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Thermodynamic Characterization of Sorption of Copper(II) ions on Rice Husk

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Abstract

This paper attempts to develop simple and easily understandable thermodynamic parameters related sorption process at the equilibrium. Batch kinetic studies were conducted for the adsorption of Cu(II) on SCRH (sodium carbonate treated rice husk). The removal were observed to increases from 92.9 to 96 % with the increase in temperature from 15° to 50° C. Equilibrium time was found to be 60 min. The overall scenario represented by thermodynamic parameters was found to be a better indicator of understanding the process mechanism. Sorption of Cu(II) on SCRH followed pseudo second-order kinetic equation. The Gibbs free energy ΔG° values for the adsorption processes of Cu(II) at 15°, 30°, 40° and 50° C was obtained as - 6.16, - 6.84, - 8.01 and - 8.53 kJ/mol respectively. The negative value, ΔG° confirms the feasibility of the adsorption process and spontaneous nature of adsorption. The values of ΔH° and ΔS° for Cu(II) were obtained as 14.37 kJ/mol and 70.92 J/mol respectively. The positive value of ΔH° indicates endothermic nature of adsorption, while positive ΔS° value confirms the increased randomness at the solid-liquid interface during adsorption. The activation energy for the sorption of Cu(II) was found as 9.00 kJ/mol indicating chemisorptions.

Keywords: Sorption, Copper, Rice husk, Thermodynamics, Activation energy.

Introduction

Rapid industrialization through the world has generated huge volumes of wastes containing toxic materials such as metal ions. The presence of heavy metals in wastewater and surface water is the major concern of public health and the environment [1]. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain. Copper is an essential nutrient, required by the body in very small amounts. Short periods of exposure can cause gastrointestinal disturbance, including nausea and vomiting. Use of water that exceeds the permissible level over many years could cause liver or kidney damage. Copper is rarely found in source water, but copper mining and smelting operations and municipal incineration may be sources of contamination [2]. High dose of copper can lead to lethargy, weakness, anorexia and damage to gastrointestinal tract [3]. The excessive intake of copper results in its accumulation in the liver and produces gastrointestinal problems [4, 5]. As one of the important toxic heavy metals, copper finds its way to the water stream from industries like electroplating, mining, electrical and electronics, iron and steel production, the non-ferrous

metal industry, the printing and photographic industries and metalworking and finishing processes [6,7,8] The reduction of the pollutant to an acceptable level is necessary when toxic metals are present in the aquatic system [9]. Prescribed limit for copper in drinking water is 0.05 mg/l as per the WHO norms and also 0.05 mg/l per ISI prescribe limits, 1983 [10]. However, the intake of excessively large doses of Cu(II) by human may lead to severe mucosal irritation, a central nervous system irritation, possible necrotic changes in the liver and kidney, etc., and the recommended maximum acceptable concentration of Cu(II) in drinking water by the World Health Organization(WHO) is 1.5 mg L⁻¹ [11,12]. As per U.S. Environmental Protection Agency (EPA) standards, the permissible limit of copper for industrial effluents to be discharged to surface water is 0.25 mg/l [13]. Increasingly stringent legislation on the purity of drinking water has created a growing interest in the development of conventional treatment processes. The traditional methods, for the treatment of copper and other toxic heavy metal contaminated wastewaters, include complexation, chemical oxidation or reduction, solvent extraction, chemical precipitation, reverse osmosis, ion exchange,

filtration, membrane processes, evaporation and coagulation. Never the less these techniques have significant disadvantages including incomplete metal removal, high consumptions of reagent and energy, low selectivity, high capital and operational cost and generation of secondary wastes that are difficult to be disposed off [14, 15]. Among these technologies, adsorption is a user-friendly technique for the removal of heavy metal. Adsorption process of heavy metals present in aqueous solution by low-cost adsorbents from plant wastes can be carried out with or without chemical modifications. In general, chemically modified plant wastes exhibit higher adsorption capacities than unmodified forms [16]. Agricultural products and by-products have been reported to be effective in removing copper. Rice husk, an abundant agricultural product, is capable of removing heavy metals and can be considered as an efficient and low-cost adsorbent for heavy metals. In recent years, attention has been taken on the utilization of unmodified or modified rice husk as a sorbent for the removal of pollutants [2,17]. Metal ion sorption can occur on rice husk through its major functional groups including proteins, polysaccharides and cellulose.

The aim of this research work was to investigate the use of SCRH for the removal of Cu(II) at different temperature ranging from 15 to 50 °C. This paper attempts to develop simple and easily understandable thermodynamic parameters related sorption process at the equilibrium, such as entropy change, enthalpy change, Gibbs free energy and activation energy of sorption. The overall scenario represented by thermodynamic parameters was found to be a better indicator of understanding the process mechanism.

Materials and methods

Preparation of Adsorbents

Fresh rice husk was obtained from a local rice mill of Silchar, Assam (India) and was passed through different sieve size. The fraction of particle between 425 and 600 μm (geometric mean size: 505 μm) was selected. Rice husk was washed thoroughly with distilled water and was dried at 60° C. This was treated with 0.1 N sodium carbonate solution at room temperature for 6 h. Excess of sodium carbonate was removed with water and the material was dried at 60° C. Sodium carbonate treated rice husk was designated as SCRH [17, 30].

Batch Kinetic Studies

All the chemicals used in the study were off analytical grade from Merck (India) Ltd. and

Qualigens Glaxo (India) Ltd. Stock solutions of 1000 mg/l were prepared for Cu(II) using copper nitrate. In order to avoid hydrolysis as well as high adsorption of species in the flask wall the stock solution was prepared with HNO₃ 2% (v/v), which were diluted with distilled water to prepare working solutions. pH of the working solutions were adjusted to 6 ± 0.2 for all studies using dilute NaOH solution. The experiments were carried out with 10 g/l of sorbent dose for initial metal concentration of 10 mg/l. The mixture was agitated using a thermal shaker at 140 rpm in the temperature range of 15° – 50° C. At the end of the experiment the sample was allowed to settle for about 1 min and the supernatant sample was analyzed for its Cu(II) concentration using atomic absorption spectrophotometer (AA-6650, Shimadzu, Japan). The kinetics for the sorption data were studied under optimized condition of pH and contact time. All the experiments were done in triplicate and means of all the three are reported. The amount of metal adsorbed per unit mass of the adsorbent was calculated as q (mg/g) = $(C_0 - C_e)V/m$ and percent removal may be calculated as $100(C_0 - C_e/C_0)$; where, q = amount of metal-ion adsorbed, at equilibrium (mg/g), C_0 =initial metal-ion concentration (mg/l), C_e =equilibrium metal-ion concentration (mg/l), V =volume of solution (l), m =adsorbent dose (g).

Results and discussion

Effect of Temperature

The kinetics of adsorption with SCRH at initial concentrations of 10 mg/l and at 15°, 30°, 40° and 50° C were studied as discussed in material methods and the results were obtained and plotted in the figures from Fig. 1. It was observed that removal of Cu(II) occurred in two stage i.e an initial rapid uptake within

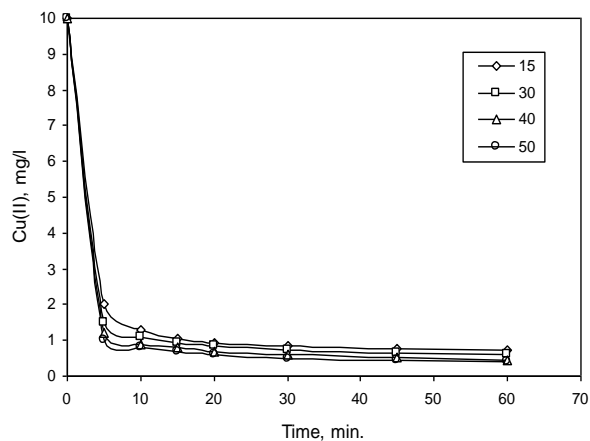


Figure-1: Kinetic profile of Cu(II) uptake at 15, 30, 40 and 50 °C.

15- 20 minute followed by subsequent slow uptake from 20 to 60 minute. At an equilibrium time of 60 minute the percentage removal increases from 92.9 to 96 % with the increase in temperature from 15° to 50° C (Fig. 2). The sorption capacity increases with increase in temperature indicating that the sorption process was endothermic and the sorption of metal ions by SCRH may involve not only physical but also chemical sorption [18, 19, 30]. The increase in sorption capacity of SCRH at high temperature may be attributed to enlargement of pore size or increase in the active surface for sorption. This could also be due to the enhanced mobility of the metal ions from the bulk solution towards the adsorbent surface and extent of penetration within SCRH structure overcoming the rate of intraparticle diffusion [19, 30]. As the temperature increase there is a greater mass transfer by collision at higher temperature. While the frequency of collision increases, probability of successive collision leading to adsorption gets higher. As a result more ions are adsorbed to give higher removal. Chemisorptions occurs when, extend of adsorption is enhance at elevated temperature. It is short and strong interaction involving orbital over lapping and electrons exchange. An increase of temperature causes an activation of active site of adsorption and higher temperature reduces mass transform resistance for ion diffusion for binding sites [27, 28]. Most potential sorption sites are situated on cellulose and hemicelluloses and pectin's on the cell wall that are active functional groups such as a hydroxyl carboxylic, carbonyl and amino group [29].

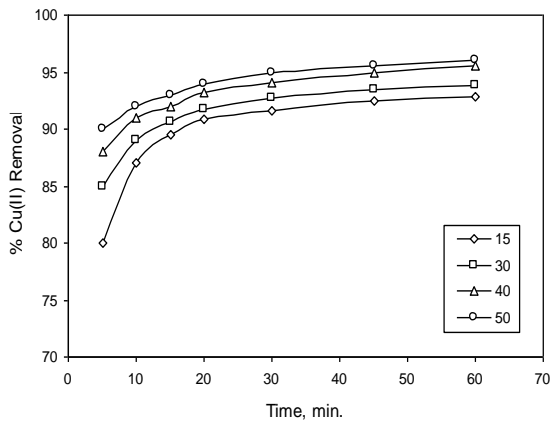


Figure-2: The rate of removal efficiency of Cu(II) at 15, 30, 40, and 50 °C.

Sorption Kinetic

Pseudo second-order kinetic model has been widely used for the sorption kinetics [20-22]. It was

observed that most of the sorption systems followed a pseudo second-order kinetic model as also reported by Ho and McKay (1999), [20] which can be expressed as

$$\frac{t}{q} = \frac{1}{h_0} + \frac{t}{q_e} \tag{1}$$

The initial sorption rate can be obtained as t approaches zero ($t \rightarrow 0$):

$$h_0 = K_{p2} q_e^2$$

where h_0 is the initial sorption rate (mg/g min), t is the contact time (min), q and q_e are the quantities of sorbate (in mg/g), sorbed at time t and at equilibrium respectively and K_{p2} is the rate constant (g/mg min). The rate constant K_{p2} was found out from the slope of the linear test plot between t/q versus time t as shown in Fig. 3 and Table 1.

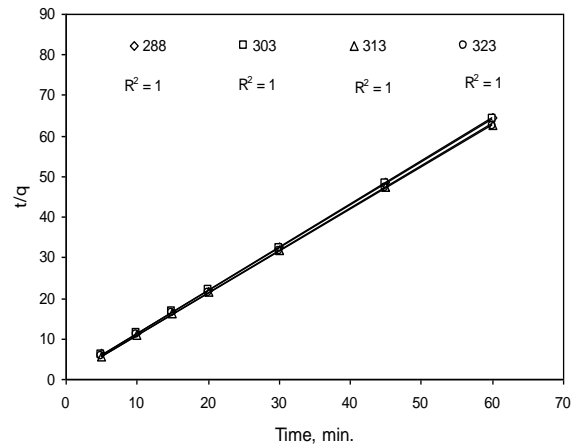


Figure-3: Pseudo second order model plot for Cu(II) at different temperature in K.

The correlation coefficients of pseudo second-order kinetic model were observed to be highest and almost equal to 1. This shows that the sorption process follow the pseudo second-order kinetics and which agrees with chemisorptions as the rate-limiting mechanism, through sharing or exchange of electron between sorbent and sorbate [20].

Table1. Pseudo second – order rate constant

Temp (° C)	K_{p2} (g/mg min)	q_e (mg/g)	h_0 (mg/g min)	R^2
15	1.299	0.942	1.1521	1
30	1.639	0.948	1.4715	1
40	1.645	0.964	1.5288	1
50	2.024	0.967	1.8925	1

Thermodynamic Parameters of Adsorption

The adsorption process of metal ions can be summarized by the following reversible process, which represents heterogeneous equilibrium.

Metal ions in solution \leftrightarrow Metal ions adsorbent. The apparent equilibrium constant (K_c) of the adsorption is defined as:

$$K_c = \frac{C_A}{C_e} \quad (2)$$

$$\Delta G^\circ = -RT \ln K_c \quad (3)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

where C_A is the solid phase concentration at equilibrium (mg/l), C_e is the equilibrium concentration (mg/l), T (K) the absolute temperature, R the gas constant (8.314 J/mol K), ΔS° the entropy change (J/mol) and ΔH° the enthalpy change (kJ/mol). ΔH° and ΔS° values were obtained from the slope and intercepts of van't Hoff plot, $\ln K_c$ versus $1/T$ (Fig. 4). The K_c value thus obtained is also used to determine the Gibbs free energy ΔG° at different temperature. The Gibbs free energy indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption [23-26]. The ΔG° values for the adsorption processes of Cu(II) at 15°, 30°, 40° and 50° C was obtained as - 6.16, - 6.84, - 8.01 and - 8.53 kJ/mol respectively using equation (3). The negative value ΔG° confirms the feasibility of the adsorption process and spontaneous nature of adsorption. The values of ΔH° and ΔS° for Cu(II), was obtained as 14.32 kJ/mol and 70.92 J/mol respectively. The positive value of ΔH° indicates endothermic nature of adsorption while positive ΔS° value confirms the increased randomness at the solid-liquid interface during adsorption [23-26].

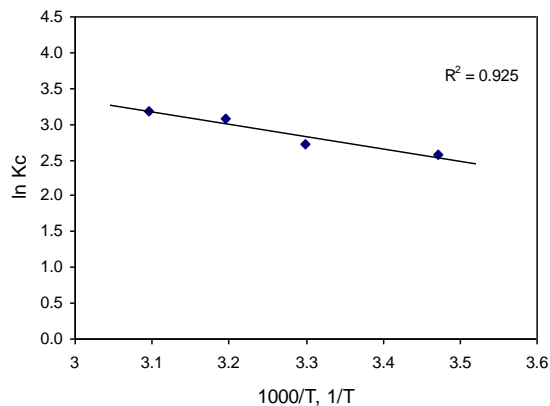


Figure-4: van't Hoff plots for Cu(II).

Enthalpy change is an energy interaction with the environment while the reaction takes place. An exothermic reaction emits heat and therefore final energy state is lower than initial energy state to give a negative enthalpy change and vice versa. Entropy is an indication for the system degree of freedom and on the reversibility of the system. For a system communicating to an external heat sink or source, entropy must be increase or remain the same. As the entropy increase, uniformity of system is improved. Hence the process occurs spontaneously. Entropy change is a measurable for reversible and irreversible heat flow through a boundary. As final entropy is greater to give positive entropy change, there is an irreversible heat flow through a system. A positive enthalpy change obtained implies that the sorption on Cu(II) ions on SCRH is endothermic. An input of energy is required to bring about the bond formation. This is because the bonding is short and as a result, energy is needed to overcome the repulsive force of attraction as ions bind in a short distance from sorbent. As external source of heat energy is needed for the endothermic reaction to occur. High temperature favors an endothermic reaction and it is deduced that chemisorptions occurs due to the formation of stronger bonds which remain bonded at high temperature [31].

Activation Energy

The increase in the pseudo-second order rate constant with temperature may be described by the Arrhenius equation which is used to calculate the activation energy for the metal ion sorption [18-20], [30] as given below:

$$\ln k_{p2} = \ln A_0 - \frac{E_a}{RT} \quad (5)$$

k_{p2} is the rate constant of sorption (g/mg min), A_0 is the temperature-independent factor (g/mg min), E_a the activation energy of sorption (kJ/mol), R the gas constant (8.314 J/mol K) and T the solution temperature (K). The kinetic profile of Cu(II) uptake at 15, 30, 40, and 50° C as shown earlier in the Fig. 1 was utilized to find the rate constant k_{p2} from the pseudo second order plot (Figs. 3) When $\ln k_{p2}$ is plotted versus $1/T$, a straight line with slope $-E_a/R$ is obtained. The magnitude of the activation energy may give an idea about the type of sorption. Two main types of adsorptions may occur: physical and chemical. In physical adsorption equilibrium is usually rapidly attained and easily reversible, because the energy requirement is small (usually no more than 4.2 kJ/mol) and since the forces involved are

week. Chemical adsorption is specific and involves forces much stronger than physical adsorption. So the activation energy for chemical adsorption is of the same magnitude as the heat of chemical reactions which means that the rate varies with temperature according to finite activation energy (between 8.4 and 83.7 kJ/mol) in the Arrhenius equation [18, 30]. The activation energy for the sorption of Cu(II), was found as 9.00 kJ/mol respectively from the slope of Fig. 5 indicating chemisorptions.

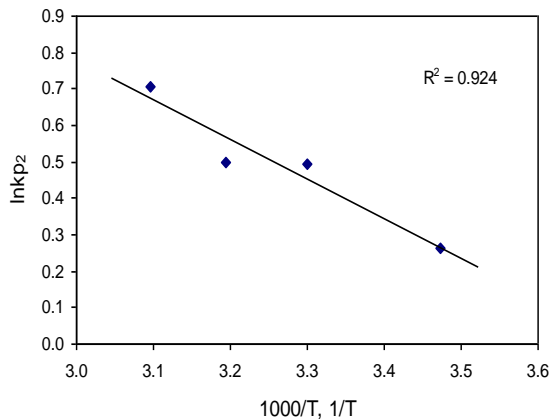


Figure-5: Plot of $\ln k_{p2}$ vs. $1/T$ plots for Cu(II)

Conclusion

Batch kinetics adsorption studies showed a rapid removal of Cu(II) by SCRH and it increases with increase in temperature (92.9 to 96 %). The sorption systems followed a pseudo second-order kinetic model with very high correlation coefficients. The sorption process was endothermic and it was further conformed by the positive value of ΔH° (14.37 kJ/mol) and further positive value of ΔS° (70.92 J/mol) confirms the increased randomness at the solid-liquid interface during adsorption. The Gibbs free energy ΔG° at 15°, 30°, 40° and 50° C was obtained as - 6.16, - 6.84, - 8.01, and - 8.53, KJ/mol respectively. The negative value, ΔG° confirms the feasibility of the adsorption process and spontaneous nature of adsorption. High temperature favors an endothermic reaction and it is deduced that chemisorptions occurs due to the formation of stronger bonds which remain bonded at high temperature. The activation energy for the sorption of Cu(II) was found as 9.00 kJ/mol confirming chemisorptions. SCRH is a favorable sorbent for the removal of Cu(II) from aqueous solutions and can be used copper removal.

References

- [1] S. Vafakhah, M.E. Bahrololoom, R. Bazarganlari, M. Saeedikhani, "Removal of copper ions from electroplating effluent solutions with native corn cob and corn stalk and chemically modified corn stalk", *J. Environ. Chem. Eng.*, vol. 2 (2014), pp. 356–361.
- [2] S. Mohan, G. Sreelakshmi, "Fixed bed column study for heavy metal removal using phosphate treated rice husk", *Journal of Hazardous Materials*, vol. 153 (2008), pp. 75–82.
- [3] R.K. Gautam, A. Mudhoo, G. Lofrano, M.C. Chattopadhyaya, "Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration", *J. Environ. Chem. Eng.*, vol. 2 (2014), pp. 239–259.
- [4] R. Gundogan, B. Acemioglu, M. H. Alma, "Copper (II) adsorption from aqueous solution by herbaceous peat", *J. Coll. Interface Sci*, vol. 269 (2004), pp. 303–309.
- [5] M.H. Kalavathy, T. Karthikeyan, S. Rajgopal and L.R. Miranda, "Kinetic and isotherm studies of Cu(II) adsorption onto H₃PO₄-activated rubber wood sawdust", *J. Coll. Interface Sci.*, vol. 292 (2005), pp. 354–362.
- [6] M. Mukhopadhyay, S.B. Noronha, G.K. Suraishkumar, "Kinetic modeling for the biosorption of copper by pretreated *Aspergillus niger* biomass", *Bioresour Technol.*, vol. 98 (2007), pp. 1781-1787.
- [7] B. M. Brauckmann, "Industrial solution amenable to biosorption". In: Volesky B, editor. *Biosorption*, Boca Raton, FL: CRC Press; 1990.
- [8] J. Zhang, H. Fu, X. Lv, J. Tang, X. Xu, "Removal of Cu(II) from aqueous solution using the rice husk carbons prepared by the physical activation process", *biomass and bioenergy*, vol. 35(2011), pp. 464 – 472 .
- [9] V.K. Gupta, C.K. Jain, I. Ali, M. Sharma, V.K. Saini, "Removal of cadmium and nickel from wastewater using bagasse fly ash-a sugar industry waste", *Water Res.*, vol. 37 (2003), pp. 4038 –4044.
- [10] A. K. Shrivastava, "A review on copper pollution and its removal from water bodies by pollution control technologies", *Indian J. Environmental Protection*, vol. 29 (2009), pp. 552-560.

- [11] S. Larous, A. H. Meniai, M. B. Lehocine, "Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust", *Desalination*, vol. 185 (2005), pp. 483 - 490.
- [12] M.M. Rao, A. Ramesh, G.P.C. Rao, K "Seshaiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls", *J Hazard Mater.*, vol. 129 (2006), pp. 123-129.
- [13] B. Zhu, T. X. Fan, D. Zhang, "Adsorption of copper ions from aqueous solution by citric acid modified soybean straw", *J Hazard Mater.*, vol. 153 (2008), pp. 300-80.
- [14] E. Eren, B. Afsin, Y. Onal, "Removal of lead ions by acid activated and manganese oxide-coated bentonite", *J. Hazard. Mater.* vol. 161 (2009), pp. 677-685.
- [15] Z. Aksu, F. Gönen, Z. Demircan, "Biosorption of chromium(VI) ions by Mowital® B30H resin immobilized activated sludge in a packed bed: comparison with granular activated carbon", *Process Biochem.* vol. 38 (2002), pp. 175-186.
- [16] W.S. WanNgah, M.A.K.M. Hanafiah, "Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review", *Bioresour. Technol.* vol. 99 (2008), pp. 3935-3948.
- [17] U. Kumar, M. Bandyopadhyay, "Sorption of cadmium from aqueous solution using pretreated rice husk", *Bioresource Technology*, vol. 97 (2006), pp. 104-107.
- [18] Z. Aksu, E. Kabasakal, "Batch adsorption of 2,4-dichlorophenoxy-acetic acid (2,4-D) from aqueous solution by granular activated carbon", *Sep. Purif. Technol.*, vol. 35 (2004), pp. 223-240.
- [19] A. Agrawal, K.K. Sahu, B.D. Pandey, "Removal of zinc from aqueous solution using sea nodules residue", *Colloids and Surfaces A: Physicochem. Eng. Aspects*, vol. 237 (2004), pp. 133-140.
- [20] Y.S. Ho, G. McKay, "Pseudo second-order model for sorption process", *Process. Biochem.*, vol. 34 (1999) 451- 465.
- [21] C.C.V. Cruz, A.C.A. da Costa, A.S.L. Henriques, "Kinetic modeling and equilibrium studies during cadmium biosorption by dead *Sargassum* sp. Biomass", *Bioresource Technol.*, vol. 91 (2004), pp. 249-257.
- [22] S. Rengaraj, Y. Kim, C. K. Joo, J Yi, "Removal of copper from aqueous solution by aminated and protonated mesoporous aluminas: kinetics and equilibrium", *J. Colloid and Interface Sci.*, vol. 273 (2004), pp. 14-21,
- [23] A.A. Asem, D.M. Ahmed, Y.M. Ahmed, "Removal of some hazardous heavy metals from aqueous solution using magnetic chelating resin with iminodiacetate functionality", *Separation and Purification Technology*, vol. 61 (2008), pp. 348-357,
- [24] A.M. Sevim, R. Hojiyev, A. Gül, M.S. Celik, "An investigation of the kinetics and thermodynamics of the adsorption of a cationic cobalt porphyrine onto sepiolite", *Dyes and Pigments*, vol. 88 (2010), pp. 25-38.
- [25] L. Wang, J. Zhang, R. Zhao, C. Li, Y. Li, C. Zhang, "Adsorption of basic dyes on activated carbon prepared from *Polygonum orientale* Linn: Equilibrium, kinetic and thermodynamic studies", *Desalination*, vol. 254 (2010), pp. 68-74.
- [26] S. Chegrouche, A. Mellah, M. Barkat, "Removal of strontium from aqueous solutions by adsorption onto activated carbon: kinetic and thermodynamic studies", *Desalination*, vol. 235 (2009), pp. 306-318.
- [27] S. Diwan, "Biosorption of Copper (II) from aqueous by non-living *Spirogyra*", *J. Environ. Res. Develop.* (2007), pp. 227-231.
- [28] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar, "Removal of heavy metal ions from aqueous solution using carbon aerogel as an adsorbent", *J Hazard. Mat.*, vol. 122, (2005), pp. 161-170.
- [29] P. M. Davaprasath, J. S. Soloman, B. V. Thomas, "Removal of Cr (VI) from aqueous solution using natural plant material", *J. App. Sc. Environ. Sanit.*, vol. 2 (2007), pp. 1-8.
- [30] U. Kumar, "Thermodynamics of the Adsorption of Cd(II) from Aqueous Solution on NCRH", *Int. J. Environmental Science and Development*, vol. 2 (2011), pp. 334-336
- [31] V.S. Sethu, Y.L. Kua, W.S. Quek, K.V. Lim, J.M. Andresen, "Adsorption thermodynamics of Cu(II) ions from water using neem leaf based biosorbents", *J. Environmental Research and Development*, vol. 6 (2011), pp. 26-33.

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