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Thermodynamic studies of Cu^{2+} and Zn^{2+} adsorption by immobilized thiosalicylic-thiolactic Bi- ligand in a batch tannery wastewater system

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Abstract
A porous solid thiosalicylic-thiolactic immobilized polysiloxane bi-ligand system has been prepared by hydrolytic Polycondensation of tetraethyl Orthosilicate with a mixture of 3-chloropropyltrimethoxysilane, methanol and sodium hydroxide as a catalyst, gelation formed after 40 min. The product was functionalized with excess ethyl chloroacetate, triethylamine and immobilized with thiosalicylic-thiolactic acid. The competitive sorption characteristic of the metal ions (Cu^{2+} and Zn^{2+}) were studied using Microwave Plasma Atomic Emission Spectrophotometer (MPAES). The immobilized thiosalicylic-thiolactic bi-ligand exhibits high potential for the extraction of heavy metals in tannery wastewater at pH 6.0, this development would improve the treatment of tannery wastewater at a low cost; batch system of extraction of metal could be employed. The adsorption effects of various weights of the adsorbent from 10 to 30 mg/60 cm^3 with mesh size of (125-150 μm) were used for the extraction of metal ion and all the masses showed significant extraction of the metal ions, Cu^{2+} percentage adsorption increases with the increase in the amount of adsorbent from 95.2-100 % while Zn^{2+} showed no significant increase with the increased in the amount of adsorbent in the treatment of tannery wastewater. Thermodynamic parameters of the study yielded negative range values for ΔG^o (Cu^{2+} -10.240 to -11.962 and Zn^{2+} - 14.369 to -14.843 $KJmol^{-1}$), positive values for ΔH^o (Cu^{2+} 40.258 and Zn^{2+} 0.000 $KJmol^{-1}$) and ΔS^o (Cu^{2+} 178.518 and Zn^{2+} 47.421 $Jmol^1K^1$) respectively, indicating spontaneous, endothermic reactions and high degree of disorderliness with respect to metal ion binding capacity to the ligand system.

Keywords: Tannery wastewater, detoxification, polysiloxane, thiosalicylic ligand, thermodynamic

1. Introduction

Leather industries play very important role in the economy of many countries, but also generate harmful wastes into water bodies (Bulus *et al.*, 2018; Evangelo and Ebel, 2007; Malarkodi *et al.*, 2007) [5, 9, 17]. During tanning alone about 300 kg of chemicals are added per ton of hides or skins (Durai and Rajasimman 2001) [7] and requires large amount of water, about 35 L of water is consumed per kilogram of raw hide or skin processed, and an average of 35,000 L of wastewater is produced per ton of raw hide or skin (Islam *et al.*, 2014) [12, 16]. Not more than 20% of the chemicals are absorbed by leather; the remainder flows out with the effluent (Muthukkauppan and Parthiban, 2018) [19]. Conventional methods used in the tannery wastewater treatments have limitations such as production of toxic sludge (Jahan *et al.*, 2014) [16] and inability to remove heavy metals at trace level. There is need for innovative technologies which require low maintenance, high energy efficiency, low cost and better operational techniques than the conventional methods, this prompted the use of polymeric modified surfaces with excellent thermal, mechanical and chemical stability properties such as polysiloxane functionalized or immobilized with ligands (El-Ashgar, 2009) have been employed as a recyclable extractant for heavy metals and in stationary phases in chromatographic techniques using simulated water but have not been tried on tannery wastewater. These immobilized ligand system could be synthesized directly by sol gel or by chemical modification of the prepared functionalized polysiloxane (El- Ashgar, 2009; 2012). A variety of spectroscopic techniques such as Fourier Transform Infra-red (FTIR) (Issa *et al.*, 2002; Nizam and Salman, 2006), Nuclear Magnetic Resonance (NMR), Scanning Electron Microscopy (SEM) (Abdussalam *et al.*, 2012; Piotr *et al.*, 2016) [1, 22] and Energy Dispersive X-ray Analysis (EDX) (Abdussalam et al., 2012; Piotr *et al*., 2016) [1, 22], have been employed to study the ligand modified polysiloxane systems. This study described the synthesis and characterization of polysiloxane-Immobilized thiosalicylic acid ligand system and its potential in the detoxification of tannery wastewater.

2. Materials and Methods

2.1 Location of the study Area

Kano state covers an area extending between latitudes 120^0 40^1 and 100^0 30^1 and longitudes 70^0 40^1 and 90^0 30^1. Climate is tropical wet and dry with mean annual rainfall of 850 mm, and a population of 9.3 million, it is a flat city drained by the Jakara river and several streams (Niger river watershed) and River Challawa (Lake Chad watershed) all are severely polluted by urban and industrial effluents. Kumbotso local government was the area of study and it lies between latitudes

11°50'S to 12°N and longitude 8°24'W to 8°40'E. It falls within the Kano State settlement zone bordering the south and west by Madobi Local Government Area, in the Northern west; Rimin-Gado, in the North by Gwale and East by Tarauni local government areas respectively (Akan *et al.*, 2009; Danazumi and Bichi, 2010) [2, 6].

2.2 Experimental

2.3 Reagents and Materials

Tetraethyl orthosilicate, 3-chloropropyltrimethoxysilane, thiosalicylic acid and methanol, where purchased from Sigma-Aldrich Chemical Company and used without further purification. Triethylamine, Ethyl chloroacetate, sodium hydroxide (LOBA Chemie). Diethyl ether (spectroscopic grade). Different pH values in the range of 2.0 – 9.0 were control using 0.1 Mol/dm^3 HCl and NaOH (Carson 2000pH Model) respectively.

2.4 Synthesis of 3-chloropropylpolysiloxanes (3-CPP)

This was prepared following the methods of Salman and Nizam (2006) and El- Nahhal *et al.,* (2002) with modifications. Tetraethyl Orthosilicate (TEOS 0.1 mol; density 0.933 g/cm^3; volume 22.29 cm^3) was dissolved in 45 cm^3 of methanol, a solution of sodium hydroxide 0.49 mol/dm^3, 14.85 cm^3 (El- Ashgar, 2009), was added and stirred for 5 min followed by the addition of 3-chloropropyltrimethoxysilane (0.05 mol; density 1.09 g/cm^3; volume 9.11 cm^3) at 40 °C and pH 10. Gelation occurred after 40 min. The product was left to stand for 12 h, dried in an oven at 110 °C for 6 h. The product was washed with successive portions of 50 cm^3 de-ionized water (to pH 6.41), methanol (to pH 6.53) and diethyl ether (to pH 6.76) respectively, and further dried for 12 h in an oven at 110 °C. The solid product formed was crushed, sieved (125-150 µm), (Issa *et al.*, 2002; El- Ashgar, 2009) and dried over $CaCl_2$.

2.5 Synthesis of immobilized thiosalicylic and Thiolactic Bi-ligand System (PITTABLS)

Immobilization of thiosalicylic-thiolactic acid ligand was carried out with respect to Salman and Nizam (2006) method with modifications. The functionalized product, was measured (3.200 g) and added to (0.05 mol, density 1.49 g/cm^3; 7.959 g and 0.05 mol; density 1.196 g/cm^3; volume 4.44 cm^3) thiosalicylic and thiolactic acids respectively in ethyl chloroacetate (0.122 mol; density 1.145 g/cm^3; volume 26.20 cm^3) and 5 cm^3 of triethylamine in a round-bottomed flask (250 cm^3) and refluxed for 12 h at 110 °C, the product formed was filtered, washed successively with 50 cm^3 portions of de-ionized water, methanol and diethyl ether, dried at 110 °C in an oven for 10 h, crushed and sieved with 125-150 µm mesh (Issa *et al.*, 2002; El- Ashgar, 2009) and dried over $CaCl_2$.

2.6 Effect of Immobilized Thiosalicylic-Thiolactic Bi-ligand System (PITTABLS) as Adsorbent

A volume of 60 cm^3 solution of the tannery wastewater adjusted at pH 6 (optimum) was transferred into 150 cm^3 conical flask and 10 mg of the polysiloxane immobilized thiosalicylic-thiolactic bi-ligand was added and adjusted in a thermostatic multi- shaker (Gallenkamp Model) at 100 oscillation for 2 hr at 30 °C. The resultant solutions were filtered using Whatman No.41 and the residual metal concentrations analysed (Cu^{2+} and Zn^{2+}) using Agilent MPAES-4200 (Bernard and Jimoh 2013; Senthil and Kirthika, 2009; Horsfall *et al.*, 2006) [3, 24, 11] This procedure was repeated for 20 and 30 mg of polysiloxane immobilized thiosalicylic-thiolactic ligand with mesh size of (125-150 µm) respectively.

2.7 Thermodynamic studies of Immobilized Thiosalicylic-Thiolactic Bi-ligand System (PITTABLS)

A volume of 60 cm^3 solution of the tannery wastewater adjusted at pH 6 (optimum) was transferred into 150 cm^3 conical flask and 20 mg of the polysiloxane immobilized thiosalicylic-thiolactic ligand was added and adjusted in a thermostatic multi-shaker (Gallenkamp Model) at 100 oscillation for 2 h at 30 °C. The resultant solutions were filtered using Whatman No.41 and the residual metal concentrations analysed (Cu^{2+} and Zn^{2+}) using Agilent MPAES-4200. (Bernard and Jimoh 2013; Horsfall *et al.*, 2006; Vasanth and Kumar 2006) [3, 11]. This procedure was repeated for temperatures of 35 and 40 °C respectively.

2.8 Digestion of Tannery Wastewater

Tannery wastewater sample of 1000 cm^3 was transferred into a conical flask and evaporated till dried. The dried sample was digested in 10:1 HNO_3:$HClO_4$ (v/v). White crystals were found in the digested samples and were dissolved in 150 ml double distilled water. The supernatant were filtered using Whatman No.41 filter paper and was read directly with Agilent MPAES-4200 (Shahida *et al.*, 2017) [25].

3. Results

Table 1: Effect of Immobilized Thiosalicylic-Thiolactic Bi-ligand Dose on the Adsorption of Heavy Metals

Metal	Blanks		Conc.	Adsorbent (mg)		
				10	20	30
Cu (ppm)	A	0.107				
	B	0.055	Cia	0.404	0.404	0.404
			Cib	0.242	0.242	0.242
			Cfa	0.018	-0.052	-0.100
			Cfb	0.018	0.000	0.000
			%ADS	92.5	100.0	100.0
Zn (ppm)	A	-0.043				
	B	-0.087	Cia	0.039	0.039	0.039
			Cib	0.039	0.039	0.039
			Cfa	-0.022	-0.032	-0.055
			Cfb	0.000	0.000	0.000
			%ADS	100.0	100.0	100.0

A = de-ionized water; B = sample blank; rC_{oi} = relative initial concentration; rC_{ef} = relative final concentration; %ADS = percentage adsorption

Table 2: Adsorption Thermodynamics for Thiosalicylic-Thiolactic Immobilized Bi-ligand System

Metal Ion	T (K)	q_e (mgg^{-1})	K_D (Lg^{-1})	lnK_D	ΔG° ($KJmol^{-1}$)	ΔH° ($KJmol^{-1}$)	ΔS° ($Jmol^{-1}K^{-1}$)	Rel.C_i (ppm)	Rel.C_f (ppm)	Cd	% ADS
Cu^{2+}	303.000	14.100	58.265	4.065	-10.240	40.258	178.518	0.404	0.033	0.209	86
	308.000	18.000	74.380	4.309	-11.035			0.404	0.020	0.222	92
	313.000	24.000	99.174	4.597	-11.962			0.404	0.000	0.242	100
Zn^{2+}	303.000	11.700	300.000	5.704	-14.369	0.000	47.421	0.039	0.000	0.039	100
	308.000	11.700	300.000	5.704	-14.606			0.039	0.000	0.039	100
	313.000	11.700	300.000	5.704	-14.843			0.039	0.000	0.039	100

4. Discussion

The leather industry contributes immensely in the generation of wastewater without proper treatment thereby contaminating or polluting the eco-system. Hence the use of Polysiloxane immobilized thiosalicylic-thiolactic ligand system was employed to adsorb some heavy metals present in the wastewater. This was made possible due to the availability of reactive sites in the polysiloxane matrix in Figure I and the mechanism of the reaction in Figure II, the protonation of COOH to COO^- by triethylamine, SH to S^-, and the presence of oxy ions contributes to the adsorption process of these heavy metals.

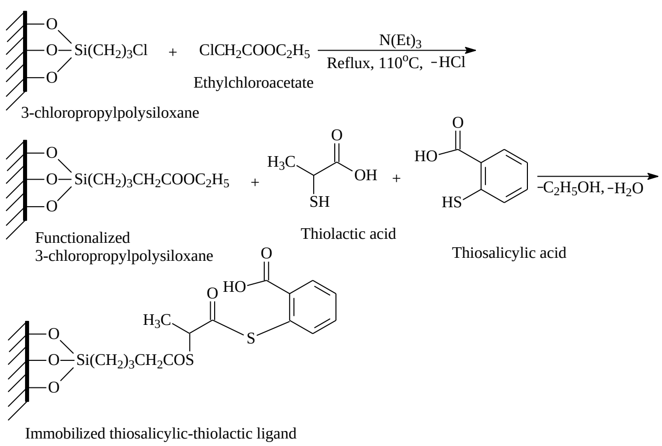

Fig 1: preparation of thiosalicylic-thiolactic Bi-ligand system

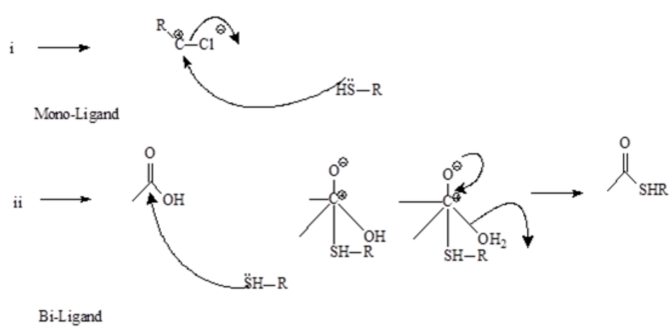

Fig 2: Reaction mechanism for thiosalicylic-thiolactic bi-ligand system

4.1 Effect of Immobilized Thiosalicylic-Thiolactic Bi-ligand Dose on the Adsorption of Heavy Metals

The adsorption effects of various weights of the adsorbent from 10 to 30 mg/60 cm^3 with mesh size of (125-150 µm) were used for the extraction of metal ion in Table 1.0. All the masses showed significant extraction of the metal ions, Cu^{2+} percentage adsorption increases with the increase in the amount of adsorbent while Zn^{2+} showed no significant increase with the increased in the amount of adsorbent in the treatment of tannery wastewater.

4.2 Thermodynamic Study of Polysiloxane Immobilized Thiosalicylic-Thiolactic Bi-Ligand System

The distribution coefficients, K_D for the extraction of Cu^{2+} and Zn^{2+} metal ions from solutions of tannery wastewater by Polysiloxane immobilized thiosalicylic-thiolactic bi-ligand system was studied at different temperatures of 30, 35 and 40 °C (Table 2.0). The results for Cu^{2+} showed that the distribution coefficients K_D increased with increase in temperature because the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles increases with increase in temperature with a resultant decrease in liquid viscosity while Zn^{2+} showed no significant change with increase in temperature. In order to determine the thermodynamic feasibility and the thermal effects of sorption, the thermodynamic parameters were evaluated using $\Delta G^o = -RT\ InK_D$ and $\Delta G^o = \Delta H^o - T\Delta S^o$, where ΔG°, ΔH°, ΔS° and T are Gibbs free energy, enthalpy, entropy and absolute temperature respectively (El-Ashgar, 2009; Parimalam *et al.*, 2011) [8, 21]. R is the gas constant (8.314 $Jmol^{-1}K^{-1}$) and K_D is the equilibrium constant. Plots of In K_D against 1/T gave the numerical values of ΔH° and ΔS° from slope and intercept respectively. The values of ΔG°, ΔH° and ΔS° are given for Cu^{2+} and Zn^{2+} in Table 2.0. The negative values of the Gibbs free energy ΔG° for all temperatures with reasonable affinity for Polysiloxane immobilized Thiosalicylic-thiolactic bi-ligands system towards Cu^{2+} and Zn^{2+}, suggests spontaneity of the adsorption process which does not required an external energy source for the system. ΔG° (Cu^{2+} -10.240 to -11.962 and Zn^{2+} - 14.369 to -14.843 $KJmol^{-1}$). Consequently, ΔG° of -15 KJ/mol are connected with physical interaction between adsorption site and metal ions which was observed in this work to be less, whereas -30 KJ/mol involves charge transfer from adsorbent surface to the metal ion to form a coordination bond this is a total deviation from the results obtained in this work. The positive values: ΔH° (Cu^{2+} 40.258 and Zn^{2+} 0.000 $KJmol^{-1}$), suggest variation of enthalpies accompanying sorption of metal ions on the Polysiloxane immobilized thiosalicylic-thiolactic bi-ligand system (indicating an endothermic process) which is facilitated by higher temperatures. The positive entropy changes: ΔS° (Cu^{2+} 178.518 and Zn^{2+} 47.421 $Jmol^1K^1$) is characterised by irregular increase in the randomness at the composite material -solution interface during adsorption procedure of the system (Zhiguang *et al.*, 2011) [28]. The results above is characterised by chemisorption process, favoured at higher temperatures. The thermodynamic parameters considered are in agreement with the work of Nizam and Zeyad (2009) [20].

5. Conclusion

The polysiloxane-immobilized thiosalicylic-thiolactic bi-ligand system has been prepared by hydrolytic Polycondensation of tetraethyl Orthosilicate with a mixture of 3- chloropropyl trimethoxysilane, methanol and sodium hydroxide as a catalyst.The immobilized ligand showed high potential for the extraction of Cu^{2+} and Zn^{2+} at an optimum pH of 6.0 in the tannery wastewater. Cu^{2+} percentage adsorption increases with the increase in the amount of adsorbent and temperature while Zn^{2+} was relatively constant and showed no significant increase with the increased in the amount of adsorbent and temperature in the treatment of tannery wastewater in a batch system. The thermodynamic parameters suggests a spontaneous and an endothermic affinity of the chelating ligand for Cu^{2+} and Zn^{2+} respectively.

6. References

1. Abdussalam Salhin Mohammad Ali, Norfarhah Abdul Razak, Ismail Ab Rahman. Study on the Preparation of a Sol-Gel Sorbent Based Thiosemicarbazone for Selective Removal of Heavy Metal Ions. World applied sciences journal. 2012; 16(8):1040-1047.
2. Akan JC, Abdulrahaman FI, Ogugbuaja VO, Reuben KD. Study of the Physico-Chemical Pollutants in Kano Industrial Areas, Kano State, Nigeria. Journal of Applied Sciences. 2009; 4(2):89-102.
3. Bernard E, Jimoh A. Adsorption of Pb, Fe, Cu, Zn from Industrial Electroplating Wastewater by Orange Peel Activated Carbon. International Journal of Engineering and Applied Sciences. 2013; 4(2):95-103.
4. Brad Busche, Robert Wiacek, Joseph Davidson, View Koonsiripaiboon, Wassana Yantasee, Shane Addleman R, *et al.* Synthesis of Nanoporous Iminodiacetic Acid Sorbents for Binding Transition Metals. Inorganic Chemistry Communications. 2009; 12:312-315.
5. Bulus Habila, Ezeh Emmanuel Chidiebere, Danladi Hassana, Igbehinadun Olajide Joseph, Shekarri Tachye Bwankhot. Determination of Heavy Metals in Tannery Wastes. International Journal of Agricultural and Biosystems Engineering. 2018 3(3):78-81.
6. Danazumi S, Bichi MH. Industrial Pollution and Implication on Source of Challawa River in Kano, Nigeria Int. Journal of Engineering and Technology IJET-IJENS. 2010; 10:01.
7. Durai G and Rajasimman M. Biological Treatment of Tannery Wastewater - A Review. Journal of Environmental Science and Technology. 2001; 4(1):1-7.
8. El-Ashgar NM. Extraction and Pre-concentration Capacity of Bi-functionalized Diamine-Thiol Polysiloxane immobilized Ligand System towards Some Divalent Cations. Journal of Iran Chemical Society. 2009; 6(4):823-830.
9. Evangelo Min H, Ebel M, Chaeffer A. Chelate Assistant Phyto Extraction of Heavy Metals from Soil. Effect, Mechanism, Toxicity and Fate of Chelating Agents. Chemosphere. 2007; 68:989-1004.
10. Flavio A Pavan, Tamia MH Costa, Edilson V Benvenutti. Adsorption of $CoCl_2$, $ZnCl_2$ and $CdCl_2$ on Aniline/Silica Hybrid Material Obtained by Sol-Gel Method. Colloids and Surfaces A: Physicochemical Engineering Aspects. 2003; 226:95-100.
11. Horsfall MJ, Abia AA, Spiff AI. Kinetic Studies on the Adsorption of Cd^{2+}, Cu^{2+} and Zn^{2+} Ions from Aqueous Solutions by Cassava (*Manihot esculenta*) Tuber Bark Waste. Journal Bio resource Technology. 2006; 97(35):283-291.
12. Islam BI, Musa AE, Ibrahim EH, Salma AA, Sharafa, Babiker M Elfaki. Evaluation and Characterization of Tannery Wastewater. Journal of Forest Products and Industries. 2014; 3(3):141-150.
13. Issa M El-Nahhal, Basher A El-Shetary, Kamal AR Salib, Nizam M El- Ashgar, Ahmed M El- Hashash. Uptake of Divalent Metal Ions (Cu^{2+}, Ni $^{2+}$ and Co^{2+}) by Polysiloxane Immobilized Triamine- Thiol and Thiol-Acetate Ligand System. Analytical Letters. 2010; 34(12):2189-2202.
14. Issa M El-Nahhal, Jane Jie Yang, Issuer Chuang, Gary E Maciel. Synthesis of Solid State NMR Structural Characterization of Polysiloxane Immobilized Thiol and Thiol-Amine Ligands. Journal of Non-Crystalline Solids. 1996; 208:105-118.
15. Issa M El-Nahhal, Nizam M El- Ashgar, Asmaa Abu-Shawish, Mona Abed El-Aziz Ahmed, Florence Babonneau. Template Synthesis of Immobilized-Polysiloxane Diamine- Thiol Tetraacetic Acid Biligand System and its Application for Determination of Metal Ions. Phosphorus, Sulphur, Silicon and the Related Elements, 2015. DOI: 10.1080/104236507.2015.101.2667.
16. Jahan MAA, Akhtar N, Khan NMS, Roy CK, Islam R, Nurunnabi. Characterization of Tannery Wastewater and Its Treatment by Aquatic Macrophytes and Algae. Bangladesh Journal of Science Industry and Research. 2014; 49(4):233-242.
17. Malarkodi M, Krishnasany R, Kumaraperumal R, Chitedeshwari T. Characterization of Heavy Metal Contaminated Soils of Coimbatore District in Tanul Nedu. Journal of Agronomy. 2007; 1:147-151.
18. Mona A Ahmed, Asmah A Abu Shaweesh, Nizam M El-Ashgar, Issa M El-Nahhal, Mohammed M, Chehimi, Florence Babonneau. Synthesis and Characterization of Immobilized- Polysiloxane Monoamine-Thiol Triacetic Acid and its Diamine and Triamine Derivatives. Journal of Sol Gel Science Technology. 2016; 78:660-672.
19. Muthukkauppan M, Parthiban P. A Study on The Physicochemical Characteristics of Tannery Effluent Collected from Chennai. International Research Journal of Engineering and Technology (IRJET). 2018; 05(03):24-28.
20. Nizam M El-Ashgar, Zeyad J Yasseen. Complexation and Thermodynamic Studies of Polysiloxane Iminobis (N-Diethylenediamineacetamide) Ligand System with Some Transition Metal Ions. Physical Chemistry an Indian Journal. 2009; 4(2):71-76.
21. Parimalam Ramachandran, Raj Vairamuthu, Sivakumar Ponnusamy. Adsorption Isotherms, Kinetics,

Thermodynamics and Desorption Studies of Reactive Orange16 on Activated Carbon Derived From A*nanas Comosus* (L.) Carbon. ARPN Journal of Engineering and Applied Sciences. 2011; 6(11):15-26.
22. Piotr Grzesiak, Joanna Lukaszyk, Elzbieta Gabala, Joanna Kurczewska, Grzegorz Schroeder. The Influence of Silica Functionalized With Silanes on Migration of Heavy Metals In Soil. Polish Journal of Chemical Technology. 2016; 18(1):51-57.
23. Sekhararao Gulipalli CH, Prasad Kailas B, Wasewar L. Batch Study, Equilibirum and Kinetics of Adsorption of Selenium Using Rice Husk Ash (RHA). Journal of Engineering Science and Technology. 2011; 6(5):586-605.
24. Senthil Kumar P, Kirthika K. Equilibrium and Kinetic Study of Adsorption of Nickel from Aqueous Solution onto Bael Tree Leaf Powder. Journal of Engineering Science and Technology. 2009; 4(4):351-363.
25. Shahida Parveen, Ram Bharose, Dharam Singh. Assessment of Physico-Chemical Properties of Tannery Waste Water and Its Impact on Fresh Water Quality International Journal of Current Microbiology and Applied Sciences. 2017; 6(4):1879-1887.
26. Vijayakumar G, Tamilarasan R, Dharmendirakumar M. Adsorption, Kinetic, Equilibrium and Thermodynamic Studies on the Removal of Basic Dye Rhodamine-B from Aqueous Solution by the Use of Natural Adsorbent Perlite. Journal of Materials and Environment Sciences. 2012; 3(1):157-170.
27. Vlasova NN, Oborina EN, Grigoryeva Yu O, Voronkov MG. Organosilicon Ion-Exchange and Complexing Adsorbents. Russian Chemical Review. 2013; 82(5):449-464.
28. Zhiguang Ma, Na Di, Fang Zhang, Peipei Gu, Suwen Liu, Pan Liu. Kinetic and Thermodynamic Studies on the Adsorption of Zn^{2+} onto Chitosan-aluminium Oxide Composite Material. International Journal of Chemistry. 2011; 3(1):18-23.