

***Solamen Vaillanti* Mollusk Powder as an Efficient Biosorbent for Removing Cobalt Ions from Aqueous Solution: Kinetic and Equilibrium Studies**

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In this research, *Solamen Vaillanti* mollusk (SVM) skin biosorbent was synthesized and used as a low-cost and environmentally friendly adsorbent to eliminate cobalt (Co²⁺) heavy metal ion from aqueous solution. The surface morphology and specific surface area of SVM were analyzed by SEM and BET analyses. Also, the impact of various effective factors like pH, temperature, contact time, biosorbent dose, and cobalt ion concentration was studied on the uptake process. According to our study, the highest biosorption efficiency of Co²⁺ (97.31%) was attained at pH 5, a mixing speed of 200 rpm, Co²⁺ ion concentration of 5 mg l⁻¹, and biosorbent dosage of 2 g l⁻¹ after 50 min. Also, the maximum biosorption capacity of SVM biosorbent was 16.23 mg l⁻¹, which was achieved at pH 5 and temperature of 25 °C. Moreover, kinetic and equilibrium studies demonstrated that the quasi-second-order kinetic model and the Langmuir isotherm model are better compatible with the experimental data. Furthermore, the reusability of the bioadsorbent showed that it can be reused in 4 cycles in the bioadsorption process.

Keywords: Aqueous solution, Biosorption, Cobalt heavy metal, Mollusk skin biosorbent

INTRODUCTION

Pollution of water resources with heavy metals due to industrial activities such as automobile industries, mines,

steel industries, etc. is one of the most important problems that can pose many risks to the environment. The presence of heavy metals in water, even at low concentrations, can cause various diseases in humans and living organisms and ultimately death. On the other hand, increasing the growth of industries and industrialization causes the accumulation of different contaminants like heavy metals, which leads to

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increased pollution of the environment and ecosystem. Heavy metals are elements with a molecular weight between 60.5-200.6. By developing industries like metal factories, mining operations, paper making, etc., the discharge of heavy metals directly and indirectly into the environment has increased. Also, heavy metals are stable elements and unlike organic compounds, which are degraded in the environment, they are not biodegradable and can accumulate in the environment and even in the body of living organisms [1-3].

Heavy metal ions are toxic and carcinogenic and have deadly impacts on the life of plants, animals, and humans. These elements can enter the water through the factory sewage. As a result, they contaminate surface and groundwater and enter the food chain. The most critical metal ions contain Pb^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Hg^{2+} , Cd^{2+} , Ni^{2+} , Cr^{3+} , Cr^{6+} and As^{3+} [4-7]. Heavy metals at low concentrations are also very dangerous. Co^{2+} is found in different forms in the environment. Cobalt has many applications in resin stabilizers, semi-conductors, nuclear medicine, plating industry, generation of glazes, paints, and polishes. Also, exposure to high concentrations of cobalt can have adverse health effects such as bone defects, lung disease, hypotension, paralysis, and genetic mutations. The maximum allowable concentration of Co^{2+} in drinking water is 0.1 mg l^{-1} [7-8]. Therefore, it is critical to eliminate Co^{2+} ions from wastewater to prevent their release into the environment. Important procedures to remove heavy metals from aquatic solutions include chemical precipitation, ion exchange, membrane filtration, coagulation, aggregation, flotation, electrochemical treatment, and sorption process. Today, the sorption process is one of the most effective and economical ways to purify water from heavy metals. The sorption process has several benefits such as flexibility in design, high performance, high selectivity, and affordable. In this process, the selection of an appropriate adsorbent with high reusability is essential. Recently, biosorbents have received much attention due to their low-cost, abundance in nature, and high reusability. Also, bioadsorbents are environmentally friendly [4,9-10]. The diversity of functional groups in the biosorbents structure plays a critical role in the uptake process [11]. Different procedures can be used to synthesize adsorbents, including chemical co-precipitation, sol-gel, micro-emulsion, *etc.* [12-13].

Different types of bacteria, fungus, agricultural wastes, polysaccharides, and chitosan are some important biosorbents, which have been extensively utilized in previous studies [11]. In addition to the above-mentioned biosorbents, some other biosorbents are used to remove organic compounds and heavy metal ions, including rice husk [14], coconut shell [15], *Moringa oleifera* leaves [16], sugarcane bagasse [17], and brewed tea waste [18].

This study investigates the removal efficiency of Co^{2+} ions from aqueous media using *Solamen Vaillantii* mollusk (SVM) powder as a low-cost biosorbent. To this end, the surface features of the biosorbent were surveyed by SEM and BET analyses. Also, the impact of operating parameters was studied on the sorption process and the best conditions with the highest removal efficiency were attained. Moreover, the kinetic and equilibrium studies of the Co^{2+} uptake process were studied. As far as we have studied, no work has been done on the removal of Co^{2+} ions using *Solamen Vaillantii* mollusk powder and its reusability. Compared to other adsorbents, cheapness and environmental friendliness are important features of this adsorbent that can make it possible to use it on an industrial scale.

MATERIALS AND METHODS

Materials

Cobalt(II) nitrate hexahydrate ($\text{CoN}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$) was purchased from Merck Co. and mollusk shell was prepared to synthesize the biosorbent. Also, HCl and NaOH (0.1 M) was utilized for adjusting the solution pH. To regulate the solution pH, a pH meter (Inolab pH 720, Germany) was used.

In order to produce the cobalt stock solution, 3.8 g of $\text{CoN}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ was added to double distilled water in a 1000 ml balloon and stirred with a magnetic-stirrer (HS6000, Iran) until completely uniform.

Preparing the *Solamen Vaillantii* Mollusk Biosorbent

To produce the biosorbent, firstly, the mollusk shells were washed several times and placed in an oven at $105 \text{ }^\circ\text{C}$ for 3 h to dry. After drying, the biosorbent was crushed with a grinder and meshed using sieve No. 25. The following



Fig. 1. Schematic of the biosorbent production and its use in eliminating Co^{2+} ions from aqueous solution.

figure indicates a procedure to generate the biosorbent and its application in removing cobalt ions.

The surface morphology of the biosorbent was investigated by SEM (Hitachi, S-4160). To this end, the biosorbent surface was covered with a thin layer of gold powder under vacuum. Also, the surface features of the biosorbent such as specific surface area and the mean pore size were determined by BET analysis.

Experimental Procedure

Biosorption experiments were done discontinuously in Erlenmeyer containing 100 ml of Co^{2+} ions solution. In this study, the impact of solution pH (3-11), biosorbent dosage (0.25-6 g l^{-1}), mixing rate (0-600 rpm), contact time (5-120 min), and Co^{2+} ion concentration (5-25 mg l^{-1}) was studied on the uptake of Co^{2+} ions from aquatic solution using the SVM. All tests were performed at 30 °C. To perform the experiments, first, the impact of pH was studied and the maximum removal efficiency was attained. For investigating the impact of pH on biosorption efficiency,

other factors were kept constant. For investigation of the impact of other factors, one parameter was changed while other parameters were considered constant. At the end of each experiment, the solution was filtered with Whatman filter paper no. 42 and the solid phase (biosorbent) was separated from the solution. Eventually, the remaining concentration of Co^{2+} ion in each sample was measured with a flame atomic absorption spectrometer (SpectraAA-10, Plus model, Varian Company). For all samples, the following equations were used to calculate the biosorption percentage (R) and biosorption capacity (q_e) [19]:

$$R (\%) = \frac{C_i - C_0}{C_i} \times 100 \quad (1)$$

$$q_e = \frac{C_i - C_0}{W} \times V \quad (2)$$

Where, C_i (mg l^{-1}), C_0 (mg l^{-1}), W (g), and V (l) are the Co^{2+} ion initial concentration, the Co^{2+} ion final concentration, weight of the biosorbent, and the solution volume, respectively. Each experiment was repeated twice and their mean was reported.

Sorption Kinetic

Sorption kinetics are used to determine the control mechanism of the sorption process. The sorption mechanism depends on the physical and chemical properties of the sorbent. In order to study the kinetic behavior of the Co^{2+} sorption process using SVM, quasi-first-order (QFO) and quasi-second-order (QSO) kinetic models were utilized. Correlation coefficients (R^2) are used to match laboratory data with kinetic models. The QFO and QSO models are described as Eqs. (3) and (4), respectively [19-21].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Here, q_e (mg g^{-1}), q_t (mg g^{-1}), k_1 (min^{-1}) and k_2 ($\text{mg g}^{-1} \text{min}^{-1}$) are the biosorption capacity at equilibrium state, the biosorption capacity at time t, the QFO model constant, and the QSO model constant, respectively.

Sorption Isotherms

Achieving an appropriate relationship is crucial for optimizing the sorption process. Sorption isotherms can be used to obtain a relationship between adsorbent and adsorbate (contaminant) [17,22]. The Langmuir and Freundlich models are the most important isotherm models that are widely utilized. Equations (5) and (6) show these isotherm models, respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (5)$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (6)$$

Where, C_e (mg l^{-1}), K_L (l mg^{-1}) and q_m (mg g^{-1}) are the equilibrium concentration of Co^{2+} ions, the Langmuir constant related to biosorption energy, and the maximum biosorption capacity for the formation of a layer on the biosorbent surface, respectively. Also, k_f and n are the Freundlich constants.

RESULTS AND DISCUSSION

Biosorbent Characteristics

The surface features of the biosorbent were studied by BET analysis. The results showed that the specific surface area, pore volume, and the mean pore diameter of the aforementioned biosorbent were $5.3 \text{ m}^2 \text{ g}^{-1}$, $0.02 \text{ cm}^3 \text{ g}^{-1}$, and 12 nm , respectively. These properties show that the SVM can be used to eliminate heavy metals from water. Also, the mean pore diameter of the biosorbent shows that this sorbent has a mesoporous structure.

Also, SEM analysis was utilized to determine the surface morphology of the SVM biosorbent and the results are demonstrated in Fig. 2. As shown in Fig. 2a, there are many holes and bumps on the surface of the biosorbent before the uptake of Co^{2+} ions. These pores on the biosorbent surface indicate that this biosorbent can be effectively used in the uptake process. Also, Fig. 2b shows the SEM image of the biosorbent after the sorption process. As shown, there are many dots on the biosorbent surface, indicating that Co^{2+} ions are adsorbed on the active sites of the biosorbent.

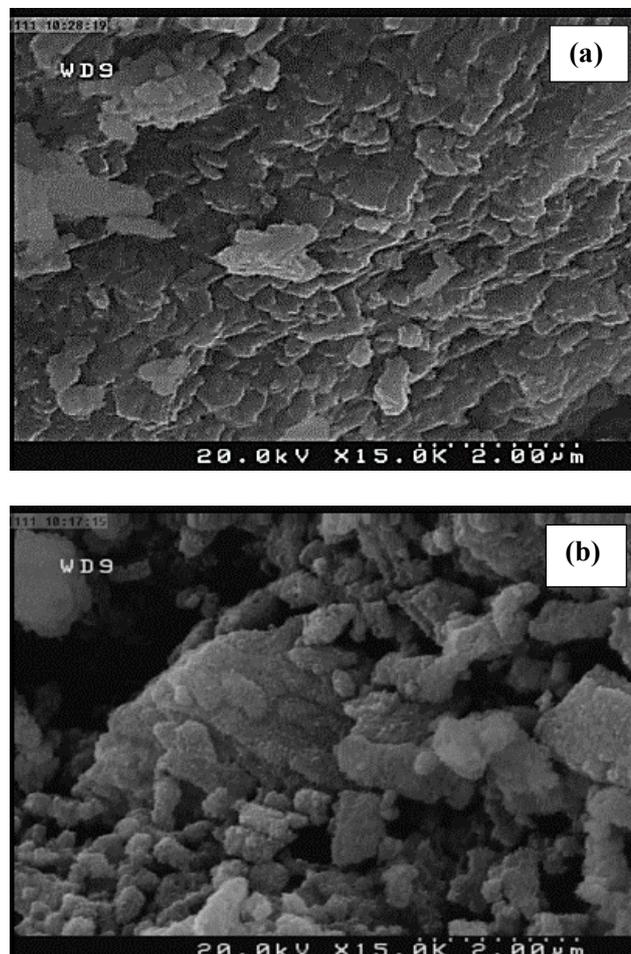


Fig. 2. SEM images of SVM with a magnification of 15.0 K before biosorption (a) and after biosorption of Co^{2+} ions (b).

Impact of Operating Parameters on the Sorption Process

The solution pH is a critical factor in the Co^{2+} sorption process because it affects the charge distribution in the solution. Acidic and basic solutions have positive and negative charges, respectively, therefore, these ions (cations and anions) can compete with charges of heavy metal ions to sit on the sorbent sites [23]. The impact of pH in the range of 3-11 was investigated on the Co^{2+} sorption efficiency using the SVM powder and the results are indicated in Fig. 3. To this end, other factors such as sorbent dosage of 2 g l^{-1} , Co^{2+} ion concentration of 5 mg l^{-1} , mixing

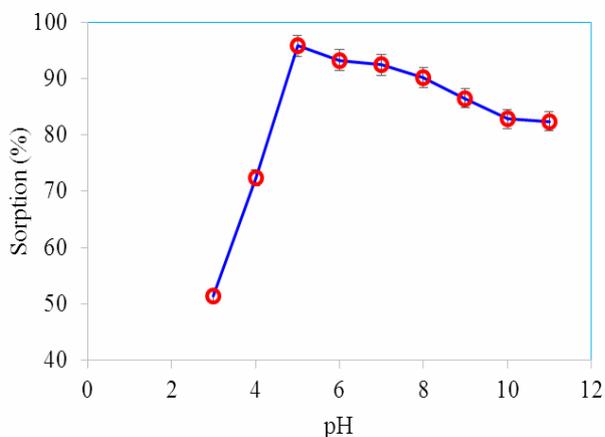


Fig. 3. Impact of pH on the Co²⁺ sorption efficiency using the SVM powder.

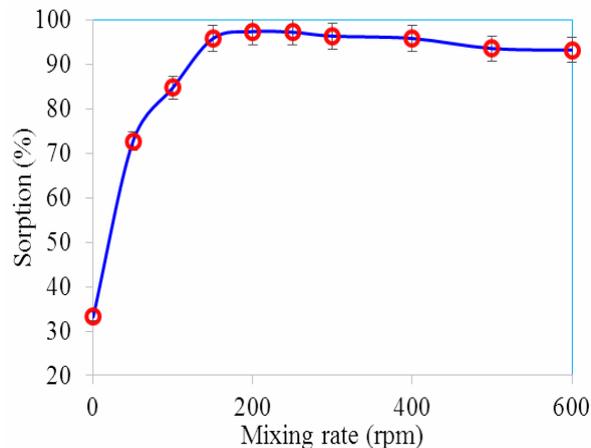


Fig. 4. Impact of mixing rate on the Co²⁺ sorption efficiency using the SVM powder.

rate of 150 rpm, temperature of 25 °C, and contact time of 50 min were kept constant. As shown, with increasing pH value from 3 to 5, the Co²⁺ sorption efficiency increased and after that, the Co²⁺ sorption efficiency slightly decreased by enhancing pH from 5 to 11. At low pH values, there are many positive charges (H⁺ ions) in the solution, so the sorption efficiency is high. While at high pH values, the concentration of hydronium ion (OH⁻) in solution increases, causing competition between OH⁻ ions and positive charges of Co²⁺ to sit on the biosorbent surface, thereby reducing the sorption efficiency [14]. The maximum Co²⁺ sorption efficiency at pH = 5 was obtained 95.76%.

Another effective factor in the Co²⁺ sorption process is the mixing rate, which impact in the range of 0-600 rpm is demonstrated in Fig. 4. Other conditions were pH = 5, sorbent dosage = 2 g l⁻¹, Co²⁺ ion concentration = 5 mg l⁻¹ and contact time = 50 min. As shown, with increasing mixing rate from 0 to 200 rpm, the Co²⁺ sorption efficiency enhanced from 33.22 to 97.31%. But, with increasing mixing rate from 200 to 600 rpm, the Co²⁺ sorption efficiency was slightly changed, indicating that the mixing rate of 200 rpm was considered as the optimal value. The lower the mixing rate, the lower the energy consumption and the more economical the adsorption process.

Sorbent dosage is one of the most important factors in the uptake process because it determines the sorption capacity of a sorbent in a specific concentration of solute

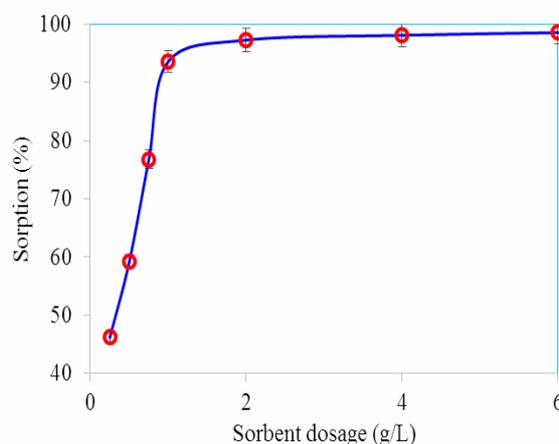


Fig. 5. Impact of sorbent dosage on the Co²⁺ sorption efficiency using SVM.

[24]. The impact of sorbent dosage on the Co²⁺ sorption efficiency using SVM in the range of 0.25 to 6 g l⁻¹ was investigated and the outcomes are shown in Fig. 5. Other conditions were Co²⁺ ion concentration = 5 mg l⁻¹, pH = 5, mixing rate = 200 rpm and constant time = 50 min. As demonstrated in Fig. 5, the Co²⁺ sorption efficiency increases significantly with raising the biosorbent dosage from 0.25 to 1 g l⁻¹, which can be due to an enhancement in the contact between biosorbent and sorbate or the large number of active sites on the biosorbent surface for uptake of cobalt ions [25]. The maximum sorption efficiency took

place at the biosorbent dosage of 2 g l⁻¹, which the sorption efficiency was 97.31%. Thereafter, no significant change in sorption efficiency was observed above 2 g l⁻¹.

In the discontinuous sorption process, the initial concentration of the pollutant plays a key role in the mass transfer between the liquid and solid phases [26]. In order to study the impact of contact time and Co²⁺ ion concentration on the sorption efficiency, the Co²⁺ sorption process was studied in different concentrations of Co²⁺ ion (5 to 25 mg l⁻¹) and different contact times (5-120 min) and the outcomes are demonstrated in Fig. 6. Other optimal conditions were pH = 5, mixing rate = 200 rpm, and sorbent dosage = 2 g l⁻¹. As indicated in Fig. 6, the Co²⁺ sorption efficiency increases with increasing contact time, but the Co²⁺ sorption efficiency decreases with enhancing Co²⁺ ion concentration. With increasing the contact time from 5 to 30 min, the Co²⁺ sorption efficiency increases with a steep slope, but with increasing the contact time from 30 to 120 min, the Co²⁺ sorption efficiency increases with a gentle slope, indicating the occupation of sorbent active sites by cobalt ions in the early time period.

Kinetic Study

In this study, the kinetic behavior of the Co²⁺ sorption process using the SVM biosorbent was studied and the results are shown in Fig. 7. To this end, the QFO and QSO kinetic models were studied and the constants and parameters of these models are reported in Table 1. According to Table 1, the QSO model due to the higher correlation coefficient (R²) in all Co²⁺ concentrations was a better model to describe the Co²⁺ ion sorption kinetic than the QFO model. Therefore, the QSO model has more compatible with the laboratory data than the QFO model. The R² values for the QSO model in all Co²⁺ concentrations are higher than 0.99, while these values for the QFO model are between 0.91 to 0.96. The results of this study are consistent with previous research [27].

Isotherm Study

In order to investigate the equilibrium behavior of the Co²⁺ sorption process using the SVM biosorbent, the Langmuir, and Freundlich models were utilized and the outcomes are depicted in Fig. 8 and the constants and parameters of these models are given in Table 2. To study

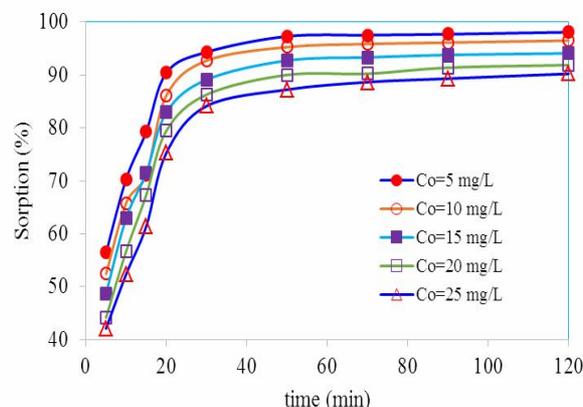


Fig. 6. Impact of Co²⁺ ion concentration on the Co²⁺ sorption efficiency in different contact times using SVM.

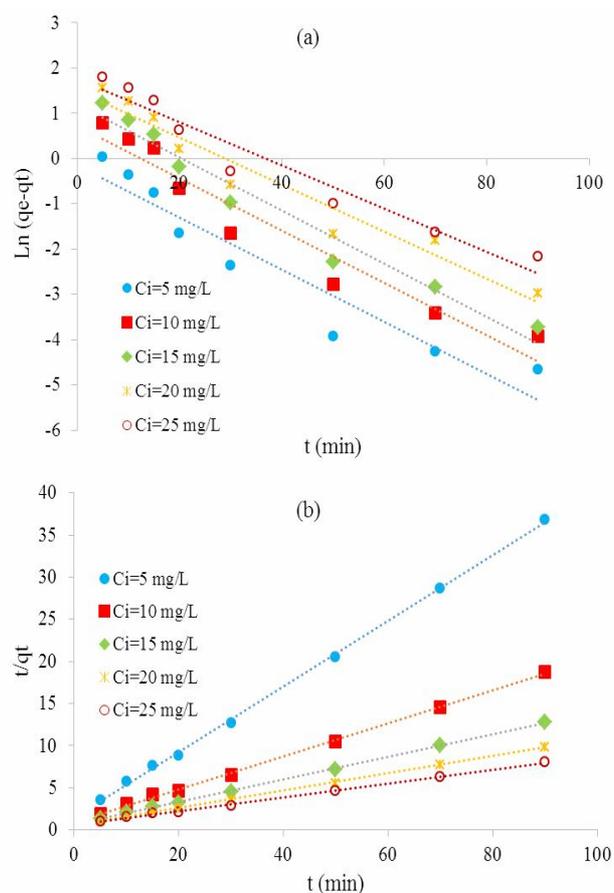


Fig. 7. The QFO (a) and QSO (b) kinetic models for uptake of Co²⁺ ions in different concentrations of Co²⁺ ion (5-25 mg l⁻¹).

Table 1. Constants and Parameters of the QFO and QSO Kinetic Models for the Co^{2+} Sorption Process Using the SVM Biosorbent

Kinetic model		Co^{2+} ion concentration (mg l^{-1})				
		5	10	15	20	25
QFO	$q_{e, \text{cal}}$	0.8571	2.0115	3.3444	3.4887	5.8159
	$q_{e, \text{exp}}$	2.4525	4.8260	7.0582	9.1890	11.2787
	k_1	0.0576	0.0576	0.0588	0.0519	0.0479
	R^2	0.9148	0.9392	0.9647	0.9455	0.9464
QSO	$q_{e, \text{cal}}$	2.5381	5.0302	7.3855	9.6805	11.9904
	$q_{e, \text{exp}}$	2.4525	4.8260	7.0582	9.1890	11.2787
	k_2	0.1179	0.0487	0.0301	0.0192	0.0130
	R^2	0.9995	0.9993	0.9993	0.9990	0.9986

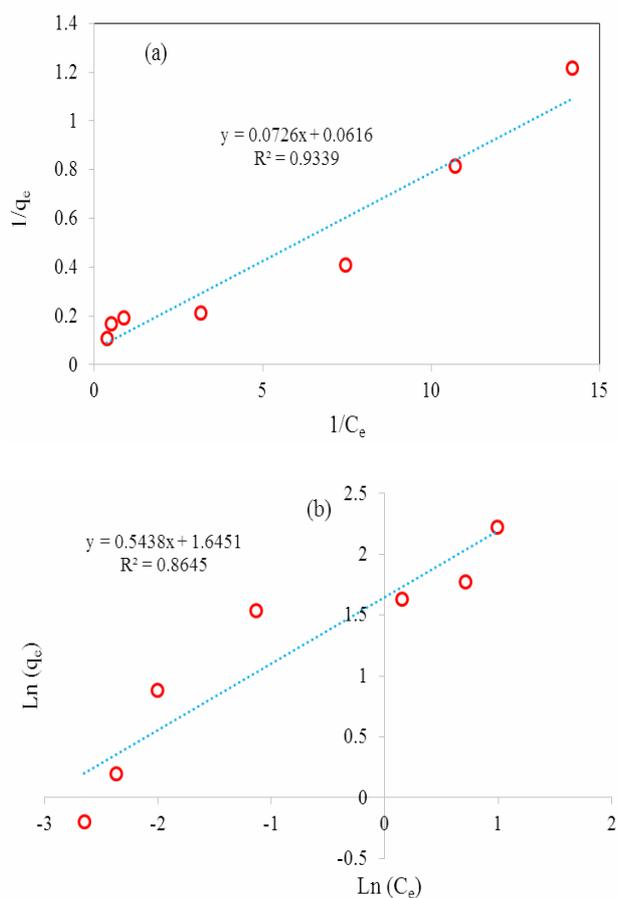


Fig. 8. The Langmuir (a) and Freundlich (b) isotherm models for the sorption of Co^{2+} ions using the SVM biosorbent.

Table 2. Constants and Parameters of the Langmuir and Freundlich Isotherm Models for the Sorption of Co^{2+} Ions Using the SVM Biosorbent

Isotherm model	Parameter	Value
Langmuir	k_L (l g^{-1})	0.848
	q_m (mg g^{-1})	16.234
	R^2	0.934
Freundlich	k_f ($(\text{mg g}^{-1}) (\text{l mg}^{-1})^{1/n}$)	5.182
	n	1.839
	R^2	0.865

the isotherm behavior of the Co^{2+} sorption process, the experiments were done at 5 mg l^{-1} Co^{2+} ion concentration, pH of 5, temperature of $30 \text{ }^\circ\text{C}$, mixing rate of 200 rpm, contact time of 50 min, and sorbent dosage in the range of 0.25 to 6 g l^{-1} . The values of the correlation coefficient for the Langmuir and Freundlich models were 0.934 and 0.865, respectively, indicating that the Langmuir isotherm model was able to describe the equilibrium behavior of the Co^{2+} sorption process using the SVM powder better than the Freundlich model. Also, the maximum Co^{2+} sorption efficiency using the Langmuir model was attained 16.234 mg g^{-1} , indicating a good value. Moreover, the constant value of the Freundlich model (n) was 1.839, indicating that the uptake process of Co^{2+} ions using the

SVM powder is physical and desirable. The results of this study are consistent with previous research [18].

Table 3 shows a comparison between the maximum sorption capacity of Co^{2+} ions using various adsorbents. According to our investigations, the biosorbent used in this study showed to have an acceptable sorption capacity and high sorption efficiency compared to other sorbents.

The Adsorbent Reusability

The stability and reusability of the adsorbent is one of the most critical features of a bioadsorbent because it shows whether the use of adsorbent is cost-effective or not. The greater the reusability, the higher the efficiency of the bioadsorbent in industrial processes [33-34]. The reusability of the SVM bioadsorbent was studied in 6 cycles and the outcomes are shown in Fig. 9. For this purpose, after using the bioadsorbent in the sorption process, the adsorbent surface was washed with H_2SO_4 acid and the adsorbent was reused to remove Co^{2+} ions from water. According to our results, the SVM biosorbent was able to remove cobalt with an efficiency of 91.33% after 4 reusing cycles, which is a significant reusability. However, after the 5th cycle, the bioadsorption efficiency was less than 90%. Therefore, the bioadsorbent can be used up to 4 times in the sorption process.

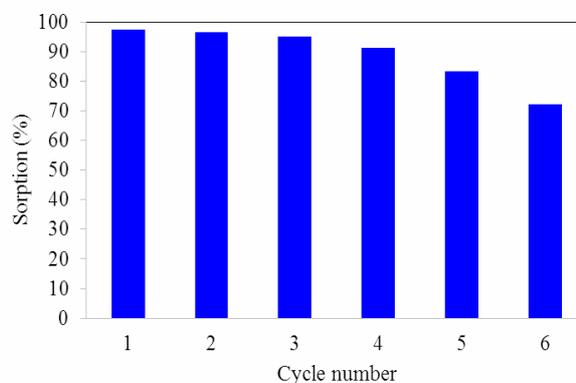


Fig. 9. The reusability of SVM in 6 reusing cycles for removing Co^{2+} ions from aqueous solution.

The Impact of Interfering Ions on the Co^{2+} Ions Adsorption

There are many ions in wastewater that can affect the adsorption efficiency of Co^{2+} ions. In this study, a solution containing various cationic ions such as Pb^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Hg^{2+} , Cd^{2+} , and Co^{2+} was made to study the impact of interfering ions on the Co^{2+} adsorption efficiency [35]. The concentration of each ion in the solution was considered 5 mg l^{-1} , and 2 g l^{-1} of the bioadsorbent was added to the solution. After 50 min, the residual concentration of these

Table 3. Comparing the Results of this Work with Previous Studies in Eliminating Cobalt Ions from Aquatic Solutions Using Various Sorbents

Sorbent	q_m (mg g^{-1})	Sorption efficiency (%)	Ref.
<i>Providencia rettgeri</i>	-	95	[1]
<i>Saccharomyces cerevisiae</i> yeast	1.768	73.4	[7]
<i>Citrus limetta</i> activated carbon	60.60	98.63	[19]
Hazelnut Shells activated carbon	13.88	-	[20]
Activated carbon/SDS	51	-	[28]
Palygorskite	8.88	-	[29]
Orange peel waste	5.128	-	[30]
Snail shell	29.41	96.5	[31]
Tabbuk clay activated by hydrogen peroxide	12.9	-	[32]
Bahhah clay activated by sodium chloride	12.55	-	[32]
SVM	16.234	97.31	Present study

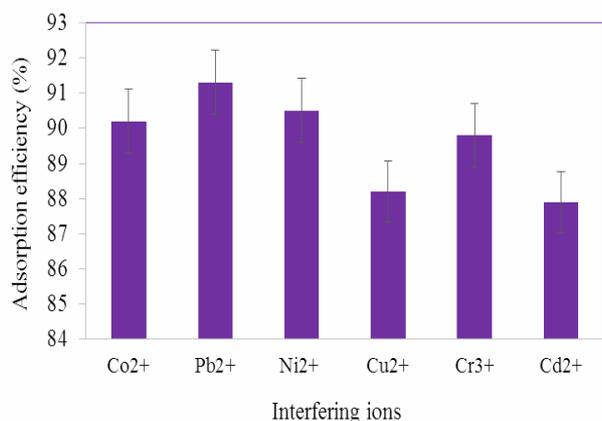


Fig. 10. Impact of various ions on the adsorption efficiency using mollusk shell powder.

ions was measured (Fig. 10). As shown in Fig. 10, the maximum and minimum adsorption efficiencies were obtained for Pb²⁺ (91.3%) and Cd²⁺ (87.9%), respectively. Also, the adsorption efficiency of Co²⁺ was 90.2%, which compared to 97.31% (adsorption efficiency without interfering ions) shows that the addition of other ions in the solution reduced the Co²⁺ adsorption efficiency by about 7%.

CONCLUSIONS

The present research investigates the sorption process of cobalt ions from aquatic solutions using an efficient biosorbent like mollusk shell powder. The surface features of the SVM biosorbent were studied using SEM and BET analyses. These analyses indicated that the biosorbent has a porous structure with a large number of bumps and holes on its surface. Also, the results of the Co²⁺ sorption process showed that the highest sorption efficiency (97.31%) was achieved at pH of 5, a mixing rate of 200 rpm, Co²⁺ ion concentration of 5 mg l⁻¹, contact time of 50 min, and biosorbent dosage of 2 g l⁻¹. Moreover, the kinetic and equilibrium studies showed that the sorption process of Co²⁺ ions using the SVM biosorbent follows the QSO kinetic model and the Langmuir isotherm model, respectively, due to a higher R² value. Regarding the advantages of the biosorbent like low-cost, biodegradability, simple procedure, and high sorption efficiency, the SVM

biosorbent is suggested as an efficient sorbent to remove Co²⁺ ions from industrial wastewater. Also, the reusability of the bioadsorbent displayed that it can be effectively used in the bioadsorption process.

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