

The Remediation of Wastewater by Adsorption on an Agro-based Waste

Mohammad Asaduddin Laskar^{*1}, Syed Kashif Ali², Sana Siddiqui³

^{1,2}Department of Chemistry, Faculty of Science, Jazan University, Jazan, Saudi Arabia

³Department of Chemistry, College of Science and Arts, Samtah, Jazan University, Saudi Arabia

*¹madasaduddinlaskar@gmail.com; ²skali_169@yahoo.com; ³sana.siddiqui1@gmail.com

Received: 24 October 2015. Revised: 25 January 2016. Accepted: 16 February 2016

Abstract - Foods and oil industries, including laboratories of traditional medicines, generate a considerable amount of waste, such as spent/used cumin seeds (binomially named *Cuminum cyminum*). The idea of using this waste for the removal of toxic metals serves a dual purpose of waste valorization as well as remediation of waste water. The preliminary work includes the optimization of the experimental parameters, namely, pH, contact time, adsorbent and metal concentrations and temperature. Fourier transform infrared spectroscopy was employed for examining the probable sites, available on the adsorbent, for interacting with the metal ions. The studied isothermal models, namely the Langmuir, Freundlich and Dubinin-Radushkevich models, collectively suggest physio-chemical sorption as the primary mode of retention of metal ions. The spontaneous nature of adsorption is indicated by the calculated thermodynamic parameters. The adsorption process was found to follow the pseudo-first order kinetic model and also followed the intraparticle diffusion up to 50 minutes of contact time. The recovered adsorbent was then subjected to several cycles of loading and elution and was found to retain 97% of the sorption capacity up to 3 cycles.

Keywords- Low Cost Adsorbent; Agricultural By-Products; Isotherm Models; Waste Valorization; Environmental Protection

I. INTRODUCTION

The uncontrolled and excessive release of heavy metals, caused by growing industrialization and urbanization, into the environment, poses serious environmental and health problems [1]. The major causes of pollution are unplanned discharge of sanitary and toxic industrial wastes, improper dumping of industrial effluent and runoff from agricultural field. One of the consequences of the introduction of toxic metal ions into the natural ecosystem is their bioaccumulation in human bodies and other living beings, which takes place through either direct intake or food chains. Hence, their removal from natural resources has become a major concern [2]. Excessive consumption of zinc may cause different health problems, such as nausea, anemia, skin irritations, and vomiting associated with stomach cramps [3]. Industries including pharmaceuticals, paints and pigments, insecticides, galvanizing, viscose rayon yarn and fiber production, newsprint paper production and cosmetics are the major contributors to zinc pollution [4].

The different techniques that have been employed for the removal of heavy metals include ion exchange, co-precipitation, adsorption [5], membrane filtration and precipitation [6]. Among these, the technique of adsorption is currently preferred over others due to its effective and economical nature in the treatment of heavy metal contaminants [7]. Moreover, resins and polymeric extractant, which require cumbersome procedures, like synthesis, purification etc, is gradually giving way to agricultural waste and/or byproducts as low cost adsorbents [8-10]. The various low cost and abundantly available agricultural by-products, such as sugarcane bagasse, rice husk, oil palm shell and neem bark, have offered efficient biosorbents for heavy metals [6].

Used cumin seeds (binomially named *Cuminum cyminum*) are a waste product of various foods and oil industries, including laboratories of traditional medicines [11]. The *Cuminum cyminum* plant belongs to the botanical family of Apiaceae. The major chemical constituents include Cuminaldehyde, Thymol, phenol, cymene and terpenoids. The different functional groups contributed by the constituent compounds and the biodegradable nature make cumin an eco-friendly and promising candidate for protection of the environment by waste valorization and remediation of waste water.

The present work aims to investigate the potential of Cumin seeds as a low-cost bio-sorbent for the removal of zinc (II) ions from aqueous media. The adsorption behavior was determined by studying the adsorption kinetics and equilibrium isotherms. The thermodynamical parameters have also been evaluated. The experimental parameters, namely amount of adsorbent, concentration of metal ion, temperature and pH, have been optimized prior to the application for the removal of the metal ions.

II. MATERIAL AND METHODS

A. Instruments and Equipments

The concentration of Zn (II) was determined by Flame atomic absorption spectrometry (Agilent, USA). The pH measurements were carried out with a pH meter (Bellstone, India). A mechanical shaker of 200 rpm (Bellstone, India) was used for the equilibrium studies. An FTIR (Fourier Transform Infra Red) spectrometer (Omicron, USA) was used for FTIR analysis. A Heating oven (Bellstone, India) was used for drying. A stainless steel grinder was used for reducing the adsorbent to powder. ASTM standard sieves were used for separating particles of the desired size.

B. Preparation of reagents and adsorbent

All reagents were of analytical grade. The solution of Zn (II) constituting compound of analytical grade was prepared in deionised water. The cumin seeds, procured from a local market (in Jazan), were extensively washed with deionised water and then left overnight in the oven for drying at a constant temperature of 80°C until a constant weight was observed. The dried adsorbent was crushed and then allowed to pass through an ASTM sieve for acquiring particles at a size of 300µm.

C. Batch method for adsorption studies

An accurately weighed amount of the adsorbent (cumin seeds) was allowed to equilibrate in contact with Zn (II) solution of an appropriate concentration [12]. The mixture was subjected to continuous shaking while maintaining a constant pH, with the appropriate buffer solution, for the optimum time. The filtrate was then subjected to FAAS for determining the concentration of Zn (II).

III. RESULTS AND DISCUSSION

A. Characterization

1) FT-IR analysis:

The nature of the interaction between the target metal ion and the adsorbent was studied by analysing the FTIR spectra of the loaded and the unloaded adsorbent (Fig. 1, 2). The broad band at 3710-3902 cm^{-1} , which may correspond to ν (NH) and ν (OH), decreased in intensity when loaded with metal, indicating the possible involvement of these functional groups in the retention of the metal. The ν (CO) of unionized carboxylates, corresponding to 1748 cm^{-1} in the spectra of the unloaded adsorbent, underwent a red shift by 102 cm^{-1} on loading with metal, indicating the participation of the CO group in the process of the retention of metal.

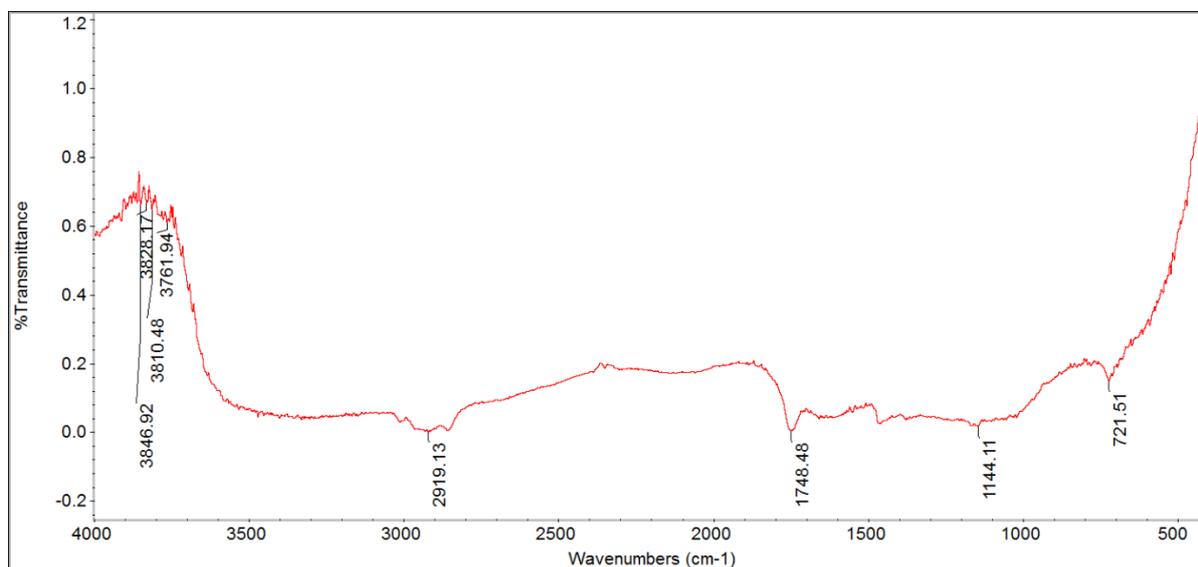


Fig. 1 FT-IR spectrum of unloaded cumin

The combined effect of double bond stretching vibration and the NH deformation band, represented by a band at 2919 cm^{-1} , undergoes a shift to 2361 cm^{-1} due to its possible role in metal retention [13]. The spectra of the metal loaded adsorbent display a band at 3390 cm^{-1} , which may represent the shift of ν (NH). Moreover, the band at 1144 cm^{-1} , corresponding to ν (C-O) and/or the bending vibration of OH, does not appear in the spectrum of the metal-loaded adsorbent, thereby indicating their role in metal binding.

2) Hydrogen capacity and water regain capacity:

The presence of an interstitial and/or trapped aqueous phase within the biomass allows easy movement of the metal phase. The water regains capacity, which reflects the hydrophilicity of the biomass (cumin seeds), may be defined as the amount of water absorbed by 1.0 g of the biomass [14].

The experiment was conducted with 2.0 g of dried ground cumin seeds. They were allowed to soak (in doubly distilled water) for 48 h, then separated out through filtration by suction. The residue of the adsorbent that was collected on the filter was then allowed to dry in air and weighed. The air-dried biomass was then dried overnight at 80° C, and then the constant weight is noted.

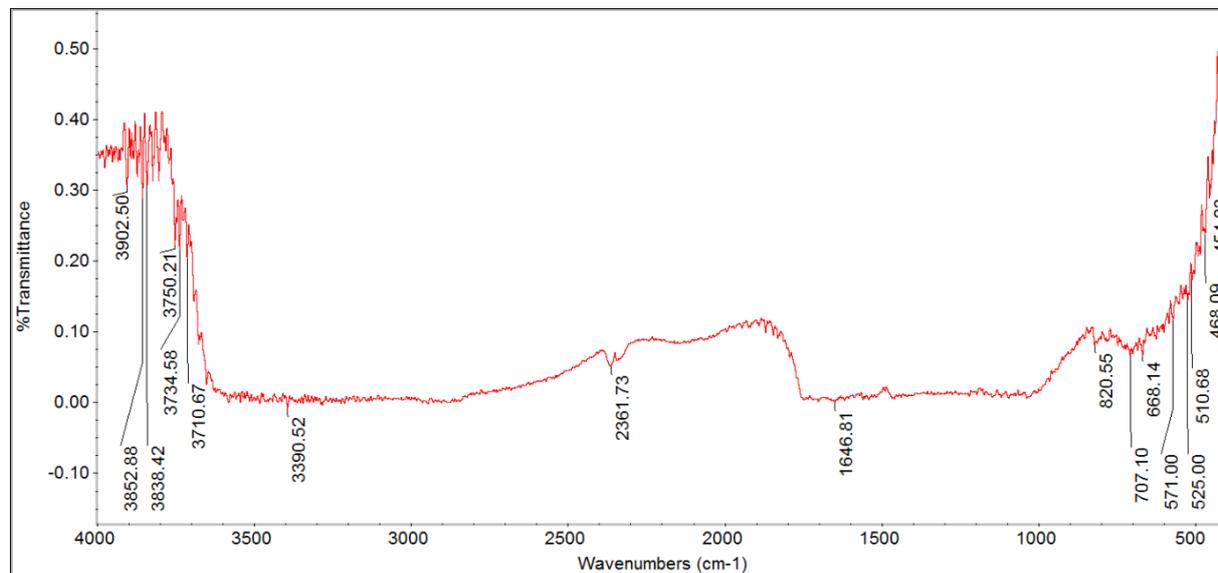


Fig. 2 FT-IR of Zn (II) loaded Cumin seeds

The water regain value was calculated as [14]:

$$W = (m_w - m_d) / m_d,$$

where m_w is the weight of the air-dried polymer after filtration by suction and m_d is the weight of the resin after drying at 80°C overnight.

The water regain capacity was found to be 5.3 mmol g⁻¹.

The overall hydrogen ion capacity was determined as follows: An amount of 1.0 g of the dried ground cumin seeds was soaked in 4.0 M HCl for 1 hr. The residue of the acid-treated biomass was then washed with distilled water until there was no leaching of free acid and subsequently dried at 60°C for 3 h. The acidified biomass was again soaked in 0.1 M NaOH solution at room temperature for 1 hr so that equilibrium was reached. The leftover alkali was then titrated against 0.1 M HCl. The overall hydrogen ion capacity was found to be 1.03 mmol /g.

3) Chemical stability:

The dried ground biomass was treated with 2 to 4 M of HCl/HNO₃/H₂SO₄ and 2 to 4 M of NaOH for 30 min (with constant stirring) and then subjected to several loading and elution cycles (after washing and drying). The sorption capacity remained constant up to 3 M of mineral acid and 4 M of NaOH. However, about 8% loss in the sorption capacity was observed with acids of >3 M and base (NaOH) of >5 M. Hence, it may be concluded that there was no degeneration of the biomass in moderately acidic and/or alkaline medium.

B. Effect of contact time

The plot of the amount of Zn (II) retained against the equilibration time (Fig. 3) suggests that the adsorption capacity increased with the increase in the contact time up to 50 min. A constant adsorption capacity of 9.99 mg g⁻¹ was observed after a contact time of 50 min, thereby giving the maximum saturation limit of the adsorbent.

C. Effect of pH on removal of heavy metal

The pH of the medium needed to be monitored, as the hydrogen ions have the potential to compete with the metal ions during the process of adsorption. A very low retention of Zn (II) ions was observed (Fig. 4) at pH 1-3; thereafter, a rapid increase in the adsorption took place up to pH 6.0. At pH > 3, the positively charged metal ion overcame the challenge posed by the H₃O⁺ ions, and, therefore, the adsorbent possessed more negatively charged sites that facilitated the binding of metal ions. At pH > 6.0, a decline in the adsorption of metal was observed, which may have been caused by the deterioration of the metal binding sites [15, 16].

D. Effect of initial concentration

In the batch equilibration method, the mass transfer resistance of metal ions between the aqueous and the solid phase may be overcome by varying the initial concentration of the metal ions, whereby the latter offers the required driving force. Therefore, with the increase in the initial metal ion concentration, there is an increase in the percentage of retention.

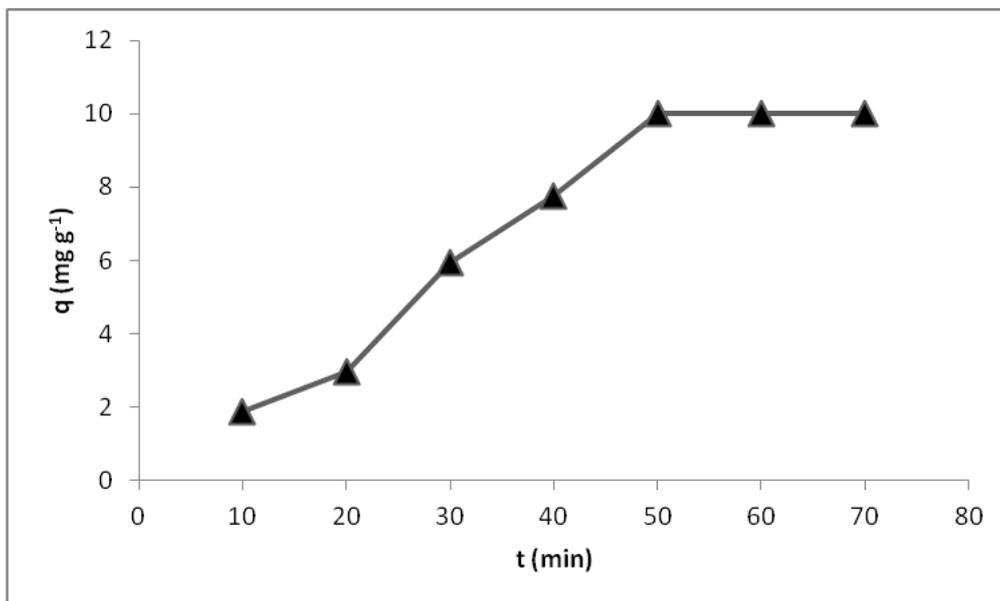


Fig. 3 Effect of contact time on the adsorption of Zn (II)

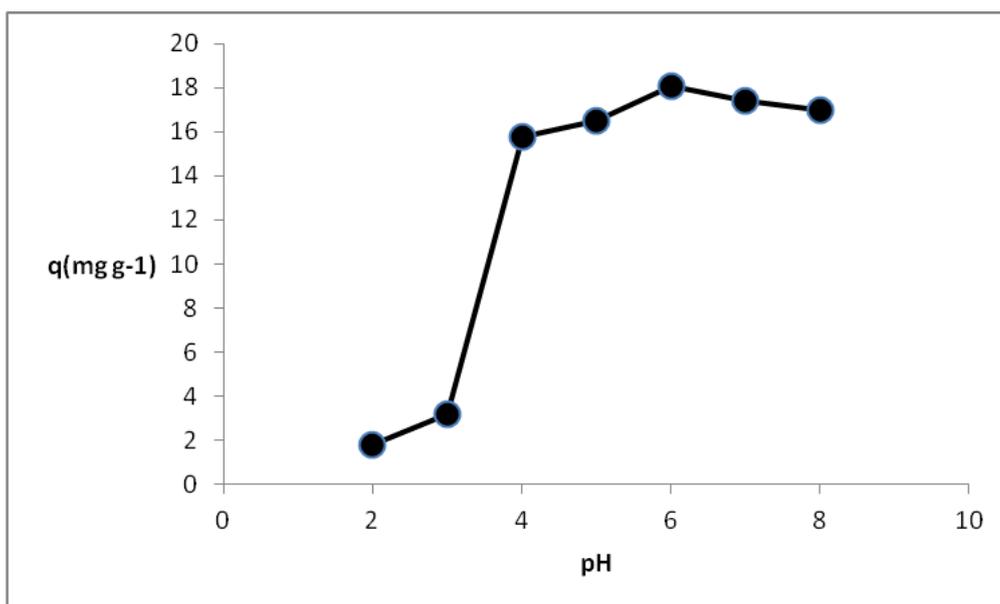


Fig. 4 Effect of pH on the adsorption of Zn (II)

E. Effect of temperature on the uptake of metal

At higher temperatures, the favorable nature of adsorption may be indicative of the involvement of some chemical interactive forces. In the range of 20-50°C, the adsorption capacity varied from 0.53 to 0.65 mmol g⁻¹ for the optimum contact time of 50 min. Before reaching the saturation limit, a kinetically controlled adsorption is suggested by the direct linear relationship between temperature and the adsorption capacity. Again, such a trend for adsorption indicates that more binding sites are available at higher temperature that leads to higher adsorption.

F. Effect of the adsorbent mass

The adsorption of Zn (II) by varied adsorbent masses reflects that the binding sites increased with the increase in the amount of the adsorbent. Hence, an increase in the adsorption capacity, from 8.0 to 9.97 mg g⁻¹ (Fig. 5), was observed.

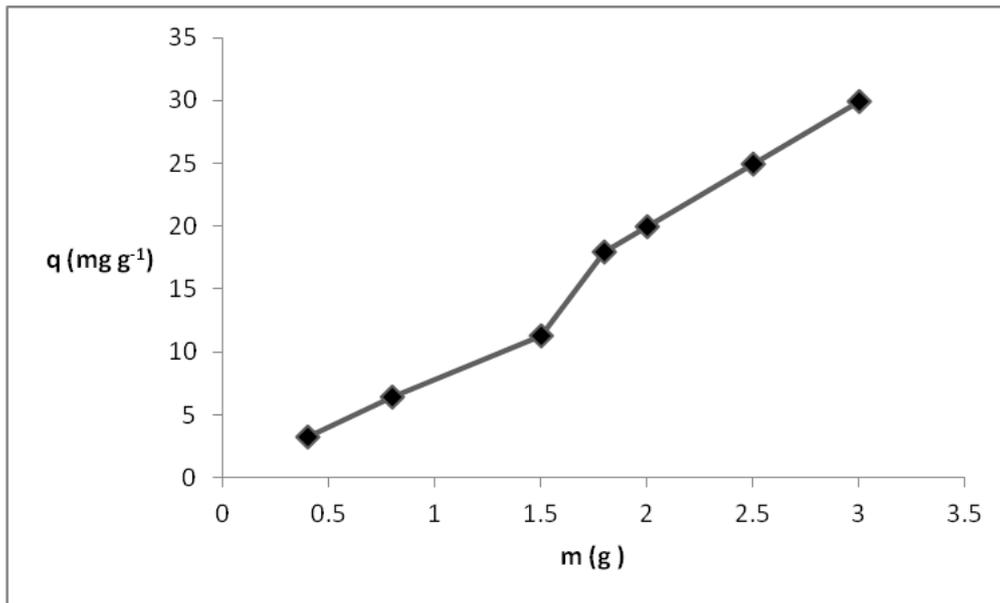


Fig. 5 Effect of the amount of adsorbent on the sorption of Zn (II) (mg)

G. Adsorption isotherm studies

Important information about the adsorption process may be obtained from the equilibrium isotherms. Hence, isotherm models, namely Langmuir, Freundlich and Dubinin-Radushkevich isotherms [17-19], have been studied at 20-50 °C.

The equation for a Langmuir isotherm is:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{q_{max}K_L} \right) \frac{1}{C_e},$$

where q_e indicates the amount of Zn (II) (at equilibrium) adsorbed by the adsorbent (mol g^{-1}); C_e , the concentration of Zn (II) (at equilibrium with the adsorbent) in the solution (mol dm^{-3}); q_{max} , the monolayer adsorption capacity of the adsorbent (mol g^{-1}); and K_L , the Langmuir adsorption constant ($\text{dm}^{-3} \text{mol}^{-1}$) related to the free energy of adsorption.

Another constant, namely the separation factor, R_L , which indicates the shape of the isotherms to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) may be represented as:

$$R_L = \frac{1}{1 + K_L C_o}$$

The Freundlich isotherm may be represented as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Here, K_F and n are Freundlich adsorption isotherm constants ($\text{dm}^3 \text{g}^{-1}$), while Dubinin-Radushkevich isotherms may be defined as:

$$\ln q_e = \ln q_m - \beta \varepsilon^2$$

where a constant, β , relates to the mean free energy of adsorption per mole of the adsorbate ($\text{mol}^2 \text{J}^{-2}$); q_m , the theoretical saturation capacity, and ε is the Polanyi potential =, $RT \ln\{1 + (1/C_e)\}$ with R ($\text{J mol}^{-1} \text{K}^{-1}$) representing the gas constant; and T (K), the absolute temperature. The free energy E (kJ mol^{-1}) of adsorption at the surface of the solid when transferred from infinity in the solution may be related to the constant, β , as:

$$E = \frac{1}{(2\beta)^{1/2}}$$

The befitting nature of the above three mentioned isotherm models (Tables 1 and 2) suggests that both homogeneous and heterogeneous sites are involved in accomplishing the process of adsorption. A probable chemical adsorption, through the ion

exchange mechanism [20], is suggestive of the homogeneous monolayer distribution of the active sites (for binding with the metal), as indicated by the Langmuir isotherm. The involvement of Langmuir isotherms is further ascertained by the value of $1/n < 1$ [21]. The value of R_L , between 0 and 1, is indicative of the favorable nature of the adsorption of metal ions. As the experimental data also befits the Freundlich isotherm, a physical sorption is reflected by the heterogeneous nature [20]. The chemical constituents of the adsorbent (cumin), namely Cuminaldehyde, Thymol, phenol, cymene and terpenoids along with their probable derivatives, may be involved during ion exchange and physiochemical reactions. Moreover, the magnitude of E (Table 2) reflects the physical nature of the adsorption process [20].

TABLE 1 VALUES OF LANGMUIR ISOTHERMS CONSTANTS FOR THE ADSORPTION OF ZN (II) AT VARIOUS TEMPERATURE

t (°C)	q_{\max} (mol g ⁻¹)	K_L (dm ³ mol ⁻¹)	r_L^2	R_L
20	5.35×10^{-4}	15.64	0.99	0.86
30	6.00×10^{-4}	10.48	0.98	0.90
40	6.22×10^{-4}	7.76	0.98	0.93
50	6.54×10^{-4}	5.20	0.97	0.95

TABLE 2 VALUES OF FREUNDLICH AND DUBININ-RADUSHKEVICH ISOTHERM CONSTANTS

Freundlich		Dubinin-Radushkevich	
n	1.02	β (mol ² kJ ⁻²)	1.25
K_F (dm ³ g ⁻¹)	145.47	E (kJmol ⁻¹)	0.58
r_F^2	0.98	r_{D-R}^2	0.98

H. Kinetics studies

In order to reach the appropriate representative rate expressions for adsorption [22], three kinetic models have been investigated.

A pseudo-first-order equation is given as: $\frac{1}{q_t} = \frac{1}{q_1} + \frac{k_1}{q_1 t}$; where q_1 and q_t are the amounts of the Zn(II) ions adsorbed at equilibrium and at time t (mg g⁻¹), respectively, and k_1 is the pseudo-first-order rate constant (min⁻¹) of adsorption.

A pseudo-second order equation may be represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t$$

where q_2 is the maximum adsorption capacity (mg g⁻¹) for the pseudo-second-order adsorption; q_t , the amount of Zn(II) ions adsorbed at equilibrium at time t (mg g⁻¹); k_2 , the equilibrium rate constant of pseudo-second-order adsorption (g mg⁻¹ min⁻¹).

The intraparticle diffusion (Fig 6) may be investigated with: $q_t = k_p t^{1/2} + C$

where C is the intercept and k_p , the intraparticle diffusion rate constant (mg g⁻¹ min^{-1/2}).

The kinetic parameters obtained (Table 3) suggest that the pseudo-first order model fits best (with correlation coefficients > 0.97), thereby indicating the probable route for the adsorption of Zn (II). However, considering the initial 50 min of the contact time (Fig. 6), the value of correlation coefficients for the intraparticle diffusion model indicates that the adsorption may be partially controlled by intraparticle diffusion.

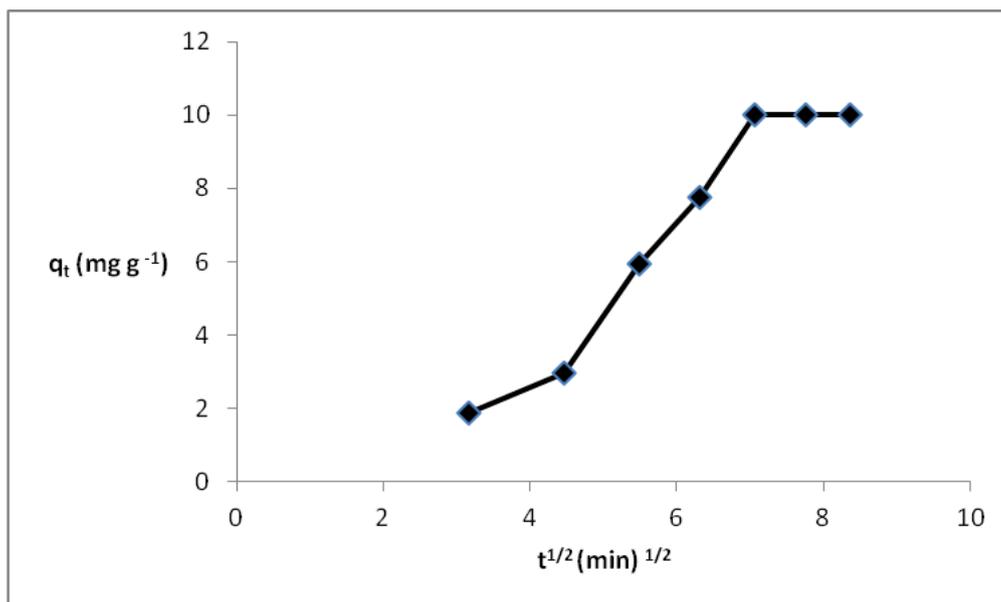


Fig. 6 Intraparticle diffusion plot for the adsorption of Zn (II) onto cumin seeds

TABLE 3 KINETIC PARAMETERS FOR THE ADSORPTION OF ZN (II)

$k_1 (\text{min}^{-1})$	349.34
$q_1 (\text{mg g}^{-1})$	65.79
r_1^2	0.98
$k_2 (\text{g mg}^{-1} \text{min}^{-1})$	30417.81
$q_2 (\text{mg g}^{-1})$	76.33
r_2^2	0.11
$k_p (\text{mg g}^{-1} \text{min}^{-1/2})$	1.99
$C (\text{mg g}^{-1})$	4.96
r_p^2	0.96

As depicted in the plot (Fig. 6), the linear portion corresponds to the bulk diffusion through the intraparticle diffusion mechanism, while the plateau may represent the attained equilibrium. Such a dual nature may indicate that the movement of the heavy metal ion through the particle-solution interface and into the pores of the particle takes place collectively with the adsorption on the available surface of the adsorbent (cumin). The intercept, which is greater than zero, is proportional to the thickness of the boundary layer effect [7]. Since the linear portion does not pass through the origin, therefore it is not the rate limiting step [23, 24].

I. Thermodynamic parameters of adsorption

The important thermodynamic parameters, namely ΔG^0 (free energy), ΔH° (enthalpy), ΔS° (entropy) and K_L (equilibrium constant) may be correlated as follows:

$$\Delta G^0 = -RT \ln K_L, \ln K_L = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}.$$

As reflected in Table 4, the negative value of Gibbs free energies is suggestive of the spontaneity of the adsorption process. Again, the positive value of ΔH° corresponds to the endothermic nature of adsorption, while the negative value of ΔS° (Table 4) indicates that there is a decrease in the randomness at the interface between the solid and the solution during the adsorption of Zn (II) onto the adsorbent.

J. Regeneration studies

For the sustainable use of the adsorbent, it should be able to regenerate for multiple uses. Hence, the metal laden adsorbent was subjected to elution with several mineral acids of varying concentrations. The best elution, with 100% recovery of the metal ions, was obtained with 0.1 M HCl. Thus, the regenerated adsorbent was employed for the loading and elution cycles. It was found that up to 3 cycles, the adsorption capacity was 97%.

TABLE 4 THERMODYNAMIC PARAMETERS CALCULATED FROM THE LANGMUIR ISOTHERM CONSTANT (KL) FOR THE ADSORPTION OF ZN (II)

t (°C)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)
20	-6.68	25.02	-61.68
30	-5.92		
40	-5.40		
50	-5.84		

IV. CONCLUSION

This method represents an alternative technique for the remediation of wastewater. A cheap bio-sorbent, with its low cost and abundant availability, promises the efficient extraction of metal ions from industrial and domestic wastewaters. Moreover, this method does not require sophisticated or cumbersome arrangements for its implementation.

REFERENCES

- [1] A. Islam, A. Ahmad and M. A. Laskar, "Flame atomic absorption spectrometric determination of trace metal ions in environmental and biological samples after preconcentration on a newly developed Amberlite XAD-16 chelating resin containing p-Aminobenzene Sulfonic Acid", *J. AOAC Int.*, vol. 98, pp 165-175, 2015.
- [2] A. Ahmad, J. A. Siddique, M. A. Laskar, R. Kumar, S. H. Mohd-Setapar, A. Khatoon and R.A. Shiekh, "New generation Amberlite XAD resin for the removal of metal ions: A Review", *J. Environ. Sci. (China)*, vol. 31, pp 104-123, 2015.
- [3] N. Oyaro, O. Juddy, E. N. M. Murago and E. Gitonga, "The contents of Pb, Cu, Zn and Cd in meat in Nairobi, Kenya", *Int. J. Food Agric. Environ.*, vol. 5, pp. 119-121, 2007.
- [4] T. K. Naiya, P. Chowdhury, A. K. Bhattacharya and S. K. Das, "Saw dust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions", *Chem. Eng. J.*, vol. 148, pp. 68-79, 2009.
- [5] R. Kumar, M. Ehsan and M. A. Barakat, "Synthesis and characterization of carbon/AlOOH composite for adsorption of chromium(VI) from synthetic wastewater", *J. Ind. Eng. Chem.*, vol. 20, pp. 4202-4206, 2014.
- [6] U. Kumar, "Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review", *Sci. Res. Essays.*, vol. 1, pp. 33-37, 2006.
- [7] M. A. Laskar, S. K. Ali and S. Siddiqui, "Characterization of the kinetics and thermodynamics for the adsorption of zinc (II) on fennel seeds", *Anal. Lett.*, (DOI:10.1080/00032719.2015.1113421).
- [8] R. Ahmad, R. Kumar and M. A. Laskar, "Adsorptive removal of Pb²⁺ from aqueous solution by macrocyclic calix[4]naphthalene: kinetic, thermodynamic, and isotherm analysis", *Environ. Sci. Pollut. Res.*, vol. 20, pp. 219-226, 2013.
- [9] Q. Wu, R. You, M. Clark and Y. Yu, "Pb (II) removal from aqueous solution by a low-cost adsorbent dry desulfurization slag", *Appl. Surf. Sci.*, vol. 314, pp. 129-137, 2014.
- [10] A. O. Jorgetto, R. I. V. Silva, M. J. Saeki, R. C. Barbosa, M. A. U. Martines, S. M. A. Jorge, A. C. P. Silva, J. F. Schneider and G. R. Castro, "Cassava root husks powder as green adsorbent for the removal of Cu(II) from natural river water", *Appl. Surf. Sci.*, vol. 28, pp. 356-362, 2014.
- [11] S. S. Handa, S. P. S. Khanuja, G. Longo and D. D. Rakesh, *Extraction Technologies for Medicinal and Aromatic Plants*, Italy: United Nations Industrial Development Organization and the International Centre for Science and High Technology, ICS-UNIDO, 2008.
- [12] A. Islam, M. A. Laskar and A. Ahmad, "Preconcentration of metal ions through chelation on a newly synthesized resin containing O, O donor atoms for quantitative analysis of environmental and biological samples", *Environmental Monitoring And Assessment*, vol. 185, pp. 2691-2704, 2013.
- [13] N. Kuyucak and B. Volesky, "The mechanism of cobalt biosorption", *Biotechnol. Bioeng.*, vol. 33, pp. 823-831, 1989.
- [14] A. Islam, M. A. Laskar and A. Ahmad, "The efficiency of Amberlite XAD-4 resin loaded with 1-(2-pyridylazo)-2-naphthol in preconcentration and separation of some toxic metal ions by flame atomic absorption spectrometry", *Environ. Monit. Assess.*, vol. 175, pp. 201-212, 2011.
- [15] R. Puranik and K. M. Paknikar, "Biosorption of lead and zinc from solutions using *Streptovorticillium cinnamomeum* waste biomass", *J. Biotechnol.*, vol. 55, pp. 113-124, 1997.
- [16] G. M. Gadd, "Accumulation of metals by microorganisms and algae", in H. J. Rehm (Ed.), *Biotechnology*, 1988, Weinheim: VCH, pp. 401-433.
- [17] I. Langmuir, "The adsorption of gases on plane surfaces of glass, mica and platinum", *J. Am. Chem. Soc.*, vol. 40, pp. 1361-1403, 1918.
- [18] H. M. F. Freundlich, "Über die adsorption in losungen", *Z. Phys. Chem.*, vol. 57, pp. 385-470, 1906.
- [19] M. M. Dubinin and L. V. Radushkevich, "Equation of the Characteristic Curve of Activated Charcoal", *Proc. Acad. Sci. U.S.S.R. Phys. Chem. Sect.*, vol. 55, pp. 331, 1947.
- [20] B. Yasemin and T. Zeki, "Removal of heavy metals from aqueous solution by sawdust adsorption", *J. Environ. Sci.*, vol. 19, pp. 160-166, 2007.
- [21] F. Haghseresh and G. Q. Lu, "Adsorption Characteristics of Phenolic Compounds onto Coal-Reject-Derived Adsorbents", *Energ. Fuel*, vol. 12, pp.1100-1107, 1998.
- [22] D. N. Jadhav and A. K. Vanjara, "A Study: Removal of Dyestuff Effluent Using Sawdust, Polymerized Sawdust and Sawdust Carbon-II", *Indian J. Chem. Tech.*, vol. 11, pp. 42-50, 2004.

[23] F. Helfferch, "*Ion exchange*", New York: Mc Graw Hill Book Co. Inc., 1962.

[24] J. Crank "*The mathematics of diffusion*", London: Clarendon Press, 1965.