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Sorption Capacity of *Bivalve molluscs* Shell in the Removal of Divalent ION from Aqueous Solutions

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Abstract : Environmental protection emphasizes the use of ecofriendly materials instead of chemicals to minimize pollution. The present work deals with the utilization of acid treated Mussel shell powder, an mollusc shell waste for the adsorption of Pb(II) from aqueous solutions. TMSP is characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDAX), Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) analyses to study the surface morphology, elemental constitution, determination of surface area and pore structures. Batch equilibration studies are verified for the operating factors viz., particle sizes/ doses of the sorbent material upon a range of initial aqueous concentrations of Pb(II) at different temperatures, agitation time and pH of the Pb(II) -TMSP system to assess the sorption capacity which is recorded as 83.6 mg/g implying its efficiency to be three fold times more than the reported values for varied sorbents by other researchers. The applicability of Langmuir and Freundlich isotherms at various initial concentrations are plotted for Pb(II) -TMSP system wherein the best straight line is well fit for Langmuir model indicating monolayer adsorption. Continuous column running for quantitative estimation of Pb(II) removal from the bulk of the solution is carried out by the chosen sorbent.
Keywords: bivalve molluscs shell, adsorption, lead ion, aqueous solution, column.

1. Introduction

Water pollution is of great global concern and its crisis is acute in India requiring evaluation and revision of water resource policies from time to time at all levels. Due to the rapid industrialization, toxic metal ions have been excessively released into the environment. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery/ paint/ pigment manufactures, tanneries, petroleum refining, pesticides, printing and photographic industries, etc[1]. The present work is focused on lead pollution, the reason being that it is lethal even at very small doses, to living beings. The observed ailments related to health issues due to lead consumption at varying levels are headache, dizziness, nausea, vommitting, chest pain, shortness of breath, tightness of chest, rapid respiration, dry cough, nephritis and extreme weakness at a concentration exceeding the recommended limit[2].

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Several technologies such as membrane separation, electrochemical precipitation, ion exchange, preconcentration, fertilization and adsorption[3] have been reported for trapping toxic ions. Of these, asorption is a promising technique due to its simplicity, high efficiency, easy handling, technical feasibility, economic viability and social acceptability[4].

Ecofriendly materials are found to possess excellent sorptive nature. The present work deals with the removal of Pb(II) from aqueous solutions using animal waste material ie; *Bivalve molluscs*Shell being litter wastes and also research work has not been reported elsewhere in analyzing its sorption potential.

2. Materials and Methods

2.1 Adsorbent preparation

Bivalve molluscs shells (Mussel Shells) were collected from the coastal areas of Tamil Nadu, India. The shells were cleaned, reduced to small sizes in a mixer blender followed by several washings in order to remove sand particles and finally sun dried for 24 hrs. The dried shells were soaked in 0.1N HCl for 4 hours to neutralize calcium carbonate present, later the dried shells were washed many times with double distilled water, air dried and segregated into different particle sizes (85 BSS, 72 BSS, 52 BSS, 36BSS and 22 BSS) using standard test molecular sieves (JAYANT Scientific Instruments Co., Mumbai). The Treated Mussel Shell Powder (TMSP) of varying sizes were stored in an air tight containers.

2.2 Particle Size Determination

Varied mesh sizes of TMSP were subjected to image microscopic analysis Binocular Microscope (OLYMPUS make, Model- CX21I) in order to determine the particle sizes. Fifteen different granular particles of each mesh size were chosen for the measurement of lengths and breadths to arrive at an average, as no two single particles are alike. By applying multiplication factors, the particle sizes were calculated. The calculated particle sizes corresponding to the mesh sizes of 85BSS, 72BSS, 52BSS, 36BSS and 22BSS are 0.18 mm, 0.21 mm, 0.30 mm, 0.42 mm and 0.71 mm respectively. The microscopic structure of TMSP (0.18 mm) is depicted in Fig 1.

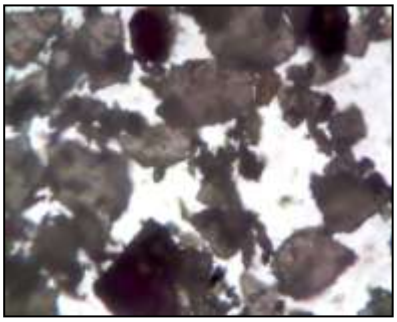

Fig1 :Optical Microscopic Image

2.3 Surface Characterization

Surface morphology of TMSP was analyzed using Scanning Electron Microscope (SEM) coupled with energy-dispersive X-ray spectroscope (EDX) (***JEOL JFM- 6390***). The surface area and volume of the pores were determined with Micromeritics ***BEL, Japan, Inc*** Surface Area Analyzer using the BET method by N_2physisorption at 77 K.

2.4 Batch adsorption experiments

The influence of varied operating parameters viz., particle sizes, (0.71 mm, 0.42 mm, 0.30 mm, 0.21 mm and 0.18 mm) dosages (200 mg, 300 mg, 400 mg and 500 mg), initial concentrations of the aqueous Pb(II) solutions, (100-1000 ppm: 100 ppm intervals) predetermined time intervals between the sorbate and sorbent species, (30 min, 60 min, 120 min) pH of the medium (3, 5, 7, 9 and 11) and temperature of the system, (293K-333 K: 10 K intervals) was experimentally verified. 50 ml of the adsorbate species taken in 250 ml Erlenmeyer flasks with the sorbent material agitated under the planned conditions in a mechanical shaker. The initial and residual Pb(II) concentrations were analyzed using Atomic Absorption Spectrophotometer : Shimadzu (AA 6200) model.

2.5 Data Evaluation

The percentage adsorption of metal ions from aqueous solutions is estimated using the following equation[5]

$$\% \text{ adsorption} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad \text{…. (1)}$$

The amounts of metal ions adsorbed (q) are calculated using the mass balance equation

$$q = \frac{V(C_i - C_e)}{W} \qquad \text{…. (2)}$$

where, V is the volume of the solution (L), m is the mass of the adsorbent (g), C_i and C_e are the initial and equilibrium metal concentrations (mg/L) respectively.

3. Results and Discussion

3.1 SEM Analysis

The surface morphologies of the unloaded and Pb(II) loaded TMSP are depicted in figures 2a & 2b. Figures 2a represents a highly porous nature of the surface with coarse textured pores of different shapes. The smooth covered pores on the surface as observed in fig 2b against fig 2a, indicate the binding of Pb(II) ions onto the surface active sites leading to diminished ruggedness of TMSP (fig 2a). This can be evidenced from the visible surface pores as depicted in figure 2a are not distinct in fig 2b.

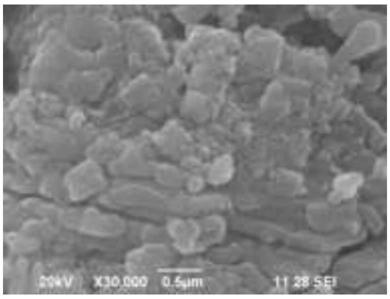

Fig 2a: Unloaded TMSP

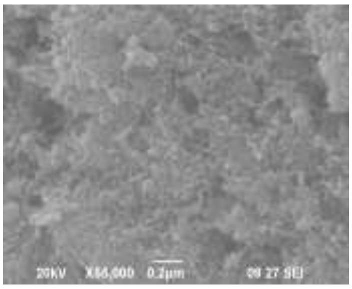

Fig 2b: Pb(II) loaded TMSP

3.2 EDAX Analysis

The EDAX spectra were recorded to analyze the elemental constitution of TMSP qualitatively. The corresponding EDAX spectra of TMSP are depicted in figures 3a and 3b, indicative of the presence of O, C, Ca and Cl, theprinciple elements of any adsorbent[6]. The appearance of new peak at an energy range of 9-15 KeV (fig 2b), confirms the adsorption of Pb(II) by TMSP.

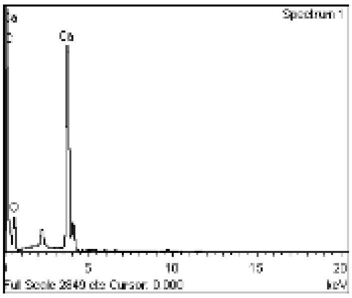

Fig 3a: Unloaded TMSP

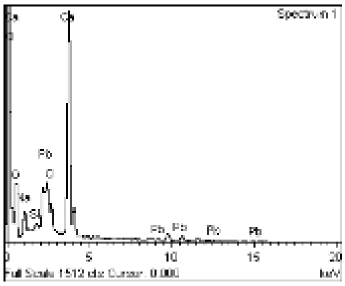

Fig3b: Pb(II) loaded TMSP

3.3 Effect of Particle sizes

The system response under the influence of varying particle sizes viz., 0.18mm, 0.32mm and 0.41mm for Pb(II)- TMSP system were experimentally verified and are illustrated in figure 4. The inverted parabolic curve suggests an increase in amount adsorbed from 29.2mg/g to 83.64 mg/g, against the particle size from 0.71mm to 0.18mm. This may be due the fact that the increase in sorption depended on the large external surface area for smaller particle sizes. 0.18mm being the size where maximum amount had been adsorbed, is fixed as the optimum particle size for further experiments.

3.4 Effect of Dosage

Figure 5 represents the experimental studies performed in order to optimize the dosage of TMSP required where maximum adsorption efficiency is found to be 83.6mg/g for a dose 1000 mg TMSP. Thenceforth, 1000 mg is fixed as the optimum dose for maximum removal of Pb(II) ions.

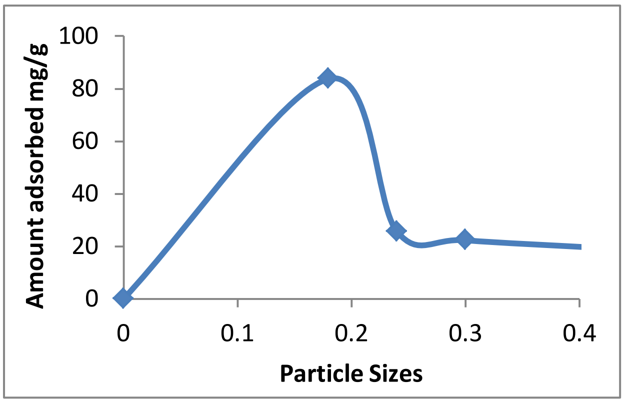

Fig 4: Influence of Particle Size

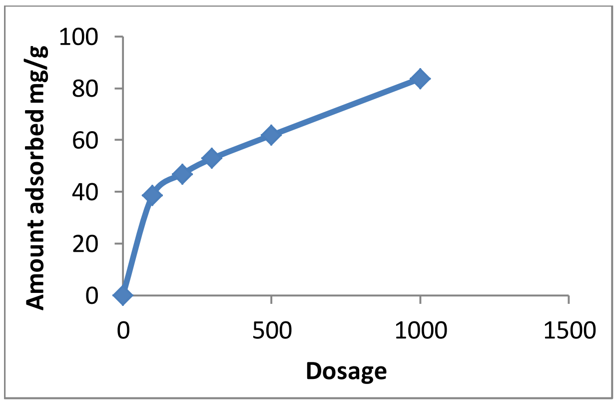

Fig 5: Influence of Dosage

3.5 Effect of Initial Concentration and Agitation Time

It is noted from the bar chart that the amount adsorbed at different initial concentrations of Pb(II) (100-1000ppm: 100ppm intervals) relates the direct proportion of Pb(II) adsorbed against increasing concentration of aqueous environments (23.81 mg/g to 83.6mg/g at 30 mins of contact time). Also, further increase in the contact time beyond 30 mins, registered a negligible effect on the adsorption rate. The mechanism of solute transfer to the solid may be due to diffusion of the fluid film around the adsorbent particle and later through the pores into the internal adsorption sites[7]. The diminished rate of adsorption at further delayed agitation time shall be probably due to the slow pore diffusion of the solute into the bulk of the adsorbent.

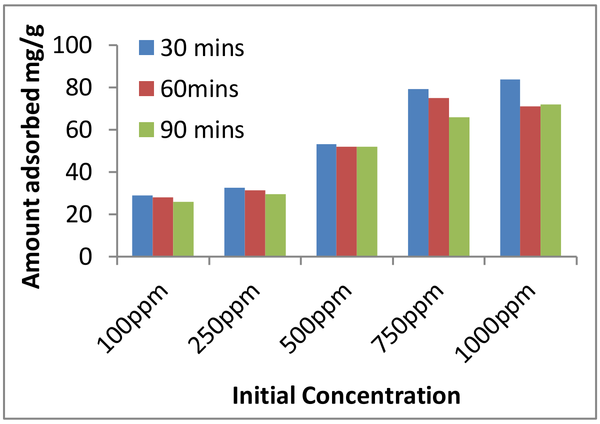

Figure 6: Influence of agitation time

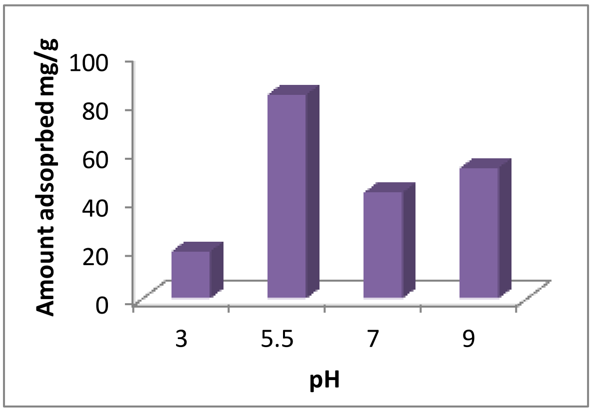

Figure 7: Influence of pH

3.6 Effect of pH

pH plays an important role in the adsorption process. The amount of Pb(II) ions adsorbed under the optimized conditions (0.18 mm & 1000 mg of TMSP, 1000mg/L of Pb(II) solutions) at varying pH environments indicated a maximum adsorption capacity to occur at pH 5.5. Mostly researchers have reported pH 5-7 to be an optimum pH for trapping heavy metal ions[8,9]. The reduced removal of Pb(II) at acidic pH 3 shall be attributed to the fact of preferential protonation of H^+ onto the sorbent surface. Similarly, Pb(II) undergo hydroxide precipitation at alkaline pH ranges (7 & 9) which hinders its availability to get adsorbed onto TMSP.

3.7 Adsorption Isotherms

A series of solutions containing different initial concentrations of Pb(II) were prepared and the batch equilibration studies were carried out to assess the applicability of the adsorption isotherms under the specified conditions, followed by further analysis to study the fit in of the isothermal plots based on the calculations of equilibrium concentrations and amount adsorbed.

3.7.1 Langmuir model

The monolayer sorption model with the linearization plot of $q_e$vsC_e was expected to give a intercept of $1/q_{max}$ and slope $1/q_m$to find the constantsq_{max} and K_a.

$$(C_e/q_e) = 1/(K_a q_{max}) + C_e/ q_{max}$$

where,

q_e = the equilibrium metal ion concentration on the sorbent (mg/g), C_e = the equilibrium metal ion concentration in solution (mg/L), q_m = the maximum monolayer adsorption capacity of the sorbent (mg/g) and K_a= the Langmuir sorption constant (L/mg) related to the free energy of sorption.

b and q_m are Langmuir constants related to the energy and maximum adsorption capacity respectively. Langmuir plot of Ce / qevsCe depicted in fig.8 shows a straight line. The Langmuir constants, b and qm were calculated from the slope (1/qmax) and intercept ($1/q_{max}.K_c$) respectively. The R^2 value of 0.9919 from the plot suggests maximum linearity and fit in of the Pb(II)- TMSP system on Langmuir adsorption isotherm.

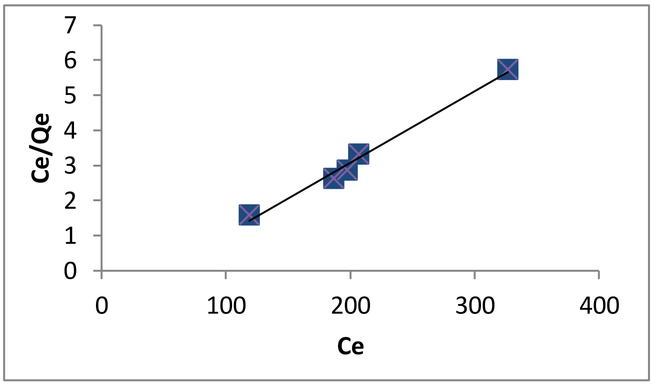

Figure 8: Langmuir Isotherm

3.7.2 Separation factor (RL)

The linearity of the Langmuir isotherm can be used to predict whether a sorption system is favourable or unfavourable. Accordingly, the essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless parameter called the separation factor or equilibrium parameter R_L, which is defined by the following relationship[10].The R_L values for all the system is between 0.006 and 0.096 (Table 1) indicating favourable adsorption.

Table 1: Equilibrium Parameter R_L for Pb(II) system

Conc. of Metal Ion (mg/L)	Pb(II)-TMSP
100	0.096
250	0.006
500	0.017
750	0.006
1000	0.016

$$R_L = \frac{1}{(1 + b\,C_i)}$$

where, C_i is the initial Pb(II) concentration (mg/L). The parameter R_L indicates the shape of the isotherm and the nature of the sorption process[11] shall be

$R_L > 1$ Unfavourable isotherm, $R_L = 1$ Linear isotherm
$R_L = 0$ Irreversible isotherm, $0 < R_L < 1$ Favourable isotherm

3.7.3 Freundlich model

The Freundlich isotherm is the most widely used non-linear sorption model. This model proposes a multilayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interaction between adsorbed molecules. The Freundlich equation is expressed linearly as

$$\log Q_e = \log K_f + 1/n \log C_e$$

The values of K_f and 1/n were obtained from the intercept and slope of a plot of log qe versus log C_e.$K_f$and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively[12]. From the slope and intercept of the plot log $q_e$vs log C_e (figure 9), values of K_f and R^2 were determined (Table 2). The constants and the correlation coefficient values (table 2) imply that Langmuir isotherm (R^2= 0.9919) is obeyed by the system less effectively as compared to Freundlich isotherm (R^2=0.9765).

Table 2: Langmuir, Freundlich and Tempkin constants data

Adsorbent	Langmuir Constants			Freundlich Constants			Tempkin Constants		
	q_m	B	R^2	K_f	1/n	R^2	B_t	A_t	R^2
TMSP	22.987	25.329	0.9919	10.593	0.476	0.9765	12.069	8.654	0.9721

3.7.4 Tempkin model

Tempkin isotherm equation contains a factor that explicitly takes into account adsorbent-adsorbate interaactions. It assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate repulsions and the adsorption is a uniform distribution of maximum binding energy[13]. The linearized form of isotherm is [14]$q_e = B_T \ln A_T + B_T \ln C_e$

where, $B_T = RT/b_T$, T is the absolute temperature in Kelvin and R is the universal gas constant, 8.314 J/mol K. The constant b_T is related to the heat of sorption. The constant A_T is the equilibrium binding constant corresponding to the maximum binding energy. The Tempkin constants A_T and b_T were obtained from the intercept and slope of the linear plots of q_e vs $\ln C_e$ as shown in figure 10.

The constants and the correlation coefficient values (table 2) imply that Tempkin (R^2= 0.9721) and Freundlich (R^2= 0.9765) isotherms are obeyed by the system less effectively when compared to Langmuir model (R^2= 0.9919).

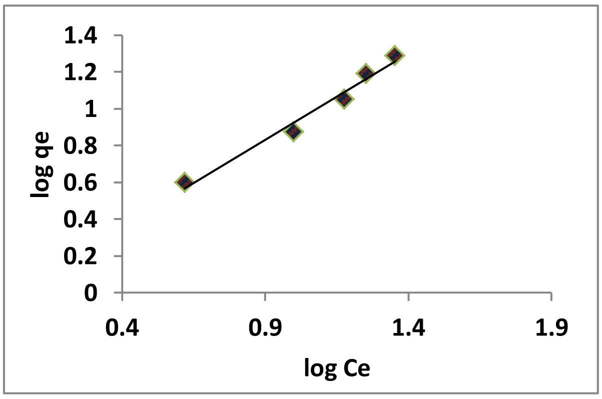

Fig 9: Freundlich Isotherm

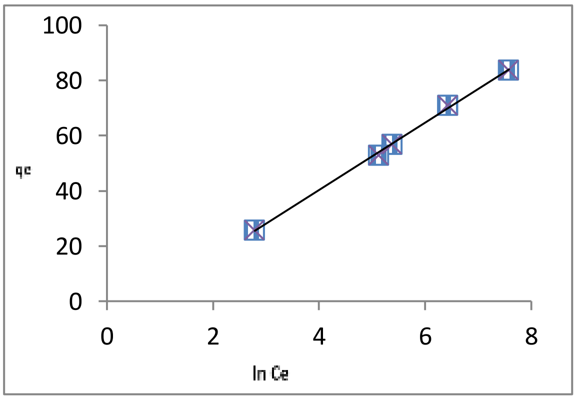

Fig 10: Tempkin Isotherm

3.8 Column Method

The results pertaining to the influential nature of variable parameters, on the basis of batch mode assessment insist the feasibility and compatibility of TMSP in trapping Pb(II) ions. Based on these observations, column experiments were performed to quantify the sorbent characteristics through the continuous column run. The inlet solutions for the column being aqueous Pb(II) ions under optimized conditions of 0.18 mm particle size of TMSP at a Pb(II) concentration of 1000 mg/L followed by extension to electroplating effluent wastewaters containing excess Pb(II) concentration.

3.8.1 Column Packing

The column is made up of cylindrical glass tube, the inner diameter being 2.5 cm and the height is 30 cm. It was packed with TMSP between two supporting layers of glass wool, spread with the glass beads at the top of the already packed glass wool layer placed at the bottom. The step by step packing is as: Glass wool layer (3 cm thickness), glass beads (2cm thickness), TMSP (50 grams: 6 cm height), glass wool (1 cm thickness). These materials were loaded from the top of the column and allowed to settle by gravity force.

500 ml of 1000 mg/L of Pb(II) solution was poured into the column from the top and the flow rate was adjusted as 100 ml collection of the outlet sample at a rate of 20 seconds time interval. At the end of passing 1 litre of the solution, a maximum efficiency of 100% of Pb(II) removal was registered. The percentage removal was observed to decline upto 90% after passing 15 litre inlet Pb(II) solution. Further decline was envisaged upto

20 litres of inlet solution and then the column went exhausted. The packed column with the experimental solutions are represented in fig 11.

Fig 11: Column Experiment

3.8.2 Desorption/Regeneration Studies

After the elution of Pb(II) ions, at quantities of 20 liters approximately, the columns packed with TMSP were washed with double distilled water followed by 0.01 M H_2SO_4 runoff, later with DD water, the collection rate being fixed as 100 ml/15mins. This desorption was carried out to assess the regeneration capacities [15,16] wherein the efficiency of TMSP was assessed as 90% recovery back against the exhausted columns.

4. Conclusion

Mussel Shell Powder (MSP) an eco-friendly and cost effective material was employed for the removal of Pb(II) ions from aqueous solutions. The unloaded and metal loaded materials were subjected to SEM, EDAX and BET studies in order to determine the surface morphological differences, elemental constitutions and surface area which supported the characteristic changes that had occurred on the loaded Mussel Shell Powder. Parametric conditions were optimized in tune of maximum percentage removal (98.1%) for Pb(II)- TMSP system by Batch mode: 0.18mm particle size, 1000 mg dosage, 30 minutes agitation time, 1000 mg/L initial concentration of Pb(II) ions, pH 5.5 of the solution medium at room temperature. The calculated correlation coefficient values from three isothermal applications viz., Langmuir, Freundlich and Tempkin indicated that Langmuir isotherm had best fit than the Freundlich and Tempkin models. Column studies were experimentally verified to quantify the sorbent characteristics and to assess TMSP efficiency in chelating Pb(II) ions from bulk of the solution. The exhausted TMSP material of the column was desorbed using 0.01M H_2SO_4 medium. The effective application of TMSP as an adsorbent to treat aqueous solution is the outcome of the present study.

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