



Quantification of Adsorptive Performance of Sea Urchin Spines on Lead by Batch Process

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Abstract: The present study investigates the adsorption capacity of Sea Urchin spine powder as a biosorbent for removing lead ions from an aqueous solution. The sea urchin spine is found to be most effective at a pH of 6 and a contact time of 57 minutes. The kinetic and isothermal models were used to evaluate the equilibrium biosorption data and finally understand the mechanism(s). The results show that the pseudo-first-order and intra-particle diffusion kinetic models provide a good correlation for the sorption of lead onto the sorbent. The peak biosorption of 83.61 % is attained at 57 min of agitation with 0.1 g/30 ml of 63 m size biosorbent mixed in 30 mL of solution ($C_0 = 20$ mg/L). The maximum biosorption capacity for lead is 14.367 mg g⁻¹ indicating the adsorptive capacity of Sea Urchin spines under favorable process conditions.

1. INTRODUCTION

Metals are natural elements extracted from the earth, and have been used for millennia in industrial products (1). Most heavy metals dissolve in water and form water solutions, accumulating at trace levels under certain environmental conditions, damaging the environment and unable to be separated with ordinary means, making them the main pollutants of seawater, soil, industry, and even treated waters (2).

1.1 Heavy metals

Heavy metal pollution is inevitable because waste from factories, refineries, waste treatment facilities and toxins are deposited directly into local water sources without being properly treated (3). Lead, mercury, arsenic, cadmium and chromium are highly toxic elements in nature.

Ion exchange, membrane, precipitation, adsorption and electrochemical technology are used to eliminate metal-rich industrial effluents (4,22). Ion exchange is a

medium for removing cat ions or ions from their diluted water solutions. The membrane process includes reverse osmosis, electrolysis and ultrafiltration. In reverse osmosis, heavy metals are removed by means of membranes, and pressure differences cause solvent movement on the membranes (5). Due to precipitation, metals soluble in water are removed and the addition of organic polymers such as aluminum, lime, iron salts, and water-soluble compounds is used. Adsorption is a surface phenomenon that removes substances from liquid or gas mixtures with porous solids and surface-active solids (6).

However, this approach is expensive both in capital and operating costs, requires pretreatment, is ineffective in high concentrations and produces high amounts of sludge, which may be harmful to the environment. As a result, the search for cost-effective, efficient and environmentally friendly wastewater treatment systems, a new technique for low-cost treatment of metal pollution wastewater, has begun. This has urged



attention to biosorption based on the binding capacities of various biological materials.

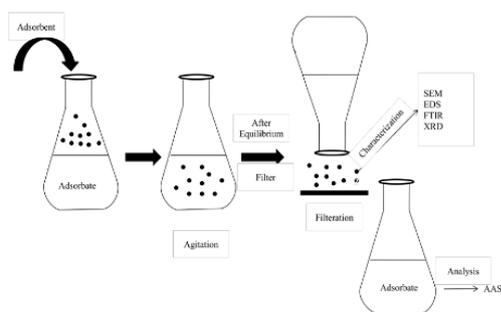


Fig.1 Batch Adsorption process in water treatment

However, the approach is costly in terms of capital and operating costs, requires pretreatment, is inefficient at high concentrations and generates large quantities of sludge, which may harm the environment. As a result, the search for cost-effective, efficient and ecological waste treatment systems, a new technology for metal pollution wastewater treatment, has begun. This focuses on the biosorption of different biological materials based on the binding capacity.

The most suitable biosorption process for studying basic kinetic and isothermal parameters is a batch experimental setup. Sorption isotherms are helpful in describing the biosorption process and comparing the sorption abilities of different biomaterials (9). Biosorption isotherms provide valuable information about the retention or mobility of a substance from the aqueous environment to the solid phase at a constant temperature and pH (10, 12, and 18). In the present study, the Langmuir, Freundlich, and Temkin models were utilized to establish the correlation between the equilibrium concentrations in the liquid phase and the solid biosorbent. These models were used to fit the experimental data. Also, the biosorption equilibrium isothermal studies for biosorption were conducted using experimental data obtained from various initial concentrations of metal ions.

2. MATERIALS AND METHODS

The sea urchin shells collected from the nearby beach were first washed with tap water. The shell, spines, and flesh were then separated. After drying for more than one day in the sunlight, the remaining organic matter was also removed from the surface. Later, the spines were once again washed thoroughly with tap water and distilled water to neutralize the sea salinity. Air-dried sea urchin spines were pulverized using a ball mill and graded to obtain a fine powder as an adsorbent. The physicochemical parameters influencing the biosorption of lead biosorption from synthetic solutions in water include: Contact time, pH, size of adsorbent, initial concentration of adsorbate in the aqueous solution, and adsorbent dosage initially by a "one variable at a time" approach i.e., fixing each parameter for optimum adsorption in a batch mode, are considered in the study to identify the optimum conditions of each variable. Initially, a "one variable at a time" approach is used, where each parameter is fixed for optimum adsorption in a batch mode. Out of all these factors, pH, adsorbent concentration, and adsorbate concentration are the most crucial. Therefore, they must be optimized to evaluate the full biosorption potential of any biomaterial and achieve maximum uptake of metal ions. The study also includes the kinetic and isothermal models to evaluate the equilibrium biosorption data and ultimately understand the mechanism(s) of lead adsorption.



Fig.2 Sea Urchin with spines

Preparation of biosorbent



Sea Urchin spines are collected and washed with water and then distilled water to remove dust and impurities (11). They are left to dry at room temperature. The spines were obtained after sun-drying for 48hrs. The dried spines are carefully powdered and sized using a sieve ranging from 63 to 212 microns (11,20). The powder is collected separately and preserved in a glass bottle as a biosorbent.

Preparation of Lead stock solution

The source for lead stock solution is lead nitrate (Pb (NO₃)₂·6H₂O). 2.12 g of 99 percent (Pb(NO₃)₂·6H₂O) is dissolved in distilled water in a 1.0-litre volumetric flask to achieve 1000 ppm (mg. L⁻¹) of lead solution in stock (8,11,20). By diluting this solution in stock, synthetic samples of various lead concentrations can be made. Solutions with different metal concentrations (20, 30, 40, 50, 60 and 70 mg. L⁻¹) (6,8,11,20) have been prepared. The pH of the aqueous solution is set to the desired level by adding 0.1 N H₂SO₄ or 0.1 N NaOH solutions. (6,8,20)

Biosorption experiments (Batch mode)

Biosorption tests were conducted in batches using a 250-mL conical flask containing a 30-mL solution with a specific concentration of lead ions at the desired pH. An appropriate quantity of Sea Urchin spine powder was added. An orbital shaker is used to shake the sample at ambient temperature (30°C) at 180 rpm until equilibrium is achieved (13). The filtrates are examined using an atomic ASM (Perkin Elmer A Analyst 3100 model) after each sample is individually filtered individually with filter papers to determine the final lead concentration.

After adjusting the pH solution within the range of 2 to 9, (14) the impact of pH on the equilibrium of biosorption was investigated. At the pH level that resulted in maximum percentage adsorption of lead, an investigation was conducted to examine the effects of varying contact time between the solution and Sea Urchin spine powder. The contact time was altered from 1 to 70 minutes. Six distinct concentrations of metal ions ranging from 20 mg. L⁻¹ and 70 mg. L⁻¹ were employed in the equilibrium studies. The biomass of Sea Urchin spine powder was varied from 0.1 g to 0.6 g to optimize the biosorption process.

The percentage removal (Eq. 1) and the metal uptake by

the adsorbent (Eq. 2) were calculated from the expressions given below:

$$\% \text{ of lead removal} = \frac{C_o - C_e}{C_o} * 100 \quad (1)$$

$$\text{Metal uptake } (q_t) = V * \frac{C_o - C_e}{1000 w} \quad (2)$$

Where C_o is the initial concentration of metal (mg L⁻¹), C_e is final metal concentration of the sample after adsorption (mg L⁻¹), w is the adsorbent weight (g), and V is the amount of metal in solution (L).

3. RESULTS & DISCUSSION

The present study investigates the adsorptive capacity of Sea Urchin spine powder as a biosorbent for removing lead metal in an aqueous solution.

Effect of Contact Time

The relationship between contact time and the percentage removal of lead is illustrated in Fig. 3 for interaction intervals varied from 1 to 70 minutes, with the optimum time being determined. Lead is adsorbed in the initial five-minute period. The percentage of biosorption exhibits a significant increase up to 70 minutes, reaching a maximum of 80%. However, beyond the 70-minute mark, the biosorption rate becomes negligible. Beyond a duration of 70 minutes, the rate of biosorption remains constant, suggesting that the system has reached equilibrium. The maximum biosorption efficiency of 83.61% was achieved after 57 minutes of agitation using 0.1 g/30 ml of biosorbent with a particle size of 63 μm, mixed in a 30 mL aqueous solution (initial concentration, C₀ = 20 mg/L). The rate of biosorption is rapid during the initial stages due to the presence of a biosorbent with a significant surface area, which facilitates lead biosorption (15, 16). It has been observed that the biosorbent surface experiences an increased adsorption of lead, primarily attributed to the Van der Waals force. Consequently, this leads to a reduction in the available surface area for further interactions. A monomolecular layer, which is only one molecule thick, is formed on the surface of the



biosorbent. At this stage, the sorbent's capacity has experienced a significant decrease (17,24).

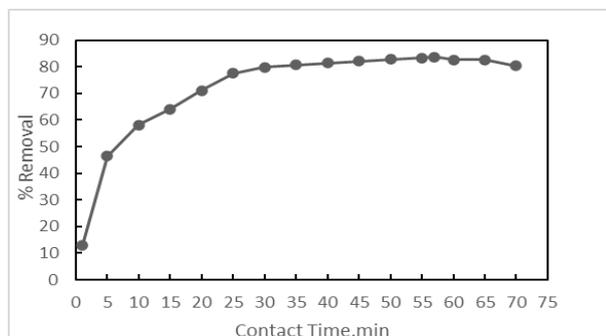


Fig. 3: Contact Time vs Lead removal (%)

Kinetics of Adsorption

The pseudo-first-order model was used to fit the experimental data, pseudo-second-order, and intra-particle diffusion kinetic models to understand the mechanisms underlying lead ions' adsorption.

The pseudo-first-order equation used was

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303 * t} \right)$$

q_e and q_t denote the quantities of lead adsorbed at equilibrium and time (t); K_1 is the pseudo-first-order (min⁻¹) rate constant. This model was inferred to be unsuitable for the system as the calculated and experimental q_e values differed, with an R^2 value much less than 1. (4,18)

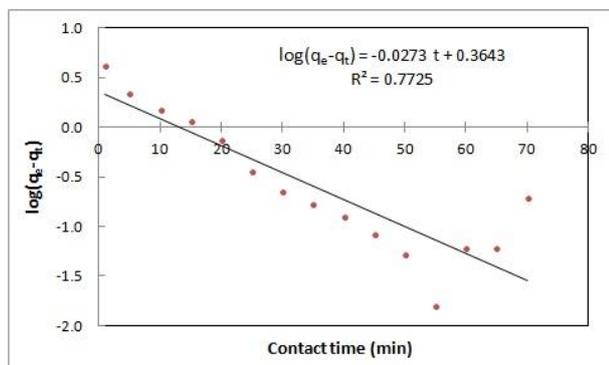


Fig.4.a pseudo-first-order biosorption of lead using sea urchin spines powder

The experimental data were then tested by the pseudo-second-order equation

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e t} \quad (4)$$

where K_2 (min⁻¹) is the rate constant for the pseudo-second-order model. The calculated q_e values agree very well with experimental data, suggesting that the pseudo-second-order kinetic model provides a good correlation for the adsorption of lead onto the adsorbent.

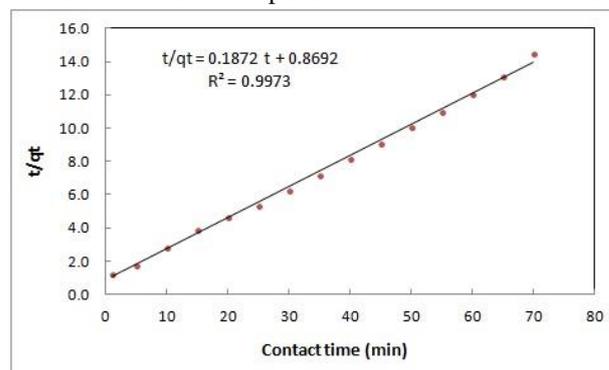


Fig.4.b pseudo-second-order biosorption of lead using sea urchin spines powder

Intra-particle diffusion model is given by the equation

$$q_t = K_{int} t^{1/2} + C \quad (5)$$

where K_{int} is intra-particle diffusion rate constant (mg g⁻¹ min^{1/2} -1) and C is the boundary layer thickness was also tested, and the values are presented in Table 1.

Because the experimental data fit the pseudo-second-order equation, the adsorption could be chemical, including valence forces via electron exchange or sharing between sorbent and sorbate.

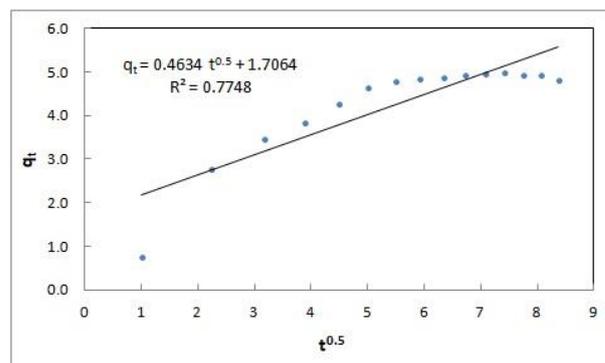




Fig.4.c Intra particle diffusion model for biosorption of lead using sea urchin spines powder

Table 1: Kinetic model equation and parameters for adsorption of lead by sea urchin spines powder

Kinetic model	Equation	Parameters
Pseudo- first order	$\log(q_e - q_t) = -0.0273 t + 0.3643$	$q_{e, calc} = 2.313 \text{ mg. g}^{-1}$
		$q_{e, exp} = 5.017 \text{ mg. g}^{-1}$
		$K_1 = 0.0628$
		$R^2 = 0.7725$
Pseudo- second order	$t/q_t = 0.1872 t + 0.8692$	$q_{e, calc} = 5.341 \text{ mg. g}^{-1}$
		$q_{e, exp} = 5.017 \text{ mg. g}^{-1}$
		$K_2 = 0.0403$
		$R^2 = 0.9973$
Intra-particle diffusion	$q_t = 0.4634 t^{0.5} + 1.7064$	$K_{int} = 0.4634 \text{ mg. g}^{-1} \text{ min}^{1/2}$
		$C = 1.7064 \text{ mg. g}^{-1}$
		$R^2 = 0.7748$

at pH 6, and then gradually decreases to 79.51% at pH 9. The observed effect is

Effect of pH
The pH level significantly affects the solubility and overall

charge of biosorption. The impact of pH on the percentage of lead removal in an aqueous solution ($C_0 = 20\text{--}70 \text{ mg/L}$ using $0.1 \text{ g}/30 \text{ ml}$ of $63 \mu\text{m}$ size biosorbent) is shown in Figure 5. The percentage of metal removal increases from 7.43% at pH 2 to 87.45%

attributed to the formation of metal hydroxides in the alkaline pH range of 7-14 (19,21). A decrease in lead biosorption is observed at a pH of 2. As the pH increases, Pb ions replace H^+ ions.

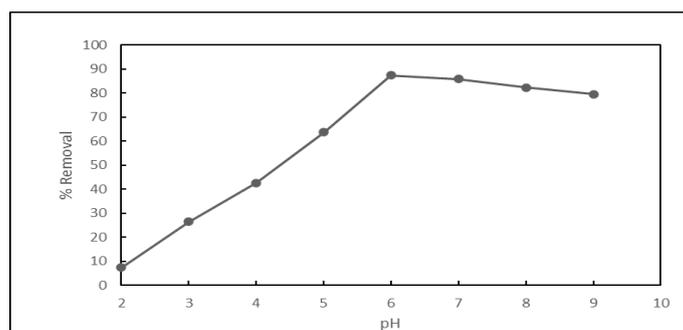


Fig.5 Effect of pH on % removal of Lead

Effect of Lead ion initial concentration

As depicted in Figure 6, the initial concentration of lead ions was systematically altered in the following manner: 20 mg/L , 30 mg/L , 40 mg/L , 50 mg/L , 60 mg/L , and 70 mg/L . Throughout the experiment, the agitation time was maintained at 57 minutes, and the pH was maintained at 6. Consequently, the percentage removal

of lead exhibited a decline from 83.61% (at an initial concentration of lead of 20 mg/L) to 71.19% (at an initial concentration of lead ions of 70 mg/L). This behavior can be attributed to the elevated levels of lead concentrations found at unbounded absorbent active sites. The relationship between the initial concentration of lead and the percentage of lead removal is depicted in Figure 6.

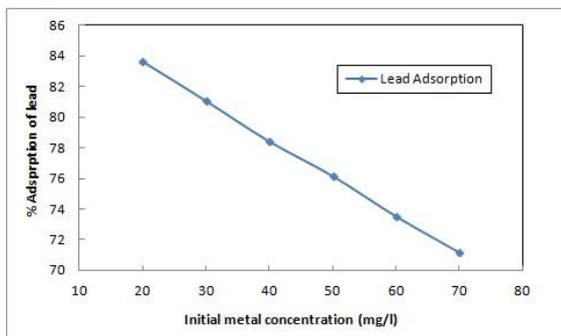


Fig. 6 Initial concentration vs. % removal of lead

Isotherms of Adsorption

The Langmuir isotherm model shows the monolayer on the sorption surface. The sorption process is assumed to occur at a specific sorption surface in this model. As a result, the molecular attraction weakens as it moves away from the sorption surface, and it is expressed as follows: (4)

$$q_e = \frac{q_{max}}{(1+b \cdot C_e)} * b * C_e \tag{6}$$

The mathematical expression for Langmuir isotherm is:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \tag{7}$$

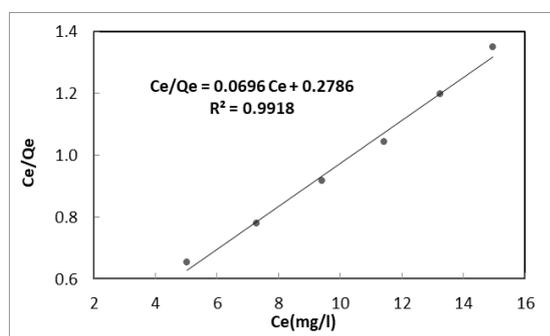


Fig.7.a Langmuir isotherm for adsorption of lead using Sea Urchin Spine powder

Where q_e = equilibrium concentration of metal ion (mg. g⁻¹)

c_e = solution's equilibrium concentration of metal ion (mg. L⁻¹)

q_m = concentration of metal ion in the solution (mg. g⁻¹)

K_L = Langmuir constant (L.mg⁻¹)

Freundlich's isotherm model considers the heterogeneity of the surface and the multilayer biosorption to the binding sites located on the surface of the sorbent and does not consider the biosorbent saturation (Freundlich, 1906). This model is expressed as follows:

$$q_e = K_f C_e^{1/n} \tag{8}$$

Where K_f is Freundlich capacity constant, and n is the affinity constant. The 'n' value between 0 and 1 suggests relatively strong biosorption of ions onto the surface of the adsorbent.

The mathematical expression for Freundlich isotherm is: (4,22)

$$\ln q_e = \frac{1}{n} (\ln C_e) + \ln K_f \tag{9}$$

Where K_f = Freundlich constant

1/n = empirical parameter of

biosorption intensity

A linearised plot was drawn for log q_e versus log c_e . The n and K_f values were calculated from the slope and the intercept, respectively. From figure.7. b, $R^2 = 0.9969$.

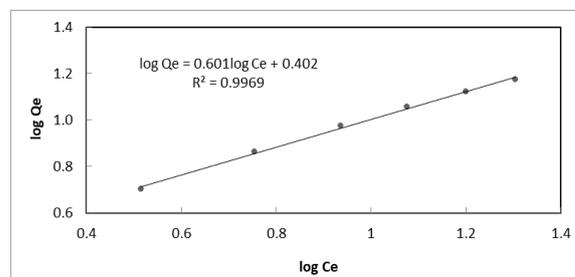


Fig.7.b Freundlich isotherm for adsorption of lead using Sea Urchin Spine powder



Temkin isotherm model indicates the interaction between adsorbate molecules and the linear form of the Temkin isotherm equation is (4,20,25)

$$q_e = \left(\frac{R_T}{b_T}\right) \ln(A_T) + \left(\frac{R_T}{b_T}\right) (\ln C_e) \quad (10)$$

R stands for the universal gas constant, and n denotes the number of atoms in T, which is the temperature. The absolute temperature (K), A_T , and b_T are Temkin constants. From (Table 2), it is clear that the Freundlich model better fits than that of the Langmuir and Temkin models when comparing the R^2 values.

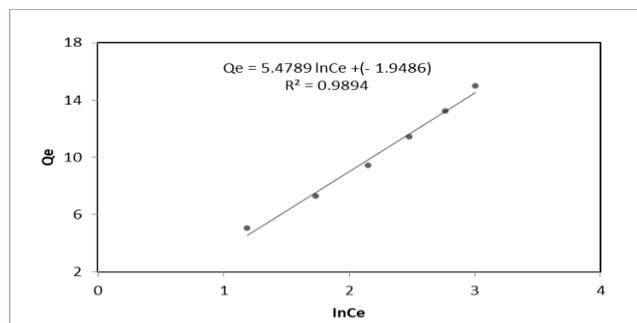


Fig.7.c Temkin isotherm for adsorption of lead using Sea Urchin Spine powder

Isothermal constants of lead adsorption onto Sea Urchin Spine powder are shown in table 2.

Table2: Isothermal equation and constants of lead adsorption onto Sea Urchin Spine powder

Isotherm	Equation	Parameter	Sea Urchin Spine
Langmuir	$Ce/Q_e = 0.0696 Ce + 0.2786$	$q_m, \text{mg/g}$	14.367
		KL	0.249
		R^2	0.9918
Freundlich	$\log Q_e = 0.601 \log Ce + 0.402$	1/n	0.601
		Kf mg/g	2.523
		R2	0.9969
Temkin	$Q_e = 5.4789 \ln Ce + (-1.9486)$	AT, L/mg	0.7007
		bT	459.78
		R^2	0.9894

5. CONCLUSION

- The use of sea urchin spines resulted in an 83.61% reduction in lead after 57 minutes of contact time.
- The removal rate increased as the pH increased from 4 to 6, with percentages rising from 42.67% to 87.45%. Further increases in pH resulted in a decrease in removal percentage.
- The Sea Urchin spine powder was found to be most effective at pH 6 with a contact time of 57 minutes.
- The Freundlich model ($R^2 = 0.9969$) is more accurate than the Langmuir model ($R^2 = 0.9918$) in predicting the equilibrium state.
- The spine powder of sea urchins has the ability to absorb up to 14.367 mg/g of lead.
- Sea urchin spine powder is a viable alternative biomass for efficiently removing lead ions, as previously discussed. It has a high biosorption capacity and is a natural, renewable material, making it cost-effective and efficient.

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