

Equilibrium, Thermodynamic and Kinetic Studies for Removal of Copper (II) from Aqueous Solution by Onion and Garlic Skin

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Summary

Removal of Cu²⁺ from aqueous solution by onion skin and garlic skin was studied as a function of various experimental parameters. FTIR analysis and Boehm titration were used to identify and estimate the surface functional groups. Point of zero charge for the onion and garlic skin was between 4.25 to 4.45 and 4.55 to 4.75 respectively. Compared to garlic skin (66.7 mg/g), the maximum adsorption capacity of onion skin (76.9 mg/g) was slightly higher (pH = 5.3, T = 303K). The pseudo second order kinetic model fitted the batch data adequately. The rate constant for onion and garlic scale in the absence of diffusional resistance was estimated to be 0.07 and 0.075 mg/g/min respectively at 303 K. The thermodynamic studies showed that the Cu²⁺ adsorption on the onion and garlic skin was spontaneous and endothermic.

Introduction

Heavy metals are known to cause toxicological problems to environmental and human health. Copper present in

industrial waste water leads to the pollution and contamination of the environment. Industries like metal cleaning, plating and metal processing, mining, refineries, paper and pulp, fertilizers, wood preservatives, etc. are the main sources of this metal emanation to the environment (Aksu & Kutsal 1999, Abu Al-Rub *et al.* 2006). Copper toxicity leads to serious health hazards like anemia, diarrhea, convulsions, gastro-intestinal malfunction (Kumar *et al.* 2006). Furthermore, it degrades the natural soil and water physiology that eventually affects the biota.

Researchers have focused upon a sustainable way of development using techniques that are environment friendly as well as cost-effective and practical. This has directed attention to the use of biological wastes. Several biosorbents such as rice husks (Jaman *et al.* 2009), wheat straws (Dang *et al.* 2009), tea factory waste (Wasewar *et al.* 2008), orange peel (Annadurai *et al.* 2002), fish scale (Espinosa *et al.* 2001), castor seed hull (Sen *et al.* 2010), wheat shell (Basci *et al.* 2009), coffee husk (Oliveira *et al.* 2008), maple sawdust (Rahaman & Islam 2009)

has been investigated for adsorbing the ion from aqueous solutions. Bhatnagar and Silanpää (2010) reviewed the use of various agro-based waste materials as low-cost adsorbents.

In this study, the effectiveness of onion skin and garlic skin for removal of Cu^{2+} from aqueous solutions was investigated. The skin is the dried up outer parchment of onion and garlic and originates as kitchen and agricultural waste. Literature survey indicates that there has been no previous study for removal of metal ions by garlic skin. Kumar and Dara (1981) studied the uptake of various metal ions by polymerized onion skin. Equilibrium and batch studies were undertaken to examine the thermodynamic and kinetic aspects of Cu^{2+} adsorption by these biosorbents. A method was described to determine the reaction rate constant in the absence of diffusional limitation.

Materials and Methods

Biosorbent Preparation

Onion and garlic skin was obtained from kitchen dumping. The skins were rinsed and washed with warm distilled water to remove dirt. The biosorbents were dried overnight in the hot air oven at around 45°C . The dried skins were stored in the laboratory desiccators to avoid moisture interruption.

The experimental studies were carried out in duplicate. Point of zero charge (PZC) was determined using the mass titration method described by Valdés et al (2002). Aqueous solutions were prepared of pH 3, 6 and 11. Increasing amount of biosorbents (0.05%, 0.1%, 0.5%, 1.0%, 3.0%, 7.0% and 10.0% w/w) were added in 20 ml of each solution and allowed to equilibrate in a temperature-controlled shaker incubator for 24h in 25°C and 100 rpm. The equilibrium pH was measured for each solution using a digital pH meter. The pH versus biomass amount

curve gave the PZC range.

Fourier transform infrared spectroscopy (FTIR) was used to identify the chemical groups present in the biosorbents. The surface functional groups of both onion and garlic skin was quantified by the method of Boehm titration (Valdés *et al.* 2002, Goertzen *et al.* 2010). Solutions of NaHCO_3 (0.1M), Na_2CO_3 (0.05M), NaOH (0.1M) and HCl (0.1M) was prepared with deionized water. The biosorbent (1g) were added to a volume of 50 ml of these solutions and shaken at 100 rpm for 24h to reach equilibrium. After filtration, the excess of base or acid was then determined by titration using the NaOH and HCl solutions.

Biosorption Studies

The copper solution was prepared by dissolving its sulfate salt (Merck) in deionized water. Equilibrium sorption studies were performed in 250 ml Erlenmeyer flask in a temperature-controlled shaker incubator at 120 rpm for 24 h. For these studies, skin for onion and garlic (0.2g) was contacted with the desired concentrations of Cu^{2+} solution at defined initial pH and temperature.

Batch studies were carried out in a vessel of diameter 12 cm with 500 ml of solution and specified amount of biosorbent. A mechanical stirrer (1500 rpm) was used to agitate the system. The concentration of the ions in the solution was measured by Atomic absorption spectrophotometer (Perkin Elmer AAnalyst 200). The amount of metal uptake by the biosorbent was calculated using the following equation:

$$(1) \quad q_t = V(C_i - C_t)/W$$

where q_t (mg/g) and C_t (mg/L) is the amount of metal ion biosorbed per gram of biomass and solution concentration at time t (min), C_i (mg/L) is the initial solution concentration, V (ml) is the volume of metal solution and W (g) is the weight of biosorbent.

Results and Discussion

Characterization of Biosorbent

The infrared (IR) spectrum obtained from FTIR of the onion and garlic skin (Figure 1a and Figure 1b) displayed a number of absorption peaks, indicating the complex

nature of the examined biomass. The results revealed biosorbent heterogeneity, evidenced by different characteristic peaks. The infrared absorption wavelengths of each peak and the corresponding functional groups are presented in Table 1a and Table 1b for onion and garlic skin respectively.

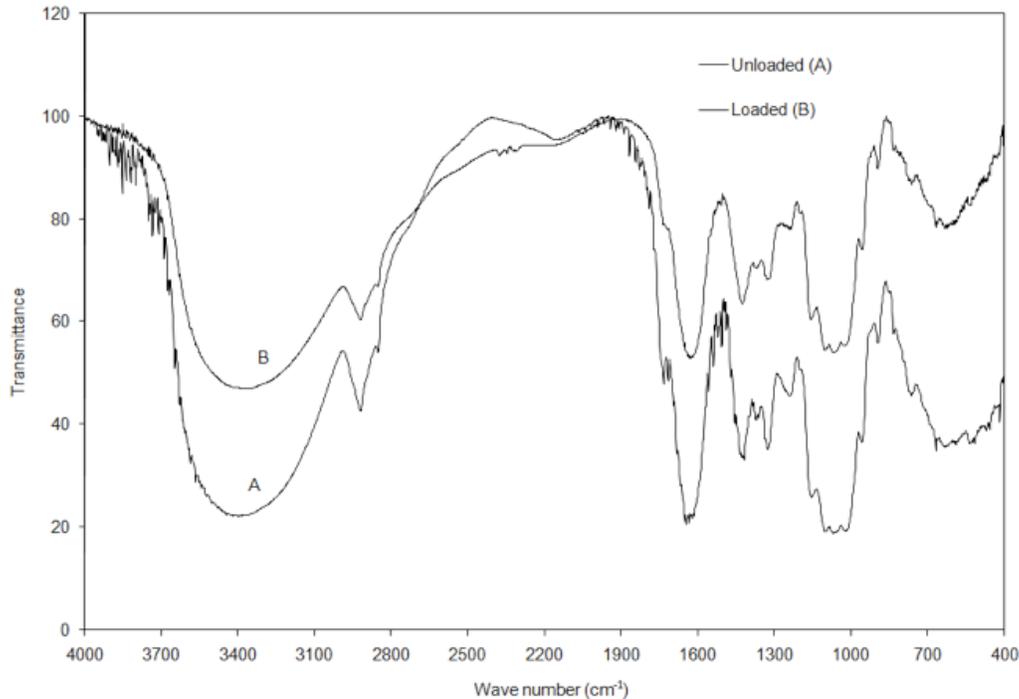


Figure 1a: FTIR analysis of loaded and unloaded onion skin.

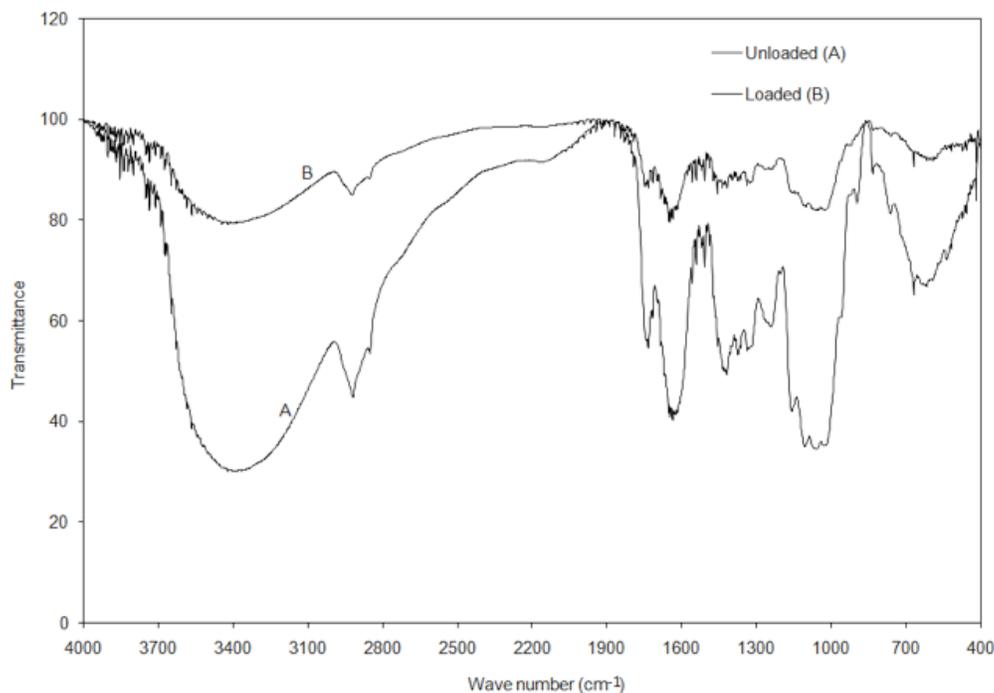


Figure 1b: FTIR analysis of loaded and unloaded garlic skin.

Wavelength range (cm ⁻¹)	Onion skin			Assignment
	Before loading of Cu(II)	After loading of Cu(II)	Differences	
3500-3000	3421	3361	-60	Bonded -OH groups
2900-2800	2852	2851	-1	CH stretching
1740-1680	17337	Absent	-	C=O carbonyl groups
1670-1640	1653	1630	-3	Carboxylic groups
1600-1500	1559	Absent	-	Carboxylic groups and N-H bending
1450-1300	1471	1426	-45	C-O stretch
1150-950	1101	1102	+1	-PO ₄ ³⁻ stretching
650-480	669	668	-1	N-containing bioligands

Table 1a: The FTIR spectral characteristics of raw onion skin before and after biosorption of Cu²⁺

Wavelength range (cm ⁻¹)	Garlic skin			Assignment
	Before loading of Cu(II)	After loading of Cu(II)	Differences	
3500-3000	3421	3393	-28	Bonded -OH groups
2900-2800	2922	2919	-3	CH stretching
1740-1680	1748	1732	-16	C=O carbonyl groups
1670-1640	1653	1647	-6	Carboxylic groups
1600-1500	1577	1559	-18	Carboxylic groups and N-H bending
1450-1300	1436	1419	-17	C-O stretch
1280-1240	1260	1243	-20	-SO ₃ ²⁻ stretching
1150-950	1105	1102	-3	-PO ₄ ³⁻ stretching
650-480	668	669	+1	N-containing bioligands

Table 1b: The FTIR spectral characteristics of raw garlic skin before and after biosorption of Cu²⁺

To determine the functional groups involved in the adsorption process, FTIR spectra obtained before and after Cu²⁺ loading were compared. As seen in Table 1a and Table 1b, the major functional groups that took part in adsorption are -OH, C=O, C-O, C-H and -COOH. The functional group -SO₃²⁻ was additionally involved in adsorption with garlic skin.

Surface functional groups were estimated based on the Boehm titration method and were found predominantly phenolic followed by basic, lactonic and carboxylic groups on both onion and garlic skin. Fig-

ure 2 shows the estimated amounts of these groups on both biosorbents. Presence of polyphenolic flavonoid called Quercetin in both onion and garlic attributes to the abundance of the phenolic group on their skin surfaces (Lombard *et al.* 2005).

Effect of pH

The effect of initial pH on adsorption capacity of onion and garlic skin is shown in the Figure 3. Diluted HCl was added to the solutions to get the desired pH values. The uptake increased with change in initial pH from 3 to 5.3 for both the biosorbents. Sim-

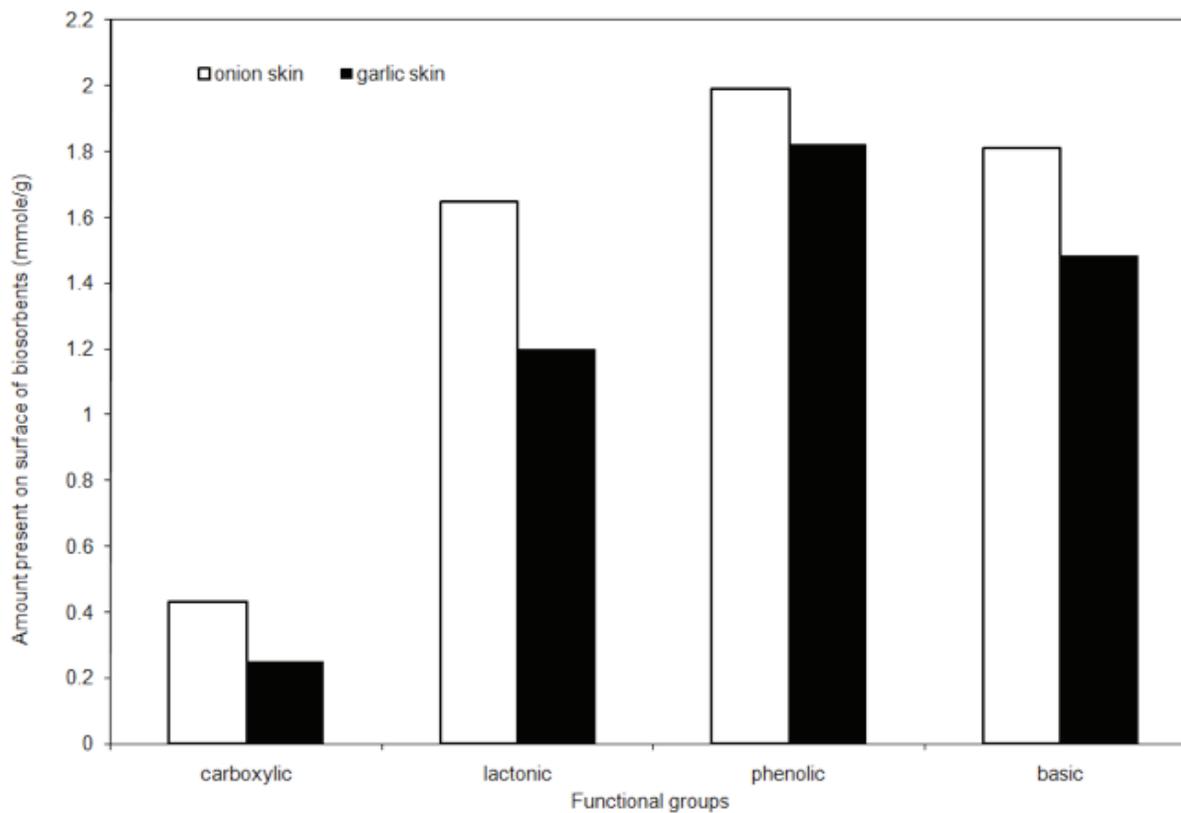


Figure 2: Amount of functional group present on onion and garlic skin.

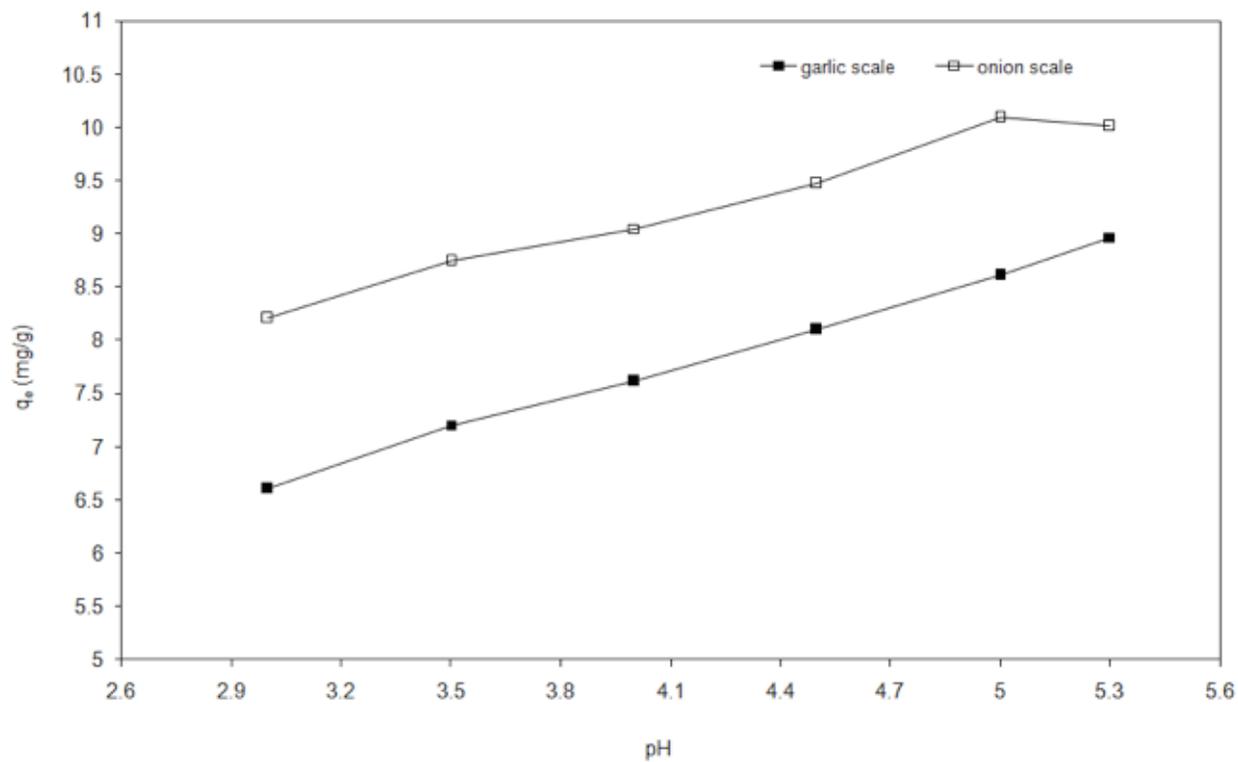


Figure 3: Effect of pH on adsorption process.

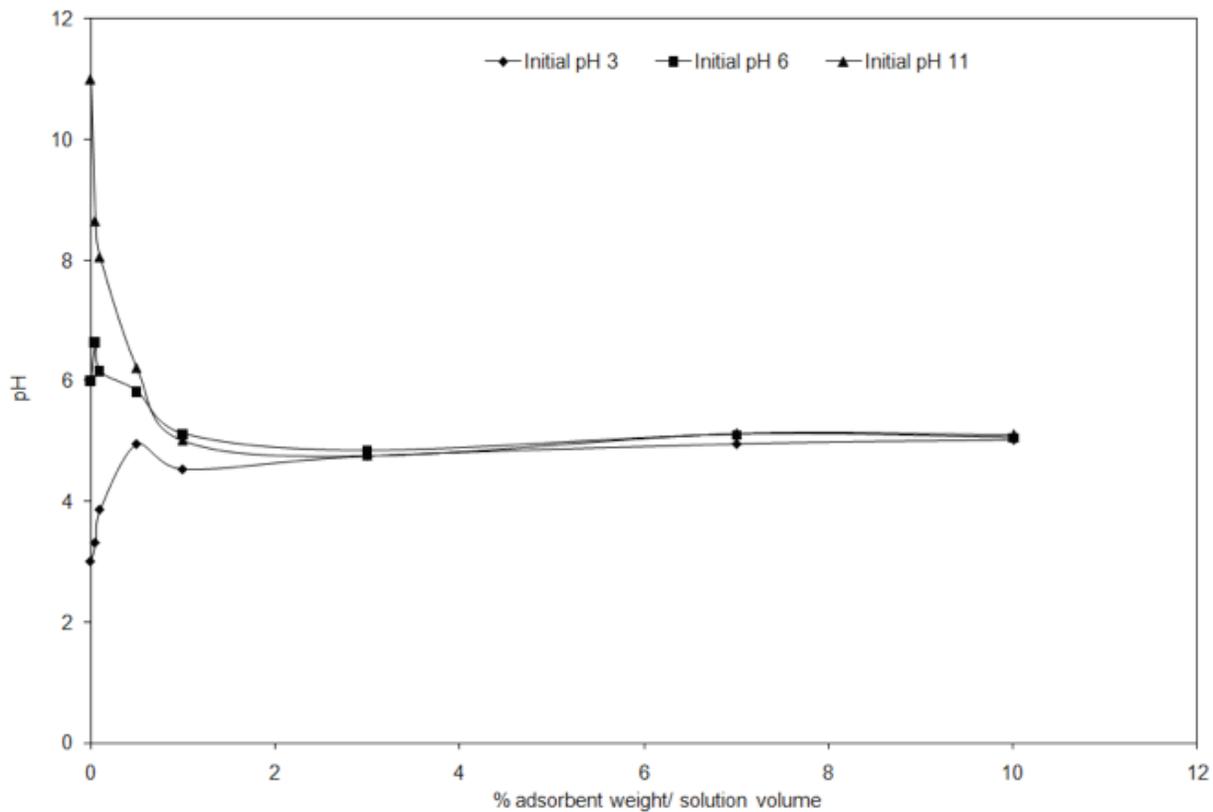


Figure 4a: Experimental curve determining the PZC value for garlic skin.

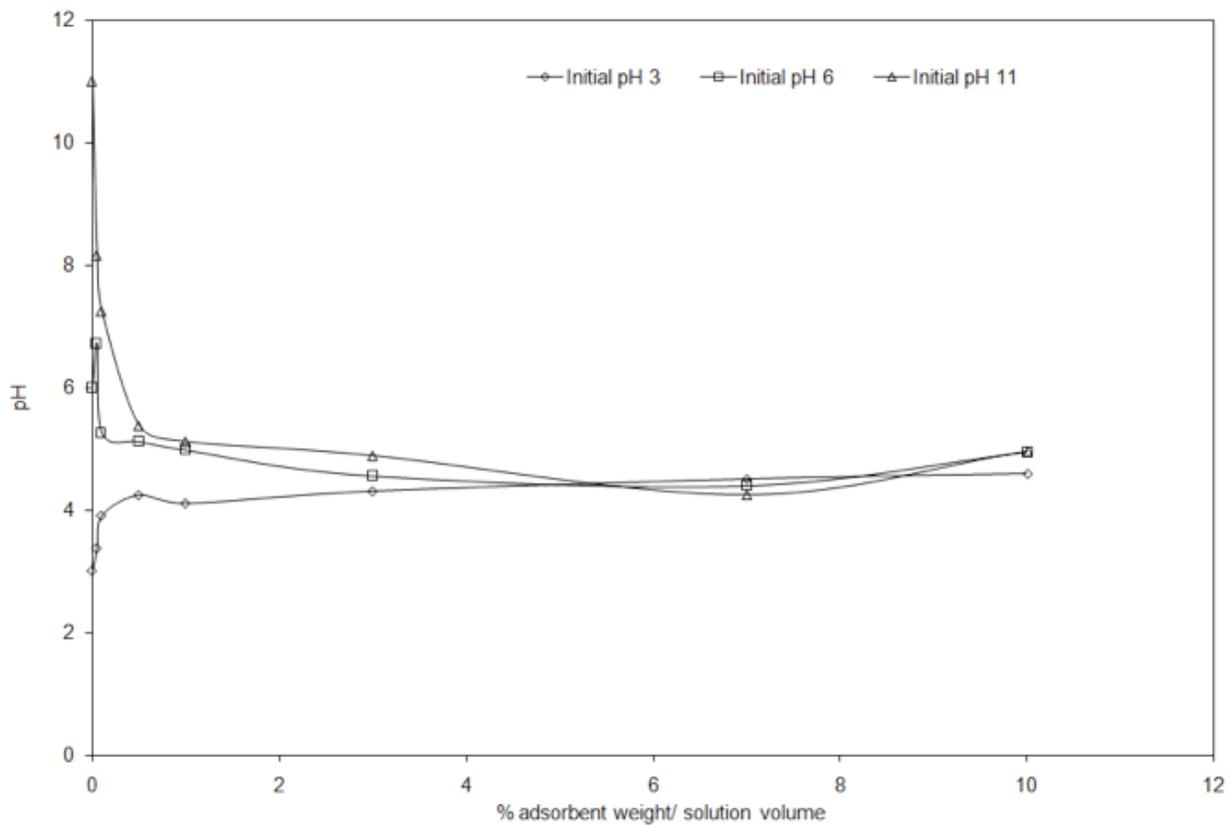


Figure 4b: Experimental curve determining the PZC value for onion skin.

ilar findings were established for several other biosorbents (Abu Al-Rub *et al.* 2006, Yahaya *et al.* 2009). Experiments were restricted to pH 5.3 as at higher pH copper precipitates out in the form of insoluble copper hydroxide.

An increase in pH results in more negative charges on the biosorbent surface that is likely to attract the positively charged Cu^{2+} ions to bind to its surface (Wahab *et al.* 2010) resulting in increased uptake. At low pH, the approach of positively charged Cu^{2+} cations will be inhibited due to the overall surface positive charge caused by protons that would restrict access to ligands by metal ions as a result of repulsive forces (Hameed & Ahmad 2009, Varshney *et al.* 2011). It is also likely that these protons will compete with Cu(II) ions for the ligands and thereby decreases the interaction of metal ions. PZC for onion and garlic skin were determined to prove the aforesaid fact. The experimental curves in Figure 4a and Figure 4b show that the PZC values are in

the range of 4.55 to 4.75 for garlic skin and 4.25 to 4.45 for onion skin. It clearly interprets that to ensure a completely negatively charged surface on the biosorbents, the pH must be maintained above 4.75 to achieve the maximum adsorption.

Biosorption Isotherms

The adsorption isotherm for garlic and onion skin at temperatures of 293 K, 303 K and 313 K are shown in Figure 5a and Figure 5b.

The Langmuir, Freundlich, Temkin and D-R isotherm models were employed to describe the uptake of Cu^{2+} by onion and garlic skins.

Langmuir

$$(2) \quad q_e/q_{max} = K_L C_e / (1 + K_L C_e)$$

Freundlich

$$(3) \quad q_e = K_F C_e^{1/n}$$

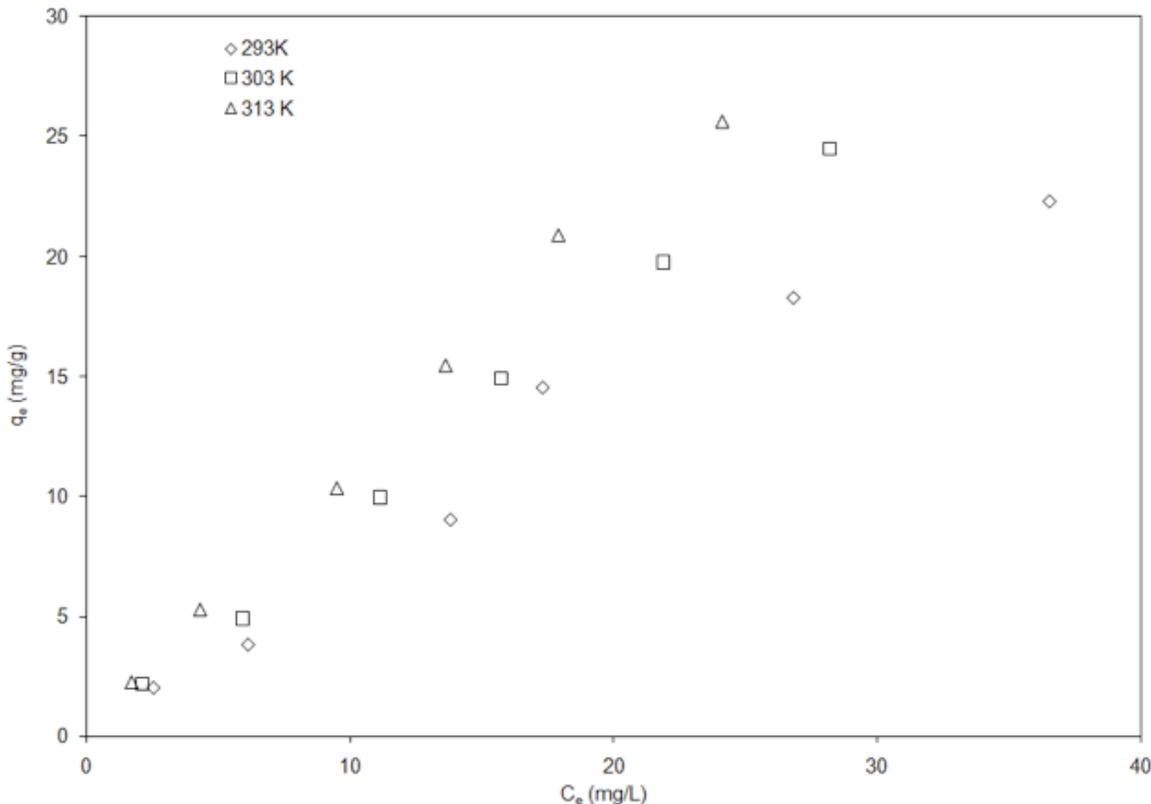


Figure 5a: Adsorption isotherm of Cu^{2+} onto onion skin (pH = 5.3).

Temkin

$$(4) \quad q_e = \frac{RT}{b} \ln(AC_e)$$

Dubinin-Radushkevich

$$(5) \quad q_e = q_{\max} \exp^{-\beta \varepsilon^2}$$

In the above equations q_e (mg/g) and C_e (mg/L) is the amount of the metal adsorbed per unit mass of adsorbent, and equilibrium metal concentration in the solution at equilibrium respectively, q_{\max} (mg/g) is the Langmuir constant related the maximum monolayer adsorption capacity and K_L (L/mg) is the Langmuir constant related to the affinity of the binding sites. The terms K_F and n in Equation (3) are related to binding energy and adsorption capacity and to the intensity of adsorption respectively. In Equation (4), $B = (RT/b)$ is related to the heat of the adsorption process. A and B are Temkin constants. For D-R model in Equation (5), β is a coefficient related to the

mean free energy of adsorption ($\text{mol}^2 \text{J}^{-2}$), and $\varepsilon = RT \ln(1 + C_e)$ is the Polanyi potential (J mol^{-1}).

The estimated value of these constants obtained by fitting the model expressions to the experimental data along with R^2 are listed in Table 2. Out of the 4 isotherm models studied, the higher values of R^2 obtained from fitting to Langmuir, Freundlich and D-R indicated that these give good fit to the experimental data over the entire concentration range studied.

Table 3 compares the values of q_{\max} obtained in this study with that of other biosorbents reported in the literature. It is seen that the adsorption capacity of the skin of onion and garlic was higher than that of many other biosorbents for this metal ion.

Biosorption Kinetics Studies

Experiments were carried out to determine

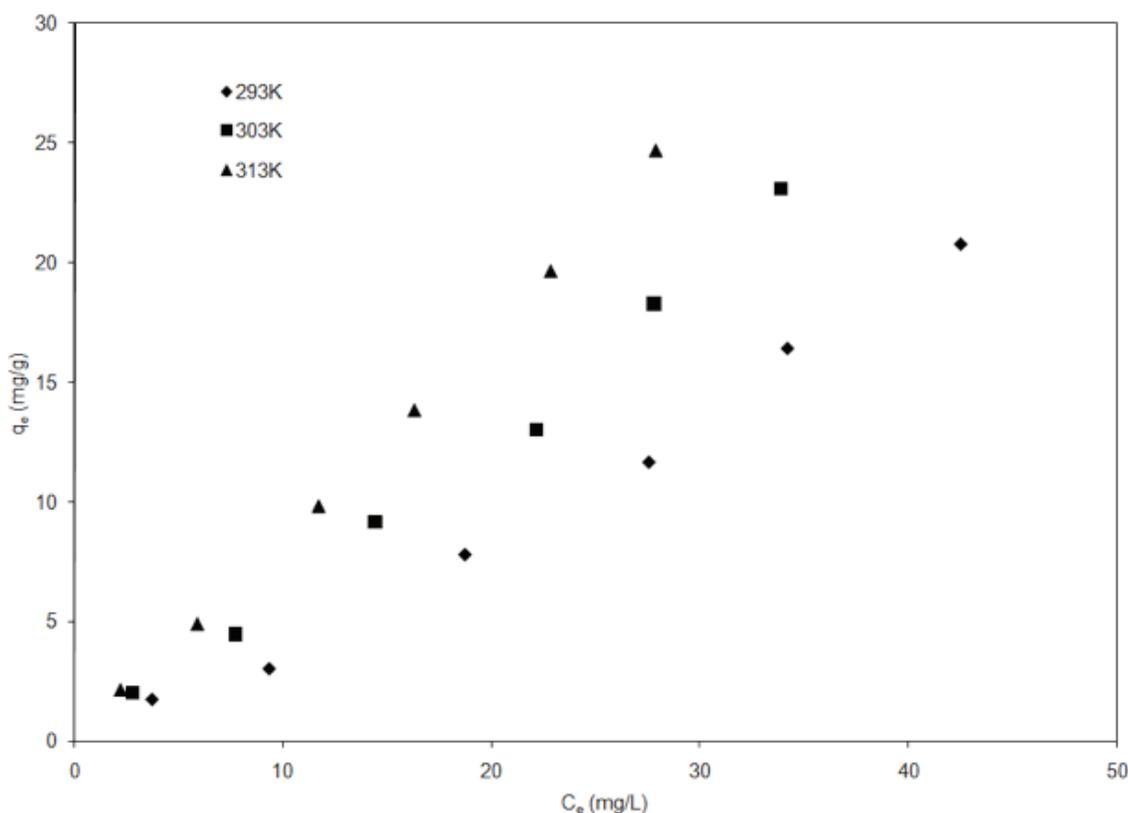


Figure 5b: Adsorption isotherm of Cu^{2+} onto garlic skin ($\text{pH} = 5.3$).

Biosorbent type	Temperature (K)	Langmuir model			Freundlich model		
		q_{max} (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	n	K_F (mg g ⁻¹)	R^2
Onion	293	66.67	0.012	0.984	1.05	0.783	0.983
	303	76.9	0.013	0.992	1.03	0.991	0.995
	313	83.3	0.016	0.998	1.07	1.36	0.998
Garlic	293	58.8	0.008	0.962	0.95	0.369	0.978
	303	66.6	0.011	0.991	1.02	0.685	0.991
	313	76.9	0.013	0.995	1.04	0.965	0.997

Biosorbent type	Temperature (K)	Temkin model			D-R model		
		A (mg L ⁻¹)	B	R^2	q_{max} (mmol g ⁻¹)	E (kJ mol ⁻¹)	R^2
Onion	293	3.07	8.92	0.88	0.0079	7.3	0.983
	303	2.57	9.39	0.903	0.0084	7.7	0.991
	313	2.05	9.51	0.905	0.0083	8.2	0.996
Garlic	293	4.74	8.4	0.861	0.0078	6.9	0.973
	303	3.46	9.04	0.852	0.0079	7.5	0.986
	313	2.65	9.4	0.88	0.0083	7.9	0.992

Table 2: Adsorption isotherm constants for onion and garlic skin

Biosorbent	q_{max} (mg/g) (T (K)/pH)	Reference
Tectona grandis	15.4 (298/5.0)	Kumar et al. 2006
Fish scale	58.5 (- / -)	Espinosa et al. 2001
Onion skin	80.6 (303/5.3)	Present study
Garlic skin	76.3 (303/5.3)	Present study
Wheat shell	8.3 (298/5.0)	Basci et al. 2009
Coffee husk	7.5 (298/4.0)	Oliveira et al. 2008
Papaya wood	19.9 (298/5.0)	Saeed et al. 2005
Sugar beet pulp	31.4 (298/4.0)	Aksu and İsoğlu 2005
Sunflower stalk	33.1 (- / -)	Sun & Shi 1998
Rice bran	27.81 (313/5.0)	Wang et al. 2009
Peanut hull	21.25 (303/5.5)	Zhu et al. 2009

Table 3: Comparison of Langmuir based maximum adsorption capacity of several biosorbents for Cu²⁺ adsorption.

the variation of the uptake of the metal ion with time at 303 K with biosorbent amount and initial metal concentration. The results for the different biomass dosage are depicted in Figure 6. These data were used for elucidating the mass transfer rate controlling mechanism and the reaction rate constant.

Intrinsic Rate Constant

The kinetic data for the studied biosorption process was analyzed by fitting pseudo first-order (Lagergren 1898) and pseudo second-order (McKay & Ho 1999) kinetic model to the experimental data. Better fit was obtained with the pseudo second-order model. The linear form of the pseudo second order model expression is:

$$(6) \quad t/q_t = t/q_e + 1/K_2q_e^2$$

where K_2 is the rate constant of the pseudo

second-order equation.

The values of the model constants for different operating parameters are shown in Table 4. The value of the experimental equilibrium adsorption $(q_e)_{exp}$ was determined by the intercept of adsorption isotherm and the overall mass balance equation. The model parameters of Equation (6) were determined using linear regression technique.

Various studies (Chowdhury and Saha (2010, 2011) have drawn attention to the drawbacks of utilizing least square regression technique with the linearly transformed pseudo second order kinetic model for determining the model constants. Non linear regression of the original form of the pseudo second order expression:

$$(7) \quad q_t = \frac{K_2q_e^2t}{1 + K_2q_e t}$$

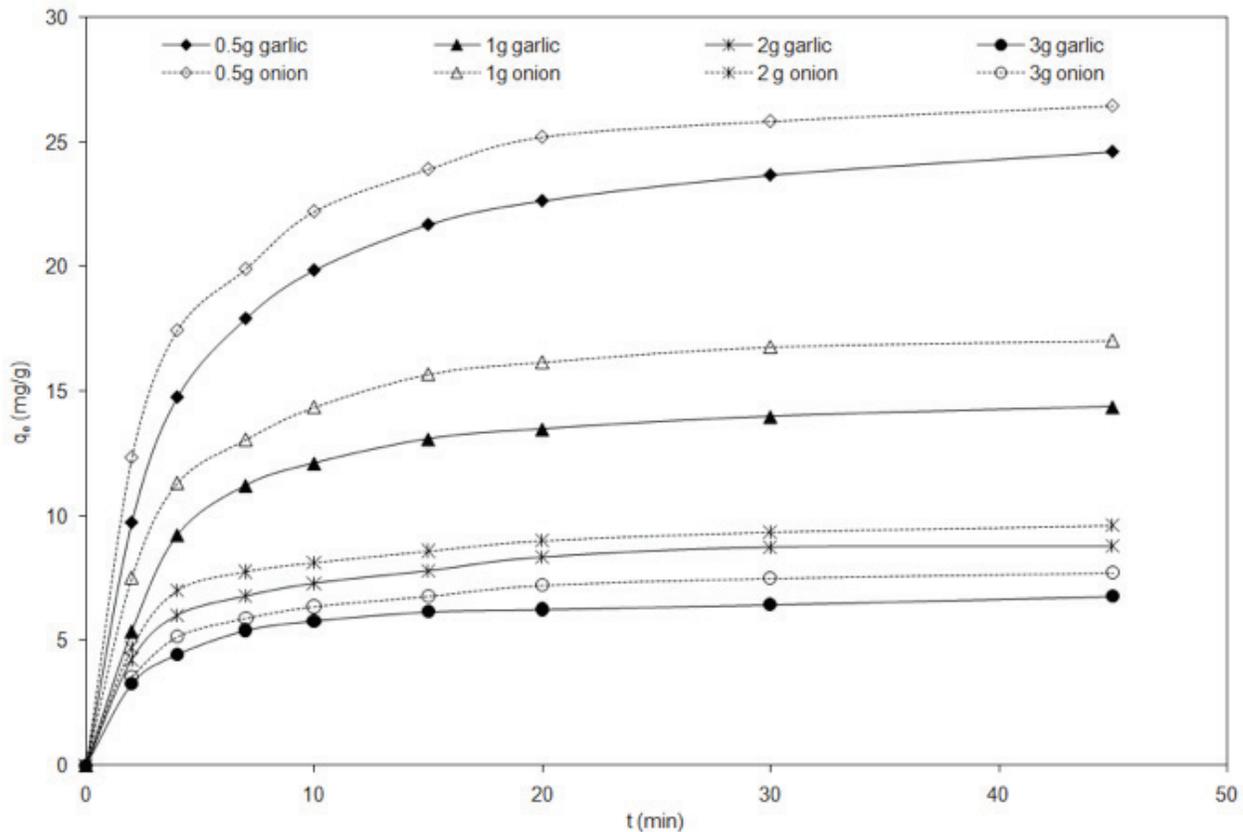


Figure 6: Effect of biosorbent dosage concentration on Cu^{2+} biosorption ($\text{pH} = 5.3$, Temperature = 303 K).

was stated to be more appropriate. The non-linear optimization method available with Microsoft Excel 2007 version (solver) was used in this study to determine the model constants of the above equation. The value of $(q_e)_{cal}$ and K_2 for garlic skin are shown within the bracket of Table 4. It is seen that there is no significant difference in the val-

ue of the parameters obtained with the two techniques. Similar result was also obtained with onion skin biosorbent.

The intrinsic rate of reaction refers only to the rate at which one chemical species is converted into another. The measurement of this can be achieved by making the process independent of physical processes such

Metal concentration (mg L ⁻¹)	Garlic skin				Onion Skin			
	$(q_e)_{cal}$ (mg g ⁻¹)	$(q_e)_{exp}$ (mg g ⁻¹)	K_2 (mg g ⁻¹ min ⁻¹)	R^2	$(q_e)_{cal}$ (mg g ⁻¹)	$(q_e)_{exp}$ (mg g ⁻¹)	K_2 (mg g ⁻¹ min ⁻¹)	R^2
20	3.53(3.54)	3.17	0.088(0.087)	0.999(0.999)	3.61	3.38	0.114	0.999
35	7.1(7.0)	6.57	0.054(0.056)	0.999(0.999)	7.54	7.5	0.061	0.999
50	9.51(9.46)	14.0	0.038(0.038)	0.998(0.992)	10.1	10.8	0.05	0.999
Biosorbent dosage (g)								
0.5	26.3(26.3)	29.2	0.012(0.0115)	1.0(0.999)	28.2	25.9	0.013	0.999
0.75	19.8(19.8)	25.4	0.015(0.015)	0.999(0.999)	21.3	20.5	0.018	0.998
1	15.17(15.17)	22.6	0.026(0.027)	1.0(0.999)	18.2	16.4	0.021	0.999
1.5	11.87(11.83)	17.1	0.031(0.032)	0.999(0.999)	12.9	13	0.035	0.998
2	9.5(9.45)	14.0	0.038(0.038)	0.998(0.992)	10.1	10.8	0.05	0.999
3	6.8(6.48)	10.9	0.06 (0.068)	0.999(0.999)	8.1	8.1	0.047	0.999

Table 4: Pseudo-second-order Kinetic rate constants related to the biosorption of Cu²⁺ biosorption onto onion and garlic skin.

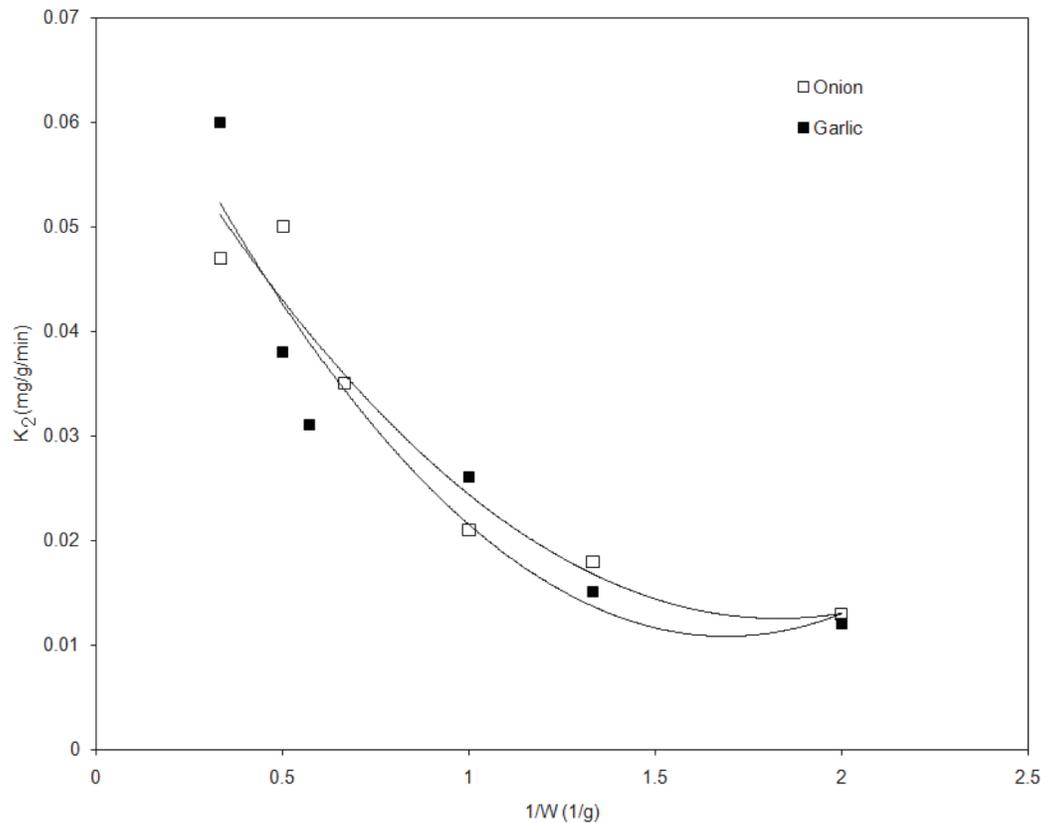


Figure 7: Variation of pseudo second order rate constant with 1/weight of biomass.

as heat, mass and momentum transfer. The change in the value of K_2 with variation of the biomass amount and initial feed concentration suggests that it is not the intrinsic reaction rate. Qualitatively, increase of metal loading in biomass (Figure 6) implies greater penetration of the sorbate into the adsorbent thereby increasing the intra particle mass transfer resistance.

The weight of the biomass gives good representation of the surface area. As W tends to infinity, the product of bulk phase mass transfer coefficient and surface area also tends towards infinite and the diffusional resistance for transport of metal ion from the bulk solution to the biosorbent-solution interface towards zero. Further, the intra particle mass transfer resistance can be neglected as the reaction can be assumed to occur at the surface of the biosorbent itself. The value of K_2 in the absence of mass transfer resistances was obtained from the intercept of the curve shown in Fig. 7 on extrapolation to $1/W \rightarrow 0$ (W is infinite). The

desired value of K_2 for onion and garlic scale are 0.07 mg/g/min ($R^2 = 0.94$) and 0.075 mg/g/min ($R^2 = 0.89$) respectively.

Thermodynamic Parameters

The chemical equilibrium constant of a reversible reaction can be related to temperature by the following expression:

(9)

$$\ln K_a = -\Delta G^0/RT = -\Delta H^0/RT + \Delta S^0/R$$

where K_a is the equilibrium constant, ΔG^0 is the change in standard Gibbs free energy, ΔS^0 is the standard entropy change, ΔH^0 is the standard enthalpy change, T is the temperature and R is the universal gas constant. The free energy change for the process was determined by using the equilibrium constants obtained from Langmuir isotherm model. Thermodynamic parameters of ΔH^0 and ΔS^0 were obtained from the slope and intercept of the plot between $\ln K_a$ versus $1/T$ (Figure 8).

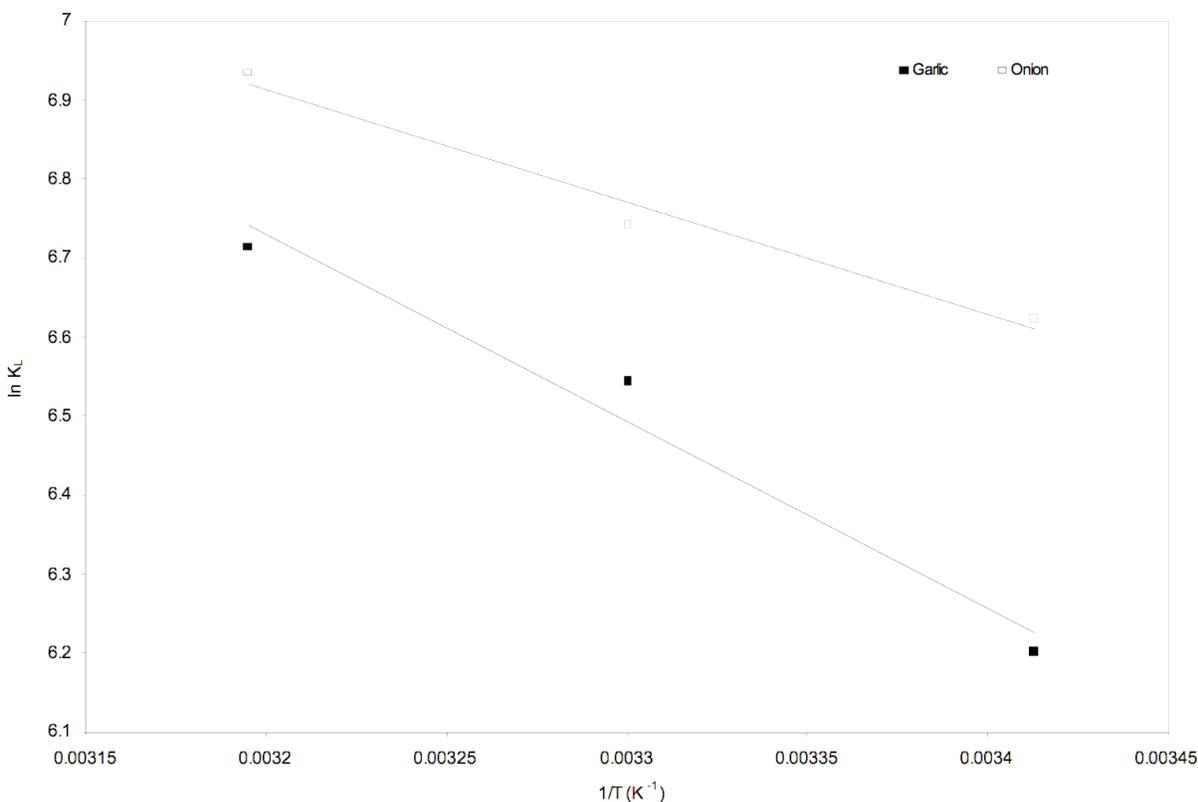


Figure 8: Plot of $\ln K_L$ versus $1/T$ for the estimation of thermodynamic parameters.

The negative values of Gibbs-free energy (~ -16.0 kJ/mol) indicated the feasibility of the process. Standard enthalpy change for onion and garlic skin was estimated to be 11.8 kJ/mol and 19.6 kJ/mol respectively. The corresponding standard change in entropy was 0.095 kJ/mol/K and 0.12 kJ/mol/K respectively. The positive values of ΔH° for Cu^{2+} removal indicated that the metal adsorption process was endothermic in nature. The positive values of ΔS° for Cu^{2+} with both biosorbent showed an increased randomness at solid solutions interface during the adsorption of Cu^{2+} on the waste biomass (Iftikhara *et al.* 2009, Özer *et al.* 2004).

Conclusions

The study showed that both onion and garlic skin are efficient adsorbents for removal of Cu^{2+} from the aqueous stream. The high adsorptive capacity of these biosorbents implies that it can be looked as an alternative to costly adsorbents like activated carbon, resins, etc. The proposed new technique for estimation of reaction rate constant in the absence of mass transfer resistances provides a means of delineating the influence of reaction kinetics and diffusional resistances on the uptake rate and result in improving contactor design.

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Discussion with Reviewers

Anonymous Reviewer: Fig. 2 shows the number of adsorption sites (carboxylic and phenolic groups) in mmole/g. Can the authors give an estimate of the spatial separation between the sites in the wet adsorbant from these measurements?

A. Chowdhury, A. Bhowal and S. Datta: The equilibrium uptake results indicated that all the adsorption sites were not occupied. This is one of the reasons which would limit the estimation of spatial separation between the sites.

Reviewer: Four thermodynamic adsorption models are numerically analyzed, but what do they show qualitatively about the molecular adsorption process, for example, if the Freundlich model is a better fit than others, can we rule some putative adsorption steps in or out?

Chowdhury, Bhowal and Datta: In the present study we have found that Freundlich isotherm model yielded best fit with the highest R^2 values at majority of the temperatures compared to other models. This concludes:

- Heterogenous surface of the adsorbents

(onion and garlic skin)

- Non-uniform distribution of heat of adsorption

The Temkin model did not give a good fit concluding that the present adsorption process is not characterized by uniform distribution of binding energy.

Reviewer: The article is appearing in Water Journal, so it is relevant to mention the role of water in the investigations. How many water molecules are accepted to be in the hydration shell of Cu, and does the heat of desorption from the ion fall into the same range (10-20 kJ/mol) as the adsorption values calculated from Fig 9?

Chowdhury, Bhowal and Datta: Cu^{2+} ion in aqueous solution exists as $\text{Cu}(\text{H}_2\text{O})_4^{2+}$. (Chemical Principles in the Laboratory by Emil J. Slowinski, Wayne C. Wolsey, William L. Masterton, Brookes/Cole, 2005). The hydration enthalpy of Cu^{2+} is -2100 kJmol^{-1} (Electronic Structure and Solvation of Copper and Silver Ions: A Theoretical Picture of a Model Aqueous Redox Reaction, J. Blumberger, L. Bernasconi, R. Vuilleumier, I. Tavernelli, M. Sprik. *J Am Chem Soc* 126 (2004) 3928-3938). Therefore, the heat of desorption of water from the Cu^{2+} is far higher than the heat of adsorption of the metal ion to the biosorbent (which is also endothermic). ■