Designing of Fabric Reinforced Polymer in the Assessment of Sorption Capacity of Mussel Shell Powder for Divalent Ion: GIS Mapping and Statistical Studies

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Abstract

This paper discusses the efficiency of acid modified mollusc shell powder in adsorbing Zn(II) ions from synthetic wastewater and actual wastewater samples discharged from electroplating industries. The chemically treated adsorbent was characterized in terms of structure and surface properties. The parameters such as, size of the sorbent particles, dosage, initial Zn(II) concentration, temperature, contact time pH and temperature were varied for optimization using batch studies. The adsorbate-adsorbent system was studied by Langmuir, Freundlich, Tempkin and DKR isotherm models. The adsorption experiments were conducted in a column packed with the acid modified mollusc shell powder. Further, a wastewater samples having surpassed Zn(II) concentration levels were collected from the industrial belt in Coimbatore, to assess the potential of the bio adsorbent. A fiber reinforced polymer fabricated with the adsorbent material installed at the effluent discharge plants achieved 100% Zn(II) removal from electroplating wastewaters. Statistical analysis performed using SPSS software showed significant correlation among the input parameters and the analytical results post-adsorption.

Keywords: Adsorption; Zinc ions; Mussel shell powder; Column Studies; Fibre Reinforced Polymers, Effluent Treatment

1. Introduction

Heavy metal contamination in water originates from anthropogenic activities such as industries like textile dyes, tannery, mining, battery, nuclear, electroplating, metal smelting, mining, paint and pigments, pesticides, chemical and manufacturing industries, domestic sewage, automobile emissions and agricultural activities. Heavy metal pollution in water causes serious environmental problems in both developing and developed countries. It is always been a threat to human health and other living beings [1]. Heavy metals ions such as Pb^{2+}, Zn^{2+}, Cr(VI), Ni+, As^{3+}, Cd^{2+} and Cu^{2+} released from industries are considered as highly toxic in nature non-biodegradable, persistent, have potential to be bio-accumulated and cannot be metabolized and posses long biological half life decomposed[2,3].Heavy metals present in contaminated water are poisonous and available in various oxidation states. They have shown better solubility in water and easily taken up by plants, thereby entering food chains and cause adverse effects to human and animals. These heavy metals are not metabolized or decomposed tend to get accumulate in soft tissues which is hazardous to human health. [4].

Although some heavy metals such as zinc, barium, lead, silver are important to human health when they are under the regulatory limit (Zn< 5 ppm; Ba<2 ppm; Pb<0.015 ppm; Ag<0.001 ppm) as recommended by the environmental protection agency (EPA); most of these heavy metals are considered to be harmful at different levels and excessive exposure to them can be fatal [5].

Zinc is very much essential it acts as nutrient for cell growth and helps in metabolism and develop immune system in human body. On the other hand, it poses a serious threat to human life when it surpassed the regular range. When exceeding consumption of it might cause gastrointestinal distress, nausea, vomiting, depression, neurological signs, irritability, loss of appetite, muscular stiffness, diarrhea and increased thirst. Its abnormal concentration could produce renal failure and stomach cancer. According to the European Environment Protection Agency the maximum permissible limit of zinc in potable water is 5 mg/L. The persons who work in metal based industries may exposure to high concentration of zinc between 100 and 500 mg per day can undergo severe health issues, such as: lethargy, hyperamylasemia, pancreatitis, pulmonary edema, renal insufficiency and neurological disturbances [6-8]. Thus, removal of zinc ions is essential to address the consequences of pollution.

Heavy metals from aqueous media and industrial effluents can be efficiently eliminated using various conventional techniques viz., solvent extraction, coagulation, Chemical precipitation [9], membrane filtration, ion exchange [10], reverse osmosis [11] electrochemical technologies, solvent extraction, coagulation/flocculation [12], ion flotation [13] and adsorption [14]. Amongst, adsorption method is found to be a efficient, cost effective and more reliable method for the removal of heavy metal ions from the contaminated water. This method is to be easily implemented and adsorbed heavy metal ions can be regenerated using simple treatment techniques [15]. Many adsorbent materials of plant and animal origin proved effective for the removal of various metal ions [16-21]. These natural materials are readily available, cheap and easily modifiable to suit the needs. In this context, this work investigates the efficiency of chemically treated mussel shell powder in the adsorption of Zn(II) ions from aqueous solutions. Mussel shell belongs to the family bivalve molluscs found in saltwater and freshwater habitats. In most marine mussels, the shell is longer than it is wide, being wedge-shaped or asymmetrical. The external colour of the shell is often dark blue, blackish, or brown, while the interior is silvery and somewhat nacreous. Mussel Shells (MS) generated by these mussel cultivation industries have some applications in the construction industry. However, when the generation of shell volume exceeds the demand, disposal of the shells becomes an environmental issue. Mussel shell is rich in calcium carbonate whose composition. The middle prismatic layer of the shell is composed of crystalline calcium carbonate and the innermost nacreous layer consists of thin layers of calcium carbonate. The chitin composition was found to be 23.25% for this shell composition. These Mussel shells (MS) being animal litter were collected from fish market to assess its sorptive nature in chelating heavy metal ions.

The elimination of zinc ions by the sorbent was studied using diverse adsorption parameters under batch and column experiments. The various isotherm models, kinetic models and thermodynamic parameters were evaluated to explain the removal process. The metal ions desorption from the used adsorbent has also experimented using various chemical agents.

2. Materials and Methods

2.1 Chemicals

Stock solution of 1000 mg/L zinc nitrate was prepared by dissolving appropriate quantity of the zinc salt in water. Aliquots of the adsorbate solutions of varying Zn(II) ion concentrations (100-1000 mg/L: 100 mg/L) were prepared by progressive dilutions from the stock solution, at natural pH conditions.

2.2 Preparation/Treatment of Adsorbent Materials

Mollusc shells were collected from shellfish processing units. The shells were cleansed using double distilled (DD) water repeatedly and converted into a coarse powder using a mortar and pestle. Then, the coarse mollusc shell powder (MSP) was kept in a flat bottom flask containing decinormal hydrochloric acid for 4 hours. Following this chemical treatment, MSP was washed well with DD water again and dried under direct sunlight. This treated powder will be mentioned as TMSP hereafter. The TMSP was crushed well to a fine dust using a laboratory blender and segregated based on the particle size as 85 BSS, 72 BSS, 52 BSS, 36BSS and 22 BSS. These adsorbent samples were stocked in sealed holders. The images of the untreated mollusc shell powder and TMSP (0.18 mm: optimized particle size) are shown in Fig 1a& 1b

Fig. 1a Untreated mollusc shell

Fig. 1b TMSP

Treated mussel shell powder samples of different mesh sizes (15 samples) were microscoped under a CX21i Binocular Microscope to determine the particle size. The dimensions of each sample were measured and averaged. Finally, the particle size was calculated using multiplication factors. The calculated particle sizes for the mesh sizes 85BSS, 72BSS, 52BSS, 36BSS and 22BSS are 0.18 mm, 0.21 mm, 0.30 mm, 0.42 mm and 0.71mm respectively.

2.3 Surface Characterization

A JEOL JFM-6390 Scanning Electron Microscope with EDX was used to study the surface structure of the treated mollusc shell powder. Similarly, a Micromeritics (BEL, Japan Inc.) Surface Area Analyzer was employed to determine the surface area and pore volume by N_2 adsorption at 77 K following BET method.

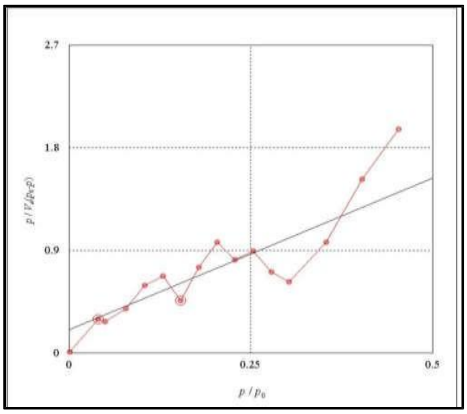


Fig.2a BET plot for TMSP

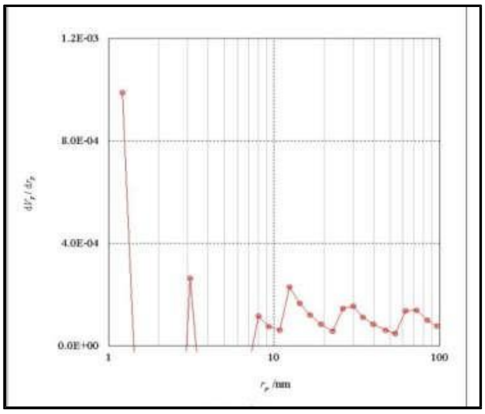


Fig.2b BJH plot for TMSP

Evaluation of the particle/ mesopore size distribution of sorbent material was carried out by BET (Fig.2a) and BJH (Fig.2b) methods. The adsorption performance is highly dependent on the internal pore structure. Pore sizes are classified in accordance with the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC manual., 1982) i.e; micropores (d<20Å), mesopores (20 Å < d< 500 Å) and macropores (d > 500 Å]. Because of the larger sizes of the liquid molecules, the adsorbents for liquid phase adsorbates should possess predominantly mesopores in the structure[22].The mesopores are responsible for the better surface area of TMSP (1.52 m2/g), possible through the activation process. The mean pore diameter value as inferred from BET plot is found to be 24.04 nm. Particles under study are found to possess mesoporous nature predominantly, as their pore diameter lie in the range of 20 Å < d < 500 Å

2.4 Batch Mode Adsorption Studies

In the batch adsorption studies, the Zn(II) samples were shaken well with TMSP in a KEMI agitator. To optimize the system for maximal adsorption, the particle size of TMSP(0.71 mm, 0.42 mm, 0.30 mm, 0.21 mm and 0.18 mm), dosage (200-500 mg 100 mg interval), pre-adsorption concentration of Zn(II) solution (100-1000 ppm; 100 ppm interval), contact time (30 min, 60 min, 120 min), pH (3, 5, 7, 9 and 11)and temperature (293K- 333 K: 10 K intervals) were varied.

The pre- and post-adsorption Zn(II) concentrations were determined using a Shimadzu (AA 6200) atomic absorption spectrophotometer. The percentage of adsorption of Zn(II) ions from the test solutions was calculated by equation (1) [23]

$$\% \text{ removal} = \frac{C0-C}{C_0} \text{ X } 100 \qquad \text{.... (1).}$$

Similarly, application of equation (2) gives the quantity of Zn(II) ions removed by the adsorbent (q).

$$q = \frac{V(C_0-C)}{W} \qquad \text{.... (2)}$$

where V, W, Ci and Ce are, respectively, volume of the solution in L, mass of the adsorbent in g, initial and equilibrium metal concentrations (mg/L).

2.5. Adsorption studies for electroplating industrial wastewater

The adsorption studies were extended to real industrial wastewater discharged from the electroplating industry located in Coimbatore, India. The wastewater containing surpassed concentration of zinc was collected for this study. The conductivity and pH of the collected wastewater were measured. The efficacy of TMSP for the removal of zinc was investigated under column experiments.

2.6. Desorption/Regeneration Studies

The revival of metal ions from the spent TMSP was carried out under batch mode conditions. Double distilled water was run through the exhausted column followed by the addition of 0.01 M H2SO4 as eluent at a collection of 100 mL/15 min. A complete Zn(II) desorption was ensured through periodic analysis of the eluted samples through exhausted medium. After desorption, the packed material was again run with DD water. The regeneration capacity was registered as 90% recovery of TMSP against the freshly packed TMSP.

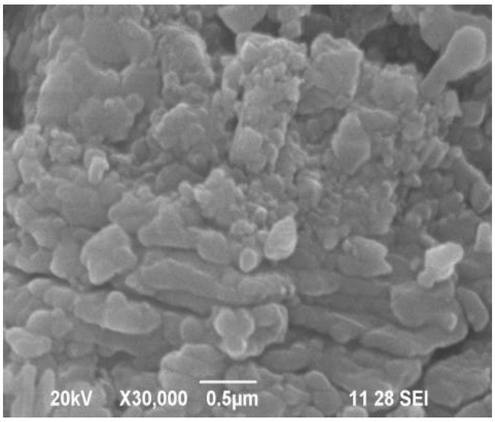
2.7 Statistical Analysis

All statistical analyses were carried out with the help of IBM SPSS (Statistical Product and Service Solutions) package version 20 using ANOVA at 95% confidence level. Pearson Product-Moment Correlation Coefficient Method was used to establish the relationship between the amount of adsorbed Zn(II) ions and the variables.

3 Results and Discussion

3.1 SEM Analysis

Figures 3a and 3b show the surface structures TMSP before and after adsorption of Zn(II) ions. From Fig 3a, it is evident that the surface of the bare TMSP is porous and rough. But, the image after Zn(II) adsorption reveals a smooth surface (Fig 3a). From, these two figures, the adsorption of Zn(II) ions onto the active sites of the surface of TMSP can be confirmed.



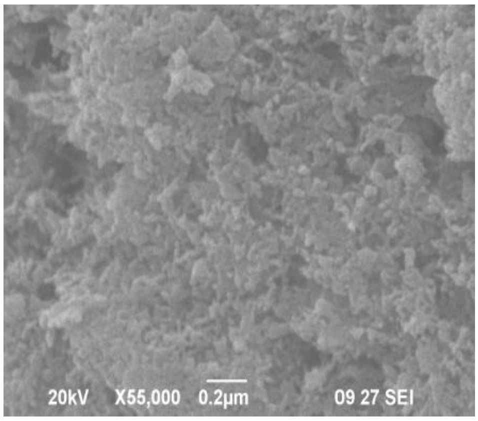
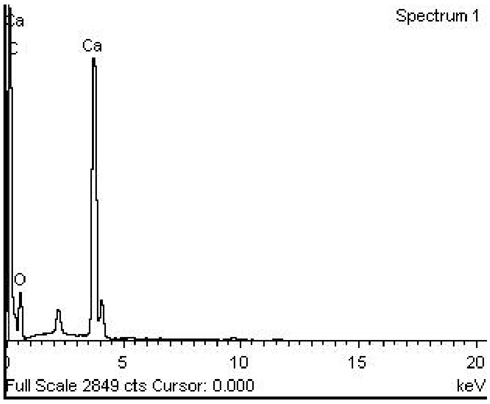


Fig 3a: Unloaded TMSP- SEM **Fig 3b: Zn (II) loaded TMSP- SEM**

3.2 EDAX Analysis



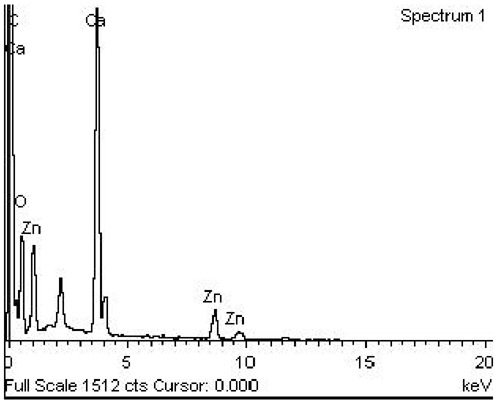


Fig. 4a Unloaded TMSP- EDAX spectra **Fig.4b Zn (II) loaded TMSP- EDAX spectra**

The chemical compositions of the adsorbent material before and after adsorption were determined by EDAX spectroscopy. Figures 4a and 4b, respectively, show the EDAX spectrum of free TMSP and Zn (II)-loaded TMSP. The EDAX spectrum of TMSP showed that oxygen, carbon, calcium and chlorine are the major elements [24]. In the spectrum of Zn (II)-loaded TMSP, a new peak observed at the energy range 8-10 KeV (Fig 4b) confirms the adsorption of Zn(II) ions onto TMSP.

3.3 FTIR Spectral Studies

FTIR spectra of unloaded and Zn(II) loaded TMSP is shown in Fig.5 . The broad intense peak at 3722 cm-1 indicative of the stretching of O-H group [25]. The peak at 1465 cm-1 corresponds to carboxylate groups. The 856 cm-1 peak relates to the presence of aromatic heterocyclic molecules. Inclines and declines in the intensities of the peaks as perceived from the figure, indicate the appropriate shifts that had occurred in the FTIR spectra of Zn(II) laden material.

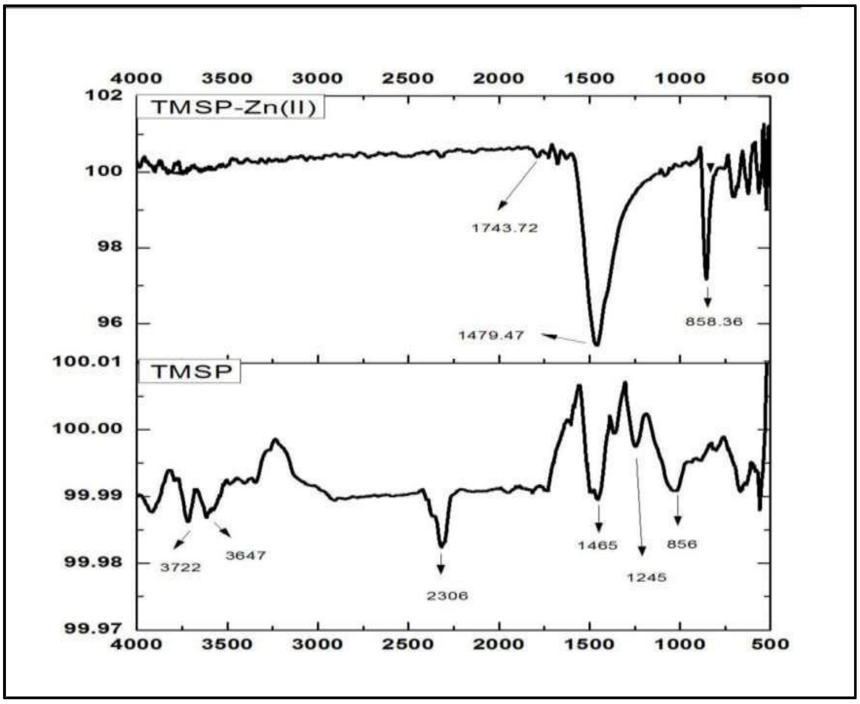


Fig.5 IR spectra of Unloaded and Zn (II) loaded TMSP

3.4 Effect of Particle sizes

The change in adsorption behavior of the Zn(II)-TMSP system with different particle size of the adsorbent (0.18 mm, 0.32 mm, 0.41 mm and 0.71 mm) was experimentally verified and illustrated in the bar diagram (Fig 6). The adsorption of Zn(II) onto TMSP was observed to increase from 19.32 mg/g to 83.76 mg/g, as the particle size decreased from 0.71 mm to 0.18 mm as expected based on the relationship between adsorption and surface area. Thus, 0.18 mm was fixed as the optimum particle size for further experiments. As per the statistical tool analysis (Table 1), the P-value (0.0297) at 95% confident level ($P<0.05$) confirms that there is a significant correlation ($r= -7395$) between the particle size of the adsorbent and the amount of solute adsorbed.

3.5 Effect of Dosage

Bar chart (Fig 7) depicts the adsorption efficiency of TMSP with dosages. The maximum Zn(II) absorption at 1000 mg TMSP is due to the increased surface area. The P-value (0.0005) at 95% confident level ($P<0.05$) shows positive correlation ($r=0.9942$) between adsorbent dosage and the amount of Zn (II) adsorbed.

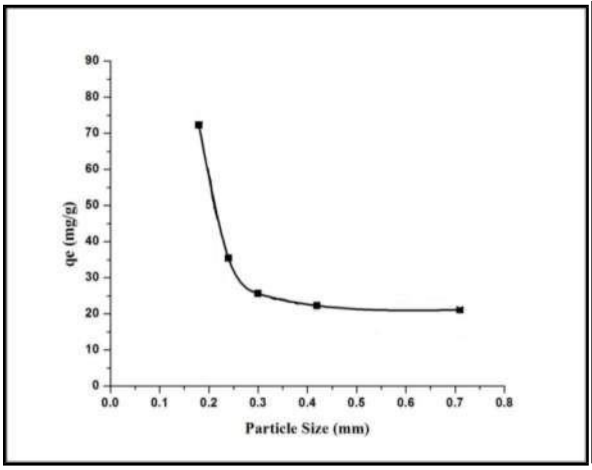


Fig 6: Particle Size-TMSP

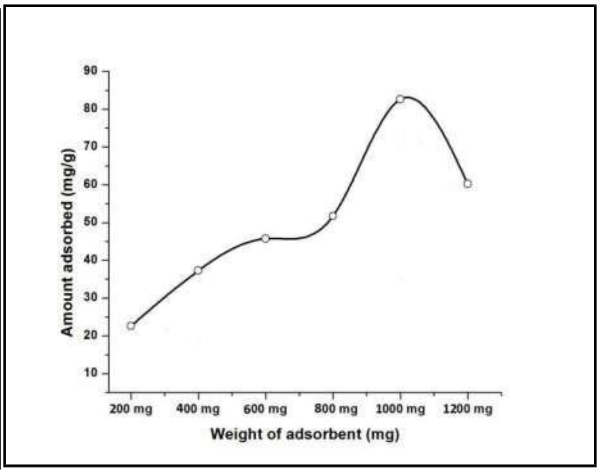


Fig 7: Dosages-TMSP

3.6 Effect of Initial Concentration and Agitation Time

The influence of contact time on Zn (II) removal is shown in the Fig. 8. The amount of Zn(II) ion adsorbed by TMSP for different values of initial Zn(II) concentrations (100-1000ppm: 100ppm intervals) at room temperature can be noted from it. It is evident that as the initial Zn(II) concentration increases, the corresponding amount of absorption also increases from 14.81 mg/g to 83.76 mg/g. Further, it is observed that the percentage of adsorption decreases with increasing initial concentration of metal ions from 100 mg/L to 1000 mg/L. This may be due to decrease in adsorbent binding site at higher initial concentration.

The maximal removal of metal ions was accomplished at a 60 min of contact time and further increase in the contact time has a negligible effect on the rate of adsorption. . Initially the rate of adsorption was increased with increase in contact time due to the appropriate residential time and higher driving force between the metal ions and TMSP [26].

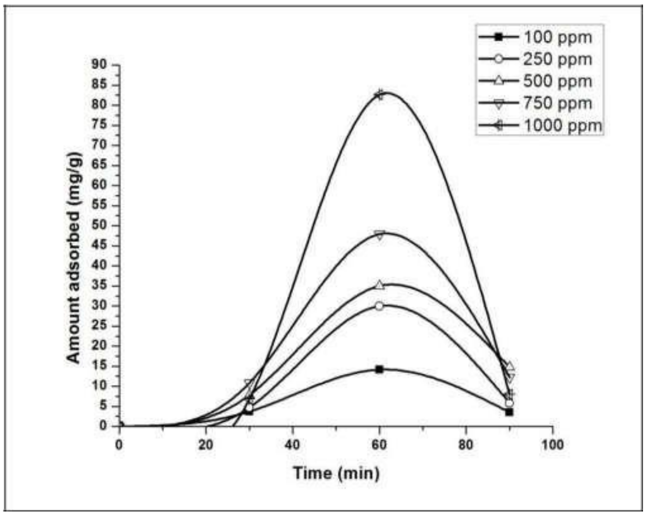


Fig.8 Effect of Initial Concentration and Agitation Time

The reduction in the rate of adsorption at increased contact time may be due to the slow pore diffusion of the solute ion into the bulk of the adsorbent [27]. The attained data was employed to explore the kinetics for the removal of zinc ions by TMSP.

3.7 Effect of pH

The toxic heavy metal ions removal from contaminated water was highly influenced by the initial pH of the solution. This is not only have an effect on the sorbent binding sites but also the metal speciation[28] It is evident from Fig. 9, the adsorption efficiency of TMSP was progressively increased with raise in the solution pH up to 5.5 This may be due to an electrostatic attraction between the surface of TMSP and metal ions. After that the decline in percent removal was observed because of the hydroxides formation. Highly acidic and alkaline pH actually hinders the removal of Zn(II) because of the interferences of hydronium (H+) and hydroxide (OH+) ions with the surface prior to adsorption, which decreases the number of active sites[29]. The calculated P-value (0.0455) at 95% confidence level ($P<0.05$), as evident from Table 2 proves the existence of significant correlation between pH and the amount of Zn (II) adsorption.

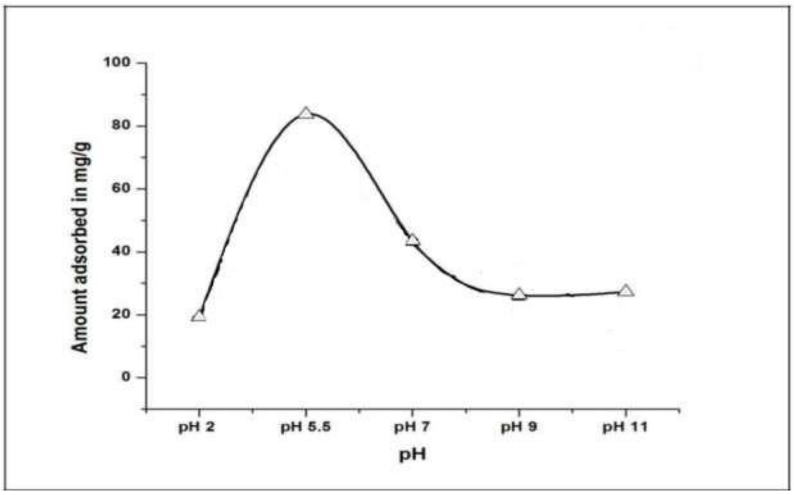


Fig.9 Effect of pH

3.8 Effect of Temperature

Temperature has a pronounced effect on the adsorption capacity of the adsorbents. The effect of temperature (293-333 K: 10 K intervals) on Zn(II) are illustrated in table 1, where the adsorption percentage was observed to increase from 67.30 to 96.00 for rise in temperatures [30,31]. The enhancement of adsorption capacity with temperature may be attributed to the increase in the mobility of ions, which can cause small pores to widen and provide more surfaces for adsorption [32, 33].

Table 1. Effect of Temperature

Adsorbent	Percentage Removal				
	293K	303 K	313 K	323 K	333 K
TMSP	67.30	95.10	95.30	95.90	96.00

3.9 Statistical Analysis

Statistically significant correlation between the experimental variables and the quantity of Zn(II) ions adsorbed onto the surface of TMSP was established by Pearson correlation analysis. These findings indicate that heavy metal pollution can be handled practicably once the factors affecting the adsorption of such ions are fixed. The Pearson correlation parameters are given in Table 3.

Table 2: Descriptive Analyses

Descriptive	Parameters (Amount adsorbed in mg/g)			
	Particle Size	Dosage	Initial Con.	pH
Mean	37.72	56.8	52.43	81.24
SD	30.79	17.29	21.69	10.99
Maximum	83.76	83.76	83.64	98.10
Minimum	19.32	38.65	33.45	67.30
Degrees of Freedom	3	4	4	3
Sum of Squares	1289.3	13.788	758.61	1812.1
Mean Square	644.66	4.596	252.87	906.07
Variance	948.38	299	470.26	120.84
Range	64.44	45.11	50.19	30.8
Skewness	1.96	1.02	1.51	0.65
Kurtosis	3.86	1.05	2.8	2.15

Table 3: Pearson correlation parameters

	Particle size	Dosage	pH
Pearson correlation	-0.739	0.994**	0.094
Sig. (2 tailed)	0.261	0.001	0.906
N	4	5	4

**Correlation is significant at the 0.01 level (2-tailed)

3.10 Adsorption Isotherm Models

Adsorption isotherms state the surface properties and affinity of the adsorbent towards the adsorbate [34]. Thus, different adsorption isotherms were applied to the Zn(II)-TMSP system under the influence of varying initial concentrations using the experimental data to understand the process. Carrying out a linear regression and validation by correlation coefficients (R^2) can authenticate the best fit between the data and type of adsorption isotherm [35].

3.10.1 ***Langmuir isotherm model***

The Langmuir model assumes the occurrence of sorption at precise homogeneous active sites that can attract only a single molecule [36]. A second layer of adsorption is excluded in Langmuir isotherm and thus only a monolayer adsorption is possible, which is expressed by the following equation

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad \text{.... (3)}$$

where

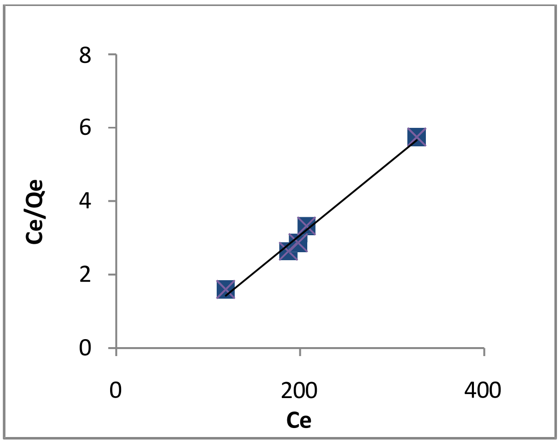
q_e = Sorption capacity of the sorbent (mg/g)

C_e = Equilibrium metal ion concentration in solution (mg/L),

q_m = Maximum monolayer adsorption capacity of the sorbent (mg/g)

b= Langmuir sorption constant (mg/L) related to the free energy of sorption.

The Langmuir constants q_m and b were determined from the slope and intercept values of the linear plot of C_e/q_e versus C_e (Fig 10). Higher the value of b, greater is the affinity of the adsorbent towards the metal ion [37]. The R^2 values (R^2= 0.9919) suggests maximum linearity and best fit of the isotherm for Zn(II)-TMSP system.



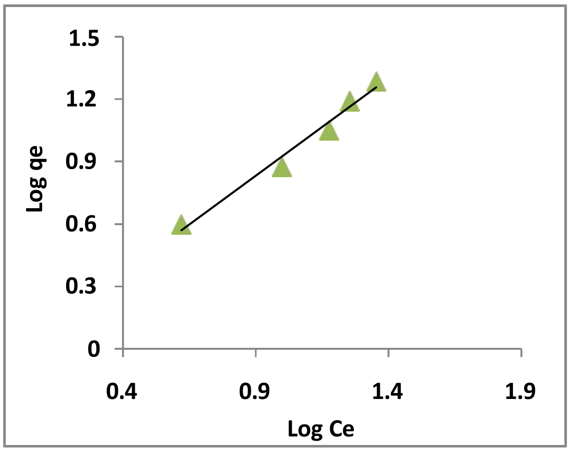


Fig 10 Langmuir Isotherm **Fig 11 Freundlich Isotherm**

3.10.2 Freundlich isotherm model

In general, the adsorption characteristics of an aqueous can be studied by applying Freundlich isotherm. Batch isothermal data fitted to the linear form of the Freundlich isotherm equation,

Log q_e = log k + 1/n log C_e...(4),

where

q_e = amount of metal ions sorbed per unit weight of the sorbent (mg/g)

C_e = equilibrium metal ion concentration (mg/L) of the metal ions in the solution

K_f and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively [38]. From the slope and intercept of the plot log q_e *vs* log C_e (Fig. 11), values of K_f and R^2 were determined (Table 4). The constants and the correlation coefficient values imply that the system does not comply well with Freundlich isotherm (R^2=0.9765) compared to its compliance with Langmuir isotherm (R^2= 0.9919).

Table 4: Isothermal Constants

Langmuir Isotherm			Freundlich Isotherm			Tempkin Isotherm			DKR Isotherm		
qm (mg/g)	B (L/g)	R^2	KF (mg/g)	1/n	R^2	A_T (L/g)	b_T	R^2	qs (mg/g)	E (kJ/mo)	R^2
122.98	25.329	0.9919	20.593	0.476	0.9765	6.982	5.966	0.9883	101.1	10.23	0.983

3.10.3 Tempkin Isotherm Model

Tempkin isotherm was applied to the adsorption data under investigation, as per equation (17). Tempkin constants A_T and b_T which are related to the equilibrium binding constant and heat of adsorption are obtained from the linear plot of ln C_e vs q_e (Fig. 12). The constants and the correlation coefficient values reported in table 4, indicate that the isotherm is obeyed by the systems effectively. Similar results were documented by earlier researchers [39, 40].

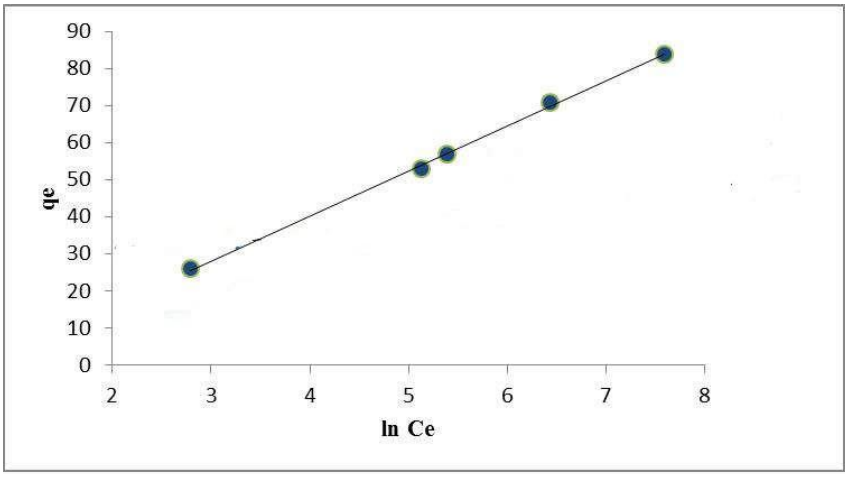


Fig. 12 Tempkin Isotherm Model

3.10.4 Dubinin–Kaganer-Radushkevich Isotherm Model

The equilibrium data were applied to the DKR isotherm model to determine the nature of sorption processes as physical or chemical. Fig.13 represents the DKR plot for Zn(II) system. The value of correlation coefficient shown in table 4, indicate that the DKR isotherm fitted well with the experimental data. The results show that the sorption of the metal ion onto the sorbent material may be carried out via chemical ion exchange mechanism, as their value lie above 8 kJ/mol. Similar results were reported for various other adsorbents [41, 42].

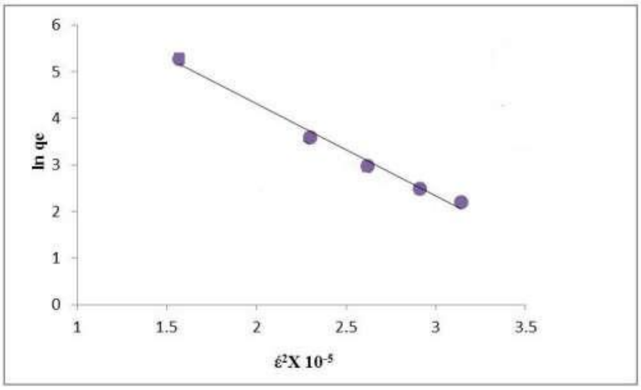


Fig. 13 Dubinin-Kaganer-Radushkevich Isotherm Model

3.11 Adsorption Dynamics

The thermodynamic parameters such as change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated. The ΔH^0, ΔS^0 calculated from the slope and intercept of Vant Hoff plot (Fig. 14) are shown in table 5. The positive values of ΔH^0 indicate the presence of an energy barrier in the adsorption process which is endothermic in nature. The negative values of ΔG^0 indicate the feasibility and spontaneous nature of adsorption of metal ions by the adsorbent [43]. The magnitude of ΔG^0 increased with temperature indicating that the sorption was more favourable at higher temperature [44]. The positive values of ΔS^0 suggest that the increased randomness at the solid-solution interface during the adsorption of metal ions in aqueous solutions onto adsorbents [45]. The low value of ΔS^0 may imply that no remarkable change in entropy occurred during the sorption of metals on the adsorbent [46]. Similar trend was observed for adsorbents such as rice bran [47], tree fern [48], and tamarind seeds [49].

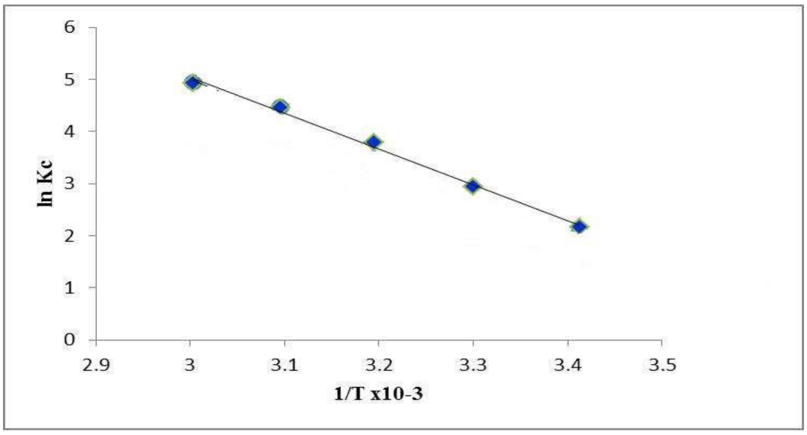


Fig.14 Vant Hoff's plot

Table 5 Thermodynamic Constants

Temp. K	TMSP		
	$-\Delta G \times 10^{-3}$ kJ/mol	ΔH kJ/mol	ΔS J/mol K
293	5.55	5.39	21.28
303	6.01		
313	8.78		
323	9.09		
333	11.98		

3.12 Column Method

The results obtained from the batch mode suggest the suitability and efficiency of TMSP in removing Zn(II) ions. Motivated by the batch mode results, the process was validated for quantification by continuous column runs. The inlet Zn(II) solutions of 1000 mg/L concentration was passed through the column packed with 300 g of 0.18 mm particle size of TMSP and the outlet solution was collected at the rate of 100 mL/2min. The maximum sorption capacity after quantification led to the extension of treating real run-off samples from electroplating industries containing excess Zn(II) concentration.

3.12.1 Column Packing

A glass column (inner diameter = 2.5 cm; height = 30 cm), shown in Fig.15 was first packed with glass wool (thickness = 3 cm) followed by glass beads (thickness = 2 cm). After making these two layers were made firm, about 50 g of the adsorbent (height = 6 cm) was carefully placed over the glass bead layer. Finally, the adsorbent was covered with another layer of glass wool (thickness = 1 cm).

Fig. 15 Zn(II)- TMSP

About 500 mL of 1000 mg/L Zn(II) solution was introduced from the top of the column and the outlet sample was collected at a rate of 100 mL/20 s. After the collection of 1 litre of residual Zn(II) solution, 100% Zn(II) removal was ensured. A gradual decline in percentage removal was observed upto 90% at the end of passing 15 litres of inlet Zn(II) solution. Further reduction was continued upto 20 litres of inlet solution, following that TMSP packed column exhausted. Pictorial representation of the packed column with the experimental solution is shown in Fig 15.

3.13 Desorption/Regeneration Studies

Double distilled water was run through the exhausted column followed by the addition of 0.01 M H_2SO_4 as eluent at a collection of 100 mL/15 min. A complete Zn(II) desorption was ensured through periodic analysis of the eluted samples through exhausted medium. After desorption, the packed material was again run with DD water. The regeneration capacity was registered as 90% recovery of TMSP against the freshly packed TMSP.

3.14 Mapping of Industrial Area-Choice of Study

Many electroplating industries were developed in Coimbatore. The electroplating units located at Kurumbapalayam area (highlighted in Table 6) were selected for the present study as numerous residential colonies nearby were subjected to heavy metal pollution due to improper and non-operative effluent treatment plants. Geographic Information System Mapping (GIS) of Sarcar Sama Kulam (study area) mapped using QGIS 3.8 software is shown in Fig 16, wherein, the green shade indicates the CODEA Industrial Park (10.5 acre) near Saravanampatti which comprises of 22 units of electroplating industries.

Table 6 Electroplating Industries in Coimbatore

S.No.	Name of the Industry	Area of location	Mode of pollution	Metal ions Present
1	Metro metal Finishers	Ellaithottam, Peelamedu	Water/Soil	Cr, Zn, Cu
2	Sangameshwari metal coating	Ellaithottam, Peelamedu	Water/Soil	Cr, Zn, Cu
3	General electroplating	Nava India	Water/Soil	Cr, Zn, Cu, Ni
4	Murugadas electroplating	Patel Road, Gandhipuram	Water/Soil	Cr, Zn, Cu, Cd
5	SilvercrownElecro plating	Mayilampatti Gandhipuram	Water/Soil	Cr, Zn, Cu
6	SIDCO	Ganapathy	Water/Soil	Cr, Zn, Cu
7	**CODEA (22 electroplating units)**	**Kurumbapalayam (SS Kulam)**	Water/Soil	Cr, Zn, Cu,Ni

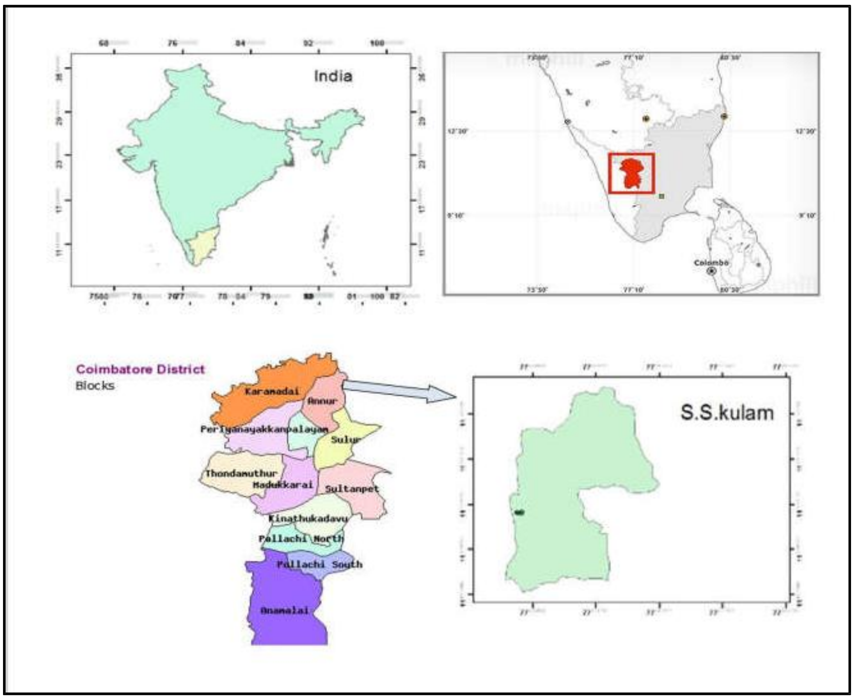


Fig. 16 GIS Mapping of Kurumbapalayam Area

3.15 Collection of Effluents

Wastewaters containing excess Zn(II) than the permissible levels were collected from various electroplating industries in Kurumbapalayam region. About 10 L of these effluent samples were collected in precleaned PET bottles of 1 L capacity from each industrial unit. Analysis of Zn(II) ion (AAS) after a series of dilutions from table 7 revealed their concentrations to exceed the permissible limits (5.0 mg/L). The recorded pH and conductivity values imply that the samples are acidic.

Table 7: Physical data of effluent Samples

S.No	Electroplating Unit	Zn^{2+} (mg/L)	Conductivity	pH
1	I	25.87	21.76	2.3
2	II	3.398	32.98	1.98
3	III	2.817	29.82	2.98
4	IV	23.298	87.87	5.35
5	V	5.876	90.79	0.57
6	VI	4.383	24.4	1.82
7	**VII**	**40.08**	**-0.693**	**3.45**

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3.15.1 Analysis of Industrial Effluents- Batch/Column Methods

Although, all the samples had excess Zn(II) concentration, batch/column experiment setup was limited to the sample collected from electroplating unit VII. The sample was diluted to 50 % and experimentally verified under optimized conditions. About 70% and 90% removal were achieved in batch and column studies, respectively.

3.16 Designing and Installation- Fiber Reinforced Polymer Column

Fiber Reinforced Polymer (FRP) Column was fabricated and installed at Kurumbapalayam, Coimbatore, Tamil Nadu with the assistance of a Design Engineer, Zion Enviro Systems Pvt. Ltd., Chennai. The dimensional and TMSP packing are shown below

FRP Column:		Column Bed
Volume	3 L capacity	TMSP – 2 kg of size 0.18mm
Diameter-	6”	
Height	20”	
Max. flow rate	100 L/h	
Mini. Flow rate	25 L/h	

The pictures representing the FRP Column, packing of material, installation and operation at field level is shown in Fig.17

Fig.17. FRP Column

The performance of the installed FRP Column was assessed by the passage of effluent sample [Zn(II)] through column inlet at a flow rate of 100 mL/5 min. About 15 L of the effluent sample was collected through the outlet and their residual concentrations were analyzed. The efficiency of the column was outstanding (0.5 mg/L of residual Zn(II) against 40 mg/L initial concentration).

4. Conclusion

Mollusc shell powder treated with HCl (TMSP) was found to be an economical and efficient adsorbent for the removal of Zn(II) ions from aqueous solutions. The unloaded and Zn(II)-loaded TMSP samples were characterized structurally and morphologically by various characterization techniques. The surface analysis of Zn(II)-TMSP showed notable changes in the surface properties. The parameters such as, particle size of the adsorbent, dosage, initial concentration of Zn(II) ions, contact time, pH and temperature were optimized for maximal Zn(II) removal by batch studies. The Langmuir, Freundlich, Tempkin and DKR isotherm models were studied to understand the type of adsorption. Langmuir isotherm showed the best fit with maximum sorption capacity of 122.9mg/g. The adsorption capacity of TMSP was also confirmed with column studies. Then, wastewaters discharged from electroplating industry with surpassed Zn(II) concentration were collected and subjected to batch/column experiments. As close as 100% of Zn(II) removal from effluent wastewaters recorded in column studies against the batch studies (85%) under similar conditions. The exhausted TMSP material of the column could be desorbed using 0.01M H_2SO_4. Based on the column results and optimized conditions observed both at the laboratory and field levels for effluent analysis, a Fibre Reinforced Polymer (FRP) column was fabricated and installed at Kurumbapalayam. Statistical studies showed a significant correlation between the experimental variables and the quantity of Zn(II) ions adsorbed.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

A data availability statement is present within the text of the manuscript.

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