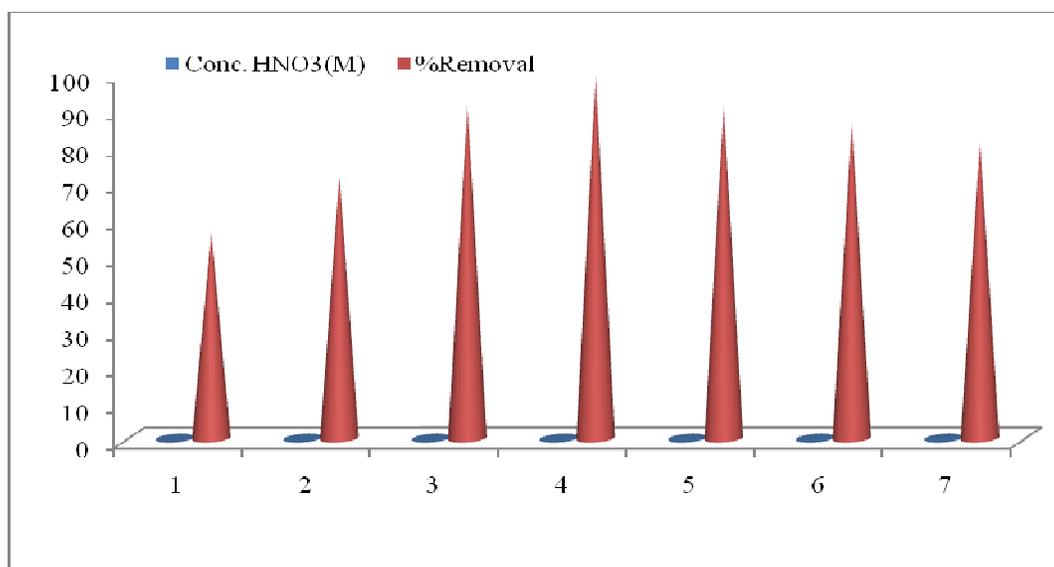


Figure-9
 Desorption studies using various strengths of HNO₃ with Cu²⁺ ions loaded PVA- ANM Microspheres

The purpose of regenerating the sorbent PVA-ANM is to minimize operating costs. The feasibility of regenerating metal absorbed PVA-ANM by 0.06 N HNO₃ by repeating the adsorption /desorption process for five consecutive cycles. Figure-10 shows the adsorption capacity of PVA-ANM retained its metal after five regenerating cycles, virtually an equivalent metal ion sorption capacity after the continual regeneration. So ion exchange mechanism is very important in reference to sorption /desorption process for adsorbent. Therefore adsorbent PVA-ANM has the potential to uptake Cu²⁺ ions repeatedly from aqueous medium.

To detect the potential of adsorbent PVA-ANM for the sorption of Cu (II) ions from waste water, PVA-ANM placed into a flask containing the industrial effluent with 53.7-59.2 mg l⁻¹ Cu²⁺ ions. The sorption capacity of PVA-ANM in a batch sorption experiment was found 44.6 mg Cu²⁺/g PVA-ANM, Thus it may be used for commercial applications.

Conclusion

The PVA-ANM microspheres were found to be terribly effective adsorbent for the removal of Cu (II) ions from sewer water. The maximum uptake of metal ions occurs at the pH 4, between temperature range 25-27°C within 120 minutes. The values of the enthalpy change (ΔH^0) and the entropy change (ΔS^0) were to be found -54.16 (kJ/mol) and -6.876 (J/mol/K), respectively. The adsorption process is feasible and spontaneous in nature. The negative ΔH^0 value indicates the exoergic nature of adsorption and the negative value of ΔS^0 suggests a decrease in the randomness at the solid/liquid interface with some structural changes within the adsorbent. The ΔG^0 values

obtained in this study for Cu (II) ions are higher than -10 kJ mol⁻¹, which indicates that physical adsorption is the predominant mechanism in the sorption method. Arrhenius activation energy of sorption E_a found 13.09 k J mol⁻¹, the positive value indicating the feasibility of the sorption process. Besides E_a value is less than 40 k J mol⁻¹ showed that the rate-limiting step of Cu²⁺ ions sorption might be physically controlled. The Arrhenius factor A was found 7.7102. The PVA-ANM might be repeatedly employed in the sorption studies by adsorption-desorption cycle while not detectable losses in their initial sorption capacities. The maximum removal of Cu²⁺ ions from aqueous medium was obtained $\geq 99\%$, which proves this adsorbent to be superior among alternative adsorbents.

Acknowledgement

Authors are grateful to UGC-DAE Consortium for Scientific Research, Indore India for FTIR and XRD and AIIMS, New Delhi, India for TEM analysis.

References

1. Hutton M. and Symon C., Quantities of cadmium, lead, mercury and arsenic entering the environment from activities, *J. of Science Total Environment.*,**57**, 129-150 (1986)
2. Jang S.H., Min B.G., Jeong Y.G, Lyoo W.S. and Lee S.C., Removal of lead ions in aqueous solution by hydroxyl apatite / polyurethane composite foams, *J. of Hazardous Materials*, **152**, 1285-1292 (2008)

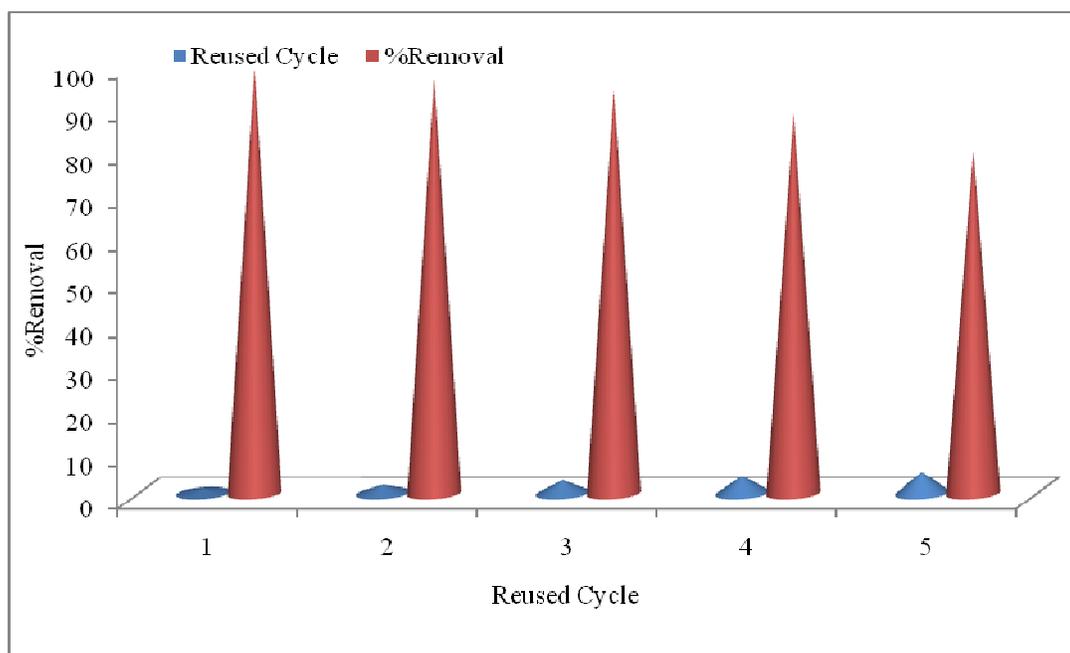


Figure-10

Sorption studies of Cu²⁺ ions using PVA-ANM Microspheres in five consecutive desorption / adsorption cycles

3. Kalavathy M. H., Karthikeyan T., Rajgopal S, Kineic and isotherm study of Cu (II) adsorption onto H₃PO₃ activated rubber wood sawdust, *J. of Colloid and Interface Science*, **292**, 354-362 (2005)
4. Peterson P. J., Peterson and Girling C. A, Other trace metals In; Lepp N. W. (Ed.) Effect of heavy metal pollution on plants Vol.-1, *Applied Science publisher, London*, 213-279 (1981)
5. Runnells D.D., Shepherd and Angino E. E., Metals in water, Determining natural background concentrations in mineralized areas, *Environmental Science Technology*, **26**, 2316 (1992)
6. Khajapai Thipyapong and Chomchai Suksai, Spectroscopic Determination Of copper(II) using Diamine Dioxime Derivatives, *Bull Korean Chemical Society*, **24(12)**, 1767 (2003)
7. Volesky B., Review Biosorption and me, *Water Research*, **41**, 4017- 4029 (2007)
8. Bailey S.E., Oline T.J., Bricka and Adrin D.D, A Review of Potentially low cost sorbents for Heavy metals, *Water Research*, **33**, 2469-2479 (1999).
9. Oboh O.I. and Aluyor E.O., The removal of heavy metal ions from aqueous solution using sour sop seed as biosorbent, *African J. of Biotechnology*, **7(24)**, 4508-4511 (2008)
10. Adouby K., Koffi Akissi L.C., Eboua Wandon N. and Yao B, Removal of heavy metal ions (Pb²⁺, Cu²⁺) in aqueous solutions by Pterygota macrocarpa sawdust, *J. of Applied Science*, **7(14)**, 1864-1872 (2007)
11. Cheung W.H., CY Ng J and McKay G, Kinetic analysis of the sorption of copper (II) ions on to Chitosan, *J. of Chemical Technique and Biotechnology*, **78**, 562-571 (2003)
12. Rimasaliba Gauthier R, Gauthier Adsorption of copper (II) chromium (III) ions onto Amidoximated cellulose, *J. of applied polymer science, John Wiley and Sons*, **15**, 1624-163 (2002)
13. Yekta Coksungur and Uren Guvence U., Biosorption of copper (II) ions by caustic treated waste baker's yeast biomass, *Turk J. Biology*, **27**, 23-29 (2003)
14. Wan Ngah W.S. and Fatinathan S., Adsorption of copper (II) in aqueous Solutions using chitosan, chitosan-GLA beads, (2007)
15. Tiwari A., Tiwari R. and Bajpai A.K., Dynamic and equilibrium studies on adsorption of Cu (II) ions onto biopolymeric cross-linked pectin and alginate beads, *J. of Dispersion Science and Technology*, **30**, 1208-1215 (2009)
16. Tiwari A., Dewangan T. and Bajpai A. K., Adsorption of Hg (II) ions onto binary biopolymeric beads of carboxy methyl cellulose and alginate, *J. of Dispersion Science and Technology*, **31**, 844-851 (2010)
17. Uheida A., Salazar-Alvarez G. and Bjorkman E, Fe₃O₄ and Fe₂O₃ nanoparticles for the adsorption of Co²⁺ from aqueous solution, *J. of Colloid and Interface Science*, **298(2)**, 501-507 (2006)
18. Khajeh and Khajeh, Synthesis of magnetic nanoparticles for biological and water applications, *nanomedicine, nanotechnology, biology and Medicine*, (2009)
19. Xiangtao Wang, Yifei Guo, Li Yang, Jing Zhao and Xiaoling Cheng, Nano materials as sorbent to remove heavy metal ions in wastewater treatment, *J. Environment Analytical Toxicology*, **2(7)**, (2012)
20. Ghanizadeh G., Ehrampoush M. and Ghaneiam M., Application of iron impregnated activated carbon for removal of arsenic from water, *Iran J. Environmental Health Sciences, Eng.*, **7(2)**, (2010)
21. Tiwari A., Soni A. and Bajpai A.K., Nanoparticles loaded alginate beads as potential adsorbent for removal of Phenol from aqueous Solution, *Synthesis and Reactivity in Inorganic, Metal, Organic and Nanometal Chemistry*, **42**, 1158-1166 (2012)
22. Tiwari A., Dhiwar C. and Bajpai A.K., Adsorption of Cr (VI) ions on composite microspheres of chitosan and Nano iron oxide, *J. of Dispersion Science And Technology*, **32**, 1661-1667 (2011)
23. Nanosafe, International conference on safe Production and use of Nanomaterials; *Conf. series*, **304**, 012022 (2011)
24. Tiwari A. and Kathane P., Superparamagnetic PVA-Alginate Microspheres as adsorbent for Cu²⁺ ions removal from aqueous systems, *Int. Research J. of Environment Sci*, **2(7)**, 1-5, 01-10 (2013)
25. Tiwari A. and Sharma N, Efficiency of superparamagnetic nano iron oxide loaded poly (Acrylamide-co- Acrylic acid) hydrogel in uptaking Cu²⁺ ions from water, *J. of Dispersion Science And Technology*, **34**, 1436-1446 (2013)
26. Tiwari A. and Sharma N, Efficiency of superparamagnetic nano iron oxide loaded poly (Acrylamide-co- maeic acid) hydrogel in uptaking Pb²⁺ ions from water, *Int. Res. J. of Environment Sci.*, **1(5)**, 1-7, 01-10 (2012)
27. Fan H.T., Fan J. Li, M.X, Guo M. and Zhang D. et al., Selective removal of arsenic (V) from aqueous solutions using a surface ion-imprinted amine-fuctionalised silica gel sorbent, *Ind Eng Chem Res*, **51**; 5216-5223 (2012)
28. Horsfall M., Spiff A. I. and Abia A. A, Studies on the influence of mercapto acetic acid (MAA) modification of cassava (manihot sculenta cranz) waste from biomass on the adsorption of Cu²⁺ and Cd²⁺ from aqueous solution,

- Bulletin of the Korean Chemical Society*, **25(7)**, 969-976 (2004)
29. Abdel-Ghani N.T., Hefny M. and El-Chaghaby G.A.F, Removal of lead from aqueous solution using low cost abundantly available adsorbents, *International J. of Environmental Science and Technology*, **4(1)**, 67-73 (2007)
30. Hossain M.A, Ngo H.H., Guo W.S and Nguyen T.V., Biosorption of Cu(II) from water by banana peel based biosorbent: Experiments and models of adsorption and desorption, *Journal of water sustainability*, **2(1)**, 87-104 (2012)
31. Sharma Neeraj and Alka Tiwari, Nano-ZnO loaded poly (acrylamide-co-itaconic acid) hydrogel as adsorbent for effective removal of iron from contaminated water, *Desalination and Water Treatment*, published on line, (2015)
32. Sharma Neeraj and Alka Tiwari, Nanomagnetite-loaded poly (acrylamide-coitaconic acid) hydrogel as adsorbent for effective removal of Mn²⁺ from contaminated water, *Desalination and Water Treatment*, published on line on 28th Jan.(2015)
33. Alka Tiwari, Dynamic and Equilibrium Studies on Adsorption of Cu(II) Ions onto Biopolymeric Cross-Linked Pectin and Alginate Beads, *Journal of Dispersion Science and Technology*, **30**, 1208-1215 (2009)
34. Sharma Neeraj and Alka Tiwari, Effective removal of Cu²⁺ ions from aqueous solution in fixed-bed micro column using nanomagnetite loaded poly (acrylamide-co-maleic acid) hydrogel as adsorbent, *Desalination and Water Treatment*, Published online: 20 Dec(2014)
35. Tulika Dewangan, Adsorption of Hg(II) Ions onto Binary Biopolymeric Beads of Carboxymethyl Cellulose and Alginate, *Journal of Dispersion Science and Technology*, **31**, 844-851 (2010)
36. Sharma Neeraj and Alka Tiwari, Assessment of Pb²⁺ ions removal efficiency of nanomagnetite-loaded poly (acrylamide-coacrylic acid) hydrogel in fixed-bed microcolumn from aqueous solution, *Desalination and Water Treatment*, Published online: 06 Dec (2014)
37. Tiwari Alka, Anjali Soni and Bajpai A.K, Nanoparticles Loaded Alginate Beads as Potential Adsorbent for Removal of Phenol From Aqueous Solution, *Synthesis and Reactivity in Inorganic Metal-Organic and Nano-Metal Chemistry*, **42**, 1158-1166 (2012)