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SEQUESTRATION OF ZINC ION USING SUGAR INDUSTRY RESIDUES: AN AVENUE TO ENVIROSAFE

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ABSTRACT

The present study focuses on the removal of zinc from aqueous solution utilising a sugar industry residues (untreated) as an adsorbent. Adsorption experiments were performed by following batch techniques, sorption capacity of the adsorbent determined as the function of pH, initial concentration of the metal solution, contact time and particle size. Various kinetic parameters were evaluated using the observed experimental data from different techniques. The morphological investigations were carried out using Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectrometer (EDAX). The results indicate that the sugar industry residues, a new cost effective industrial based sorbent material holds great potential for the extraction of Zn(II) from the aqueous solution with maximum removal of 95.55% at pH value of 5.

KEY WORDS : Zinc removal, Sugar industry waste, Solution, Sorbent

INTRODUCTION

Industrialization is a big challenging issue nowadays and is mainly related to environmental pollution. The waste water discharged from the industries carries a lot of toxic heavy metals which are harmful to the environment (Barakat, 2011). Heavy metals which are fatal to the environment include lead, mercury, cadmium, arsenic, copper, zinc, and chromium at high concentrations. The main sources of heavy metals to the environment are mining operations, secondary metal production, coal combustion, rubber tyre wear and phosphate fertilizers (Amalina Amirah Bt Abu Bakar *et al*., 2016). In recent studies, it was pointed that the heavy metals were found to remain high in drinking water, soil by means of direct usage and indirect transfer. Direct usage includes consumption by the human society in every area of modern consumerism like construction materials, cosmetics, medicines, processed foods. Indirect transfer of heavy metals includes the discharge from the industries to the water sources. Some metals like copper, iron play an important role for the functioning of critical enzyme systems. Most other metals have no proper role in living organisms and remain toxic even at trace levels of exposure. The metals which are considered to be toxic turn to be harmful in nature by their increased dosage (Hazrat Ali, 2019). They degrade the environment by the contamination with the natural resources, particularly water. The presence of heavy metals in the waste waters has a tendency to bio accumulate through the food chain and remain persistent in the environment. Their presence not only affects the human beings but also the aquatic species too. Owing to these environmental, biological, communal health issues in view, it is considered necessary to attempt and provide an easy, feasible, economical, reliable method for the removal of heavy metals. Several methods have been devised for the treatment of heavy metals which include chemical precipitation, lime coagulation, ion exchange, reverse osmosis, ozonation, solvent extraction, electroplating and electrodialysis (Tonni Agustiono Kurniawan, 2006). In certain cases, biosorption is used as natural method for the removal of heavy metals by utilising the microorganisms, microphytes, macrophytes as adsorbents (Sri Lakshmi Ramya Krishna Kanamarlapudi *et al.,* 2018). A cost effective, environmentally friendly technique i.e., adsorption is used as a best method for the removal of heavy metals (Subhas Sarkar, 2018) where natural adsorbents, industrial by- products can be used as asorbent material either with or without modification.

The objective of the present research is to figure out the sorption capacity of the raw sugar industry residues (SIR) as an adsorbent for the removal of heavy metal, Zinc [Zn(II)] from aqueous solutions so as to facilitate its adsorption ability in comparison with other adsorbents. The optimal condition for increasing the efficiency of this removal process was also investigated.

Experimental Methods

Sugar industry waste (semi-solid material after processing) was collected from the nearby sugar industry located in Palani area, Coimbatore district, Tamilnadu, India and sun-dried for 15 days. The dried material were well grounded, sieved to different particle sizes and sealed in a tight lid separate container for further adsorption studies. Deionised distilled (DD) water was employed throughout the study for the batch adsorption studies.

Adsorbate solution was prepared by dissolving 4.5502 g of $Zn(NO_3)_2$ in 1000 mL distilled water. The stock solution was then diluted to the required concentrations. All experiments were carried out at room temperature and clear solutions obtained during the study were measured using Atomic Absorption Spectrophotometer (Shimadzu AA 6200). The pH of the solutions was monitored and adjusted to the desired value using 0.1M NaOH/HCl as required. The surface morphology of the adsorbents was visualized on JEOL 6360 model scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Characterisation of the sorbent material

The investigation on adsorbent is presented in Table 1. Surface morphology of the sorbent material was examined by SEM and is represented in Fig. 1, 1(a). It was observed that the sorbent material morphology was found to vary before and after adsorption process i.e., dense surface texture with little grooves on the surface gets shifted to smooth surface. EDAX analysis of SIR indicates that carbon, oxygen are the major constituents in the sorbent and the results suggest that they are capable of binding metal ions.

Table 1. Characterisation of the adsorbent

Properties	Adsorbent
pH	6.1
Surface area (m^2/g)	3.282
Carbon content (%)	41.03
Moisture content (%)	3.42
Ash content (%)	10.66
Bulk Density (g/cc)	0.56

Batch Studies

The particle size of the sorbent material has greater influence on the adsorption studies. The adsorption of Zn(II) studied for various particle sizes viz., 0.18

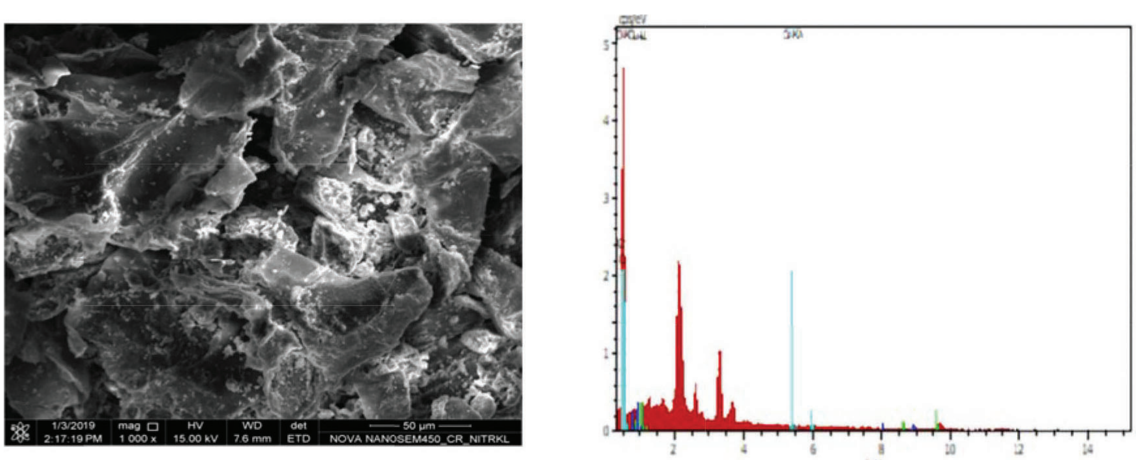


Fig. 1. SEM & EDAX images of SIR.

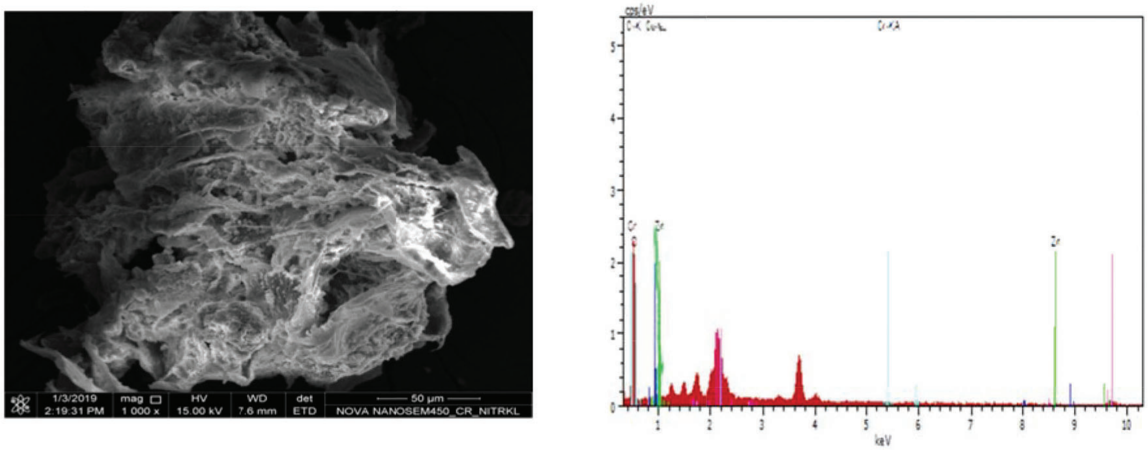


Fig. 1 (a). SEM & EDAX image of Zn(II) loaded SIR.

mm, 0.24 mm, 0.30 m, 0.42 mm, 0.71 mm reveals that the adsorption of metal ion increase with decrease in particle size of the adsorbent as smaller size of the material takes shorter time to equilibrate and is associated with larger surface area which removes more metal ions (Al-Anber, 2011). Consequently, adsorbent particle sizes of 0.18 mm have been selected for the batch experiments.

pH of the metal solution is a very critical parameter in the abstraction of Zn(II) from aqueous solution. The effect of pH on the percentage removal of Zn(II) by SIR is shown in Figure 2. When pH is raised from 3 to 11, removal of Zn(II) was increased slowly from 3 to 5, and thereafter drops slowly. This may be attributed to the competition between the hydrogen and metal ions on the sorption sites, at low pH values (Mamatha *et al.,* 2013). Formation of soluble hydroxy complexes makes sorption studies impossible at higher pH values. Consequently, the working pH value for Zn(II) removal was chosen as 5.0 and the adsorption experiments were performed at this pH value.

The effect of agitation time at different initial Zn(II) concentration, specific uptake by the adsorbent is shown in Figure 3. It was observed that the maximum adsorption occurs at 100 mg/L and further increase in the concentration of the metal ions results in saturation of the adsorbent sites. It was evident (Figure 2) that the maximum sorption had occurred at 30 min for Zn(II) and smooth curves obtained further endorsing no more metal sorption from the solutions (Kannan, 2001; Madu *et al*., 2011).

The effect of adsorbent dosage was studied at various dosages of the sorbent material like 50 – 200 mg in the removal of Zn(II). It was observed that with the increase in dose of the adsorbent, adsorption efficiency was found to rise due to large number of binding sites (Hawari *et al*., 2009). The results indicate that high adsorption efficiency occurs with the increase in dose of the adsorbent upto a certain limit, then it remains almost dropped

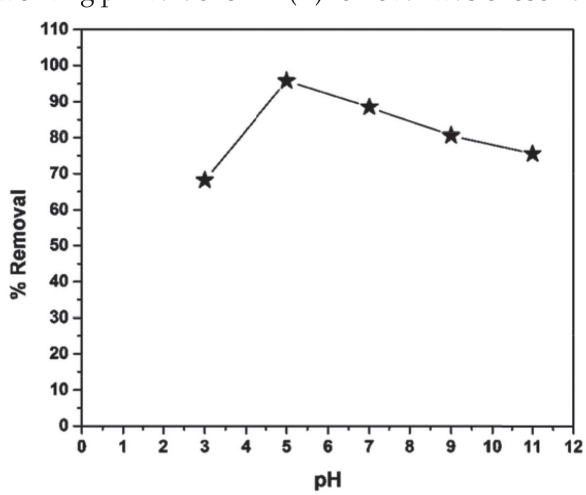


Fig. 2. Effect of pH

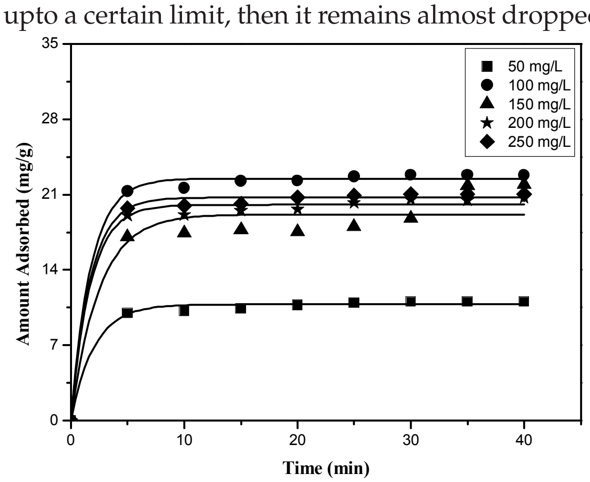


Fig. 3. Effect of agitation time and initial concentration

due to agglomeration and 200 mg of adsorbent dosage is fixed as optimum for studies.

Adsorption Isotherms

Adsorption isotherm explains the interaction between the adsorbate and adsorbent. An equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed. The mathematical models developed by Langmuir, Freundlich and Tempkin isotherms were applied to the equilibrium data in order to understand the sorption mechanism and surface characteristics. Langmuir isotherm is based on the adsorption happening at specific adsorption sites. The Langmuir isotherm equation (Silkeschiewer, 2009; Gupta, 2008) is expressed as follows:

$$C_e/q_e = C_e/q_m + 1/bq_m$$

where, q_m is maximum adsorption capacity (mg/g); b is the Langmuir sorption constant (mg/L); C_e is equilibrium metal ion concentration in solution (mg/l); q_e is equilibrium metal ion concentration on the sorbent (mg/g). A linear plot is obtained from Ce/qe against Ce over the entire concentration range of metal ions where maximum sorption capacity (q_m) calculated as 49.26 represents monolayer coverage of the sorbent with sorbate. The investigated correlation coefficient (R^2) values indicate the suitability of Langmuir model to the selected system.

Freundlich isotherm is applicable to the adsorption processes that occur on heterogeneous surface. The linear form of the Freundlich equation (Kalavathy, 2005) is as follows,

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

Where q_e is amount of metal ion adsorbed per unit weight of the adsorbent (mg/g); C_e is equilibrium metal ion concentration (mg/l); K_f is adsorption capacity; 1/ n is adsorption intensity. The calculated K_F and 1/n values from the freundlich adsorption isothermal plots are listed in Table 2. Smaller K_F values and $1/n$ values (lying between 0 and 1) suggests that the adsorption of metal ions onto the surface of sorbent supports physisorption process.

Tempkin isotherm model considers the effect of adsorbate / adsorbent interactions. The linear form of Tempkin isotherm model (Demirbas, 2008) is given by the following equation,

Table 2. Isothermal Constants

	Parameters	Zn(II) - SIR
Langmuir Isotherm	q_m (mg/g)	49.26
	b (L/g)	0.07
	R^2	0.9904
Freundlich Isotherm	K_F(mg/g)	1.83
	1/n	0.49
	R^2	0.8064
Tempkin Isotherm	A_T(L/g)	1.14
	B_T (J/mol)	5.12
	R^2	0.9287

$$q_e = \frac{RT}{b}\ln AT + \frac{RT}{b}\ln C_e$$

whereq_e is the amount of metal ion adsorbed per unit weight of adsorbent (mg/g); $C_e$is equilibrium concentration (mg/l); b is heat of adsorption (J/mol). Tempkin isothermal data (Table 2) reveals that the heat of adsorption (B_T) remains higher whereas tempkin isotherm constant (A_T) remains lower. This nature indicates a weaker interaction between the sorbate and sorbent in the process (Yuh-Shan Ho, 2000).

Adsorption Kinetics

The kinetic study of an adsorption plays an important role because it affords an important insight into the reaction pathways and mechanism of the reaction. Pseudo first order, Pseudo second order kinetic models, Elovich models are applied to the experimental data.

The pseudo first-order kinetic model has been widely used to predict the metal adsorption kinetics. The metal adsorption kinetics following the pseudo first-order model (Ho, 1999a) is given by,

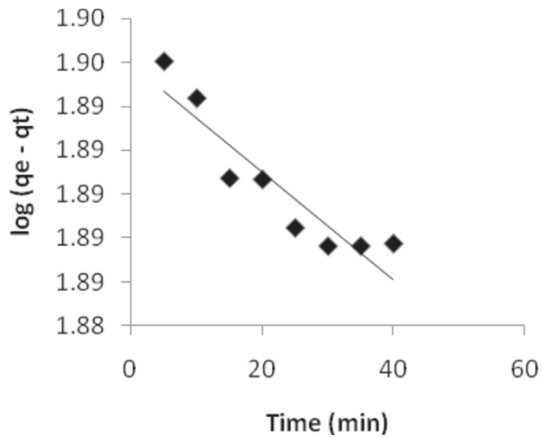
$$\frac{dq}{dt} = k_1\,(q_e - q_t)$$

Where k_1 is rate constant of the pseudo first-order adsorption; q_t is the amount of adsorption at time t (mg/g); q_e is the amount of adsorption at equilibrium (mg/g).

The adsorption kinetic data can be further analyzed using pseudo second-order kinetics (Mckay, 1999 b,c). This is represented by,

$$\frac{dq}{dt} = k_2\left(q_e - q_t\right)^2$$

The linear plots corresponding to pseudo first order and pseudo second order kinetic models are shown in Figure 4. The equilibrium rate constants along with SSE are listed in Table 3. The data (Table



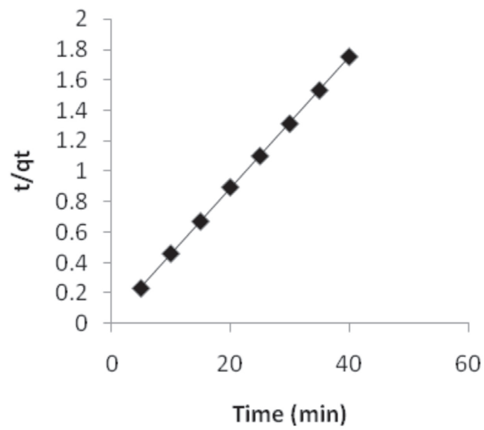


Fig. 4. Pseudo First and Second Order Plot – Zn(II)

3) reveals that the pseudo second order model fitted the experimental record well with a correlation coefficient (R^2) close to unity at low concentration and SSE values are found to be minimum.

The Elovich equation has been applied if the adsorbing surface remains heterogeneous. The Elovich model equation is expressed (Suresh Gupta, 2009) as

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$$

where α is initial adsorption rate (mg/g min); β is adsorption constant (g/mg)

The adsorption rate (α) for Zn(II) shows notable change in their fixed concentration followed by the decline at higher concentration range.

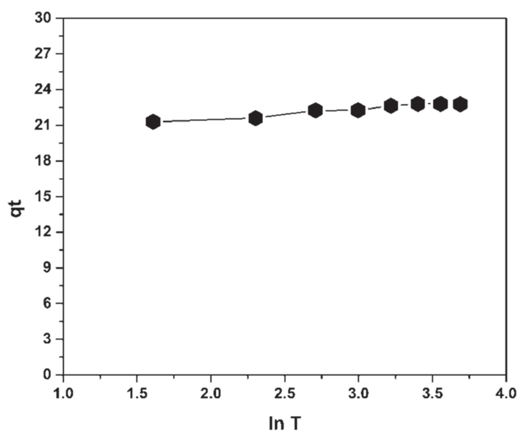


Fig. 5. Elovich Plot

CONCLUSION

The ability of sugar industrial residues, an industrial based sorbent material for removing Zn(II) metal ions from aqueous solution was studied with various parameters such as pH, initial concentration, adsorbent dosage, particle size. The maximum removal percentage was obtained at pH 5 with a dose of 200 mg. The experimental data was found to follow the monolayer coverage of the metal ion on the sorbent surface and best fit the sorption process. Adsorption isotherm and intensity value showed that there is greater affinity for zinc extraction from aqueous solution that initiates a challenge in the water treatment process. Further, this study may extend to detoxify the pollutants

Table 3. Kinetic Constants

Conc. of Metal Ions (mg/L)	$q_e$exp (mg/g)	Pseudo First Order Kinetics				Pseudo Second Order Kinetics			
		q_{e1} (mg/g)	$k_1 \times 10^{-2}$ (min^{-1})	R^2	SSE	q_e^2 (mg/g)	$k_2 \times 10^{-2}$ (min^{-1})	R^2	SSE
Zn(II) - SIR									
50	11.03	3.04	0.92	0.8967	1.63	10.07	0.11	0.9997	0.39
100	22.80	3.72	0.46	0.8588	2.52	18.79	0.11	0.9999	0.81
150	21.80	4.78	0.23	0.7055	2.38	18.05	0.24	0.9999	0.79
200	20.53	4.78	0.12	0.9456	2.29	4.21	1.18	0.9994	1.64
250	21.03	5.14	0.03	0.8733	2.30	17.63	0.10	0.9998	0.75

values are found to be minimum.

from the industrial effluents.

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