

## Treatment of Wastewater Containing Co(II) Ions Using Eggshell Nanoparticles: Kinetic and Equilibrium Investigations

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The sorption potential of eggshell nanoparticles as a cheap sorbent was studied in the removal of cobalt ions from aqueous solutions. Also, Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET), and Dynamic Light Scattering (DLS) analyses were employed to measure the features of eggshell nanoparticles. The highest uptake efficiency was 97.43%, which was attained at stirring rate of 200 rpm, contact time of 60 min, 4 g l<sup>-1</sup> eggshell dose, Co(II) ion concentration of 20 mg l<sup>-1</sup>, temperature of 30 °C, contact time of 60 min, and pH 6. Also, the adsorption process followed the Langmuir isotherm model. Moreover, the pseudo-second-order kinetic model could describe the kinetic behavior of Co(II) ions adsorption better than the pseudo-first-order and intraparticle diffusion kinetic models. Further, the eggshell sorbent showed significant reusability, so the removal efficiency of Co(II) after 4 reutilize cycles did not change significantly and could remain its removal efficiency above 90%. Moreover, the adsorbent was able to eliminate effectively contaminants such as 5-day Biochemical Oxygen Demand (BOD<sub>5</sub>), Chemical Oxygen Demand (COD), and heavy metal ions from a real wastewater. Additionally, the influence of interfering ions including Zn(II), Pb(II), Cr(III) and Cr(VI), Hg(II), and As(III) was studied on the sorption performance of Co(II) ions, and the results revealed that Pb(II) and As(III) had the highest and lowest sorption efficiency, respectively.

**Keywords:** Cobalt ions, Eggshell nanoparticles, Adsorption isotherm, Kinetic behavior

### INTRODUCTION

Heavy metals are one of the stable, non-biodegradable pollutants that can enter water and soil in the environment

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and be sorbed by plants and thus enter the food chain [1,2]. These ions are toxic and dangerous for humans. Cobalt (Co) is utilized extensively in many industries such as batteries, hard-facing alloys, production of pigment, fuel, and other industries [3]. According to the World Health Organization (WHO), the permeable quantity of Co(II) ion in potable water is 2 µg l<sup>-1</sup> [4]. Accumulation of Co(II) ions in the human body

causes many diseases and disorders including myocardial disorders, thyroid disorders, skin sensitivity, and cancer [5]. There are plenty of processes for Co removal from effluents, including ion exchange, reverse osmosis, electro dialysis, chemical precipitation, coagulation, and sorption [3,6]. The sorption process is a simple, and cheap method with high efficiency. The sorption process has advantages over other techniques, which can be attributed to the small area of the land used (half or a quarter compared to the biological process), low sensitivity to flow changes, no influence of toxic materials in the process, high flexibility in design, very high removal of inorganic materials, *etc.* [7,8]. Diverse kinds of substances can be employed in this process, among which biosorbents have been considered much attention owing to their low cost, availability, and no need for the generation process. Eggshells [9], sawdust of palm tree, sour lemon and eucalyptus [10], rice and corn husk biochar [11], *Microcystis aeruginosa* bioadsorbent [12], tea residues [13], orange peel waste [14], and sewage sludge-derived biochar [15] are some important biosorbents. Eggshell is considered as an abundant waste material in the environment, which is a rich source of calcium. Annually, more than 4 million tons of eggshells are produced in China [16]. Almost 95% of eggshell is calcium carbonate and the rest of its content is organic matter. To produce a sorbent with high efficiency, it is better to calcinate eggshells in temperatures above 800 °C. In these temperatures, the eggshell turns into CaO. These types of catalysts have high reusability and stability, and after several reuses, their performance reduces because they may be converted to Ca(OH)<sub>2</sub> [17,18]. In addition, to evaluate the sorption behavior of adsorbents, kinetics and isotherms are very helpful. By utilizing isotherm models, some important factors such as maximum sorption capacity and type of sorption process (*i.e.*, physical or chemical) can be specified. Also, the rate of sorption of contaminants on the sorbent surface is determined by kinetic models [19,20].

The goal of this project is to evaluate the sorption potential of eggshell nanoparticles in Co(II) ions removal from aqueous media. The surface attributes of eggshells were evaluated by DLS, SEM, and BET analyzes. Also, the kinetic and equilibrium behaviors of the sorption process were studied. Moreover, the recyclability of eggshell nanoparticles was investigated in multiple cycles in order to evaluate the

stability of these nanoparticles in wastewater. Besides, the capability of eggshell nanoparticles was assessed to purify a real wastewater and some crucial factors such as BOD<sub>5</sub>, COD, metal ions, and pH were measured before and after adding adsorbent.

## CHEMICAL AND PROCEDURES

### Materials

Cobalt(II) nitrate hexahydrate (CO(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, purity >99%, Merck Co.) with a molar mass of 291.03 g mol<sup>-1</sup> was utilized to generate cobalt solution. Also, acetic acid (purity ≥ 99.8 and molar mass of 60.05 g mol<sup>-1</sup>) and NaOH (purity ≥ 99 and molar mass of 40 g mol<sup>-1</sup>) were prepared from Merck Co., and utilized in this study.

### Producing Eggshell Nanoparticles

The eggshell was prepared from local restaurants. Then, the membrane into the structure of the eggshell was isolated. Next, it was cleansed several times with water. After that, the washed eggshells were dried at 100 °C for 2 h in an oven. Next, they were pulverized by a mechanical ball mill. This technique is a useful process for the top-down production of nanoparticles. In this process, the material particles are ground due to friction with the grinding grains and collision at high speed, which ultimately leads to the reduction of particle size in the nanoscale. After this process, the particle size reached 70 nm [21]. To specify its particle size, eggshells were dissolved into a solution containing ethylene glycol. It was then stored in polyethylene plastic bags at room temperature. Particle size distribution of eggshell was obtained using a Particle Size Analyzer (PSA) device (Horiba, Japan, model lb550). To study the changes on the surface of eggshells before and after sorption, SEM (Hitachi S-4160, Japan) analysis was done. Further, the surface features such as specific surface area and pore size of eggshell, BET (Belsorp, mini II, Japan) analysis was applied.

### Batch Experiments of Adsorption

In this study, the experiments were done discontinuously in 250 ml Erlenmeyer flasks containing 100 ml of cobalt ion

concentration. Then, the impact of pH (2-10), eggshell concentration (1-5 g l<sup>-1</sup>), cobalt ion concentration (10-50 mg l<sup>-1</sup>), stirring speed (0-400 rpm), and time (5-130 min) as effective parameters were studied on the cobalt ion sorption. In order to obtain optimal pH value, several solutions with different pHs containing 2-10 were made and the laboratory conditions were the temperature of 30 °C, 10 mg l<sup>-1</sup> cobalt ion concentration, 3 g l<sup>-1</sup> eggshell dosage, and 200 rpm stirring speed. After 40 min, the remaining concentration of Co(II) ions was measured by a flame atomic absorption device (SpectrAA240, Varian, Australia). After that, the influence of other factors on the sorption of Co(II) was assessed. At the end of each test, the sorption efficiency (R) and sorption capacity (q<sub>e</sub>) were determined as follows:

$$R(\%) = [(C_i - C_0)/C_i] \times 100 \quad (1)$$

$$q_e = (C_i - C_e) * V/w \quad (2)$$

Here, C<sub>i</sub>, C<sub>0</sub>, C<sub>e</sub>, V, and W are initial cobalt concentration (mg l<sup>-1</sup>), final cobalt concentration (mg l<sup>-1</sup>), equilibrium cobalt concentration (mg l<sup>-1</sup>), solution volume (liter), and sorbent weight (gram), respectively [22].

Also, the zero point charge (pH<sub>zpc</sub>) of the adsorbent was studied in order to determine the net surface charge of the adsorbent. To determine pH<sub>zpc</sub>, several solutions with different pH values (2-10) were prepared and after adding eggshell nanoparticles to the solutions, their final pH was measured.

### Treatment of Real Wastewater and Reusability

The capability of eggshell nanoparticles in the treatment of a real sample of wastewater was evaluated. To do so, different chemical and physical attributes of the wastewater were measured before and after adding eggshell nanoparticles, including BOD<sub>5</sub>, COD, pH, and concentration of Hg(II) and Co(II) metal ions.

Also, the reusability of the eggshell nanoparticle in the elimination of cobalt ions was studied in multiple cycles. The tests were done under optimal situations and after each step, the structure of eggshells was cleansed with HNO<sub>3</sub> and water to delete any impurity and metal ions from its surface and prepare the sorbent in the next step of sorption.

### Impact of Interfering Ions

The influence of several ions in the solution on the removal efficiency of cobalt ions on the surface and active sites of eggshell nanoparticles was investigated. To investigate this key factor, a solution containing various metal ions such as zinc (Zn(II)), lead (Pb(II)), chromium (Cr(III) and Cr(VI)), mercury (Hg(II)), and arsenic (As(III)) was made. The experiment was done at a temperature of 30 °C, stirring rate of 200 rpm, pH 6, and eggshell dose of 4 g l<sup>-1</sup>. The concentration of each ion in the solution was considered as 20 mg l<sup>-1</sup> and after 60 min, the sorption process was stopped and the residual concentration of each ion was measured.

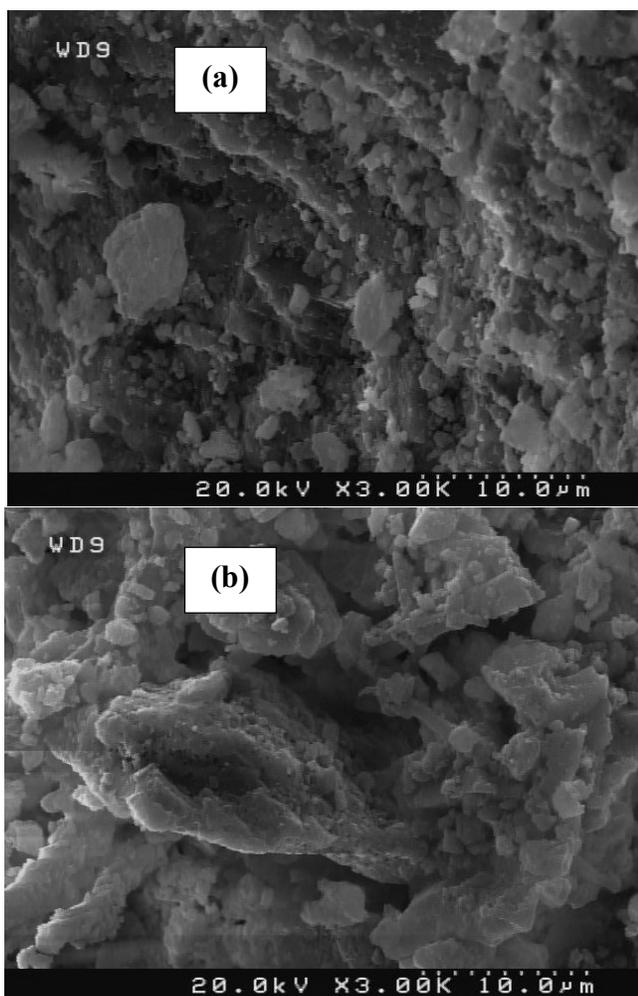
## RESULTS AND DISCUSSIONS

### Characterization of Eggshell Nanoparticles

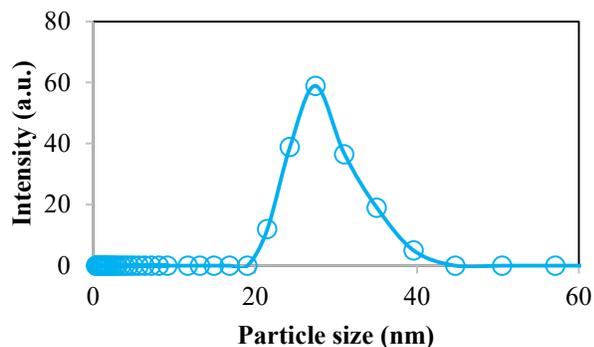
In order to investigate the surface changes as well as morphological features on the eggshell surface, SEM analysis was employed. In order to evaluate the surface features of eggshell nanoparticles such as porosity and active sites, the surface of nanoparticles was covered with a thin layer of gold. As shown in Fig. 1a, there are many pores on the adsorbent surface. Also, many ups and downs are seen on its surface, which indicates that eggshell nanoparticles have sufficient active sites for the adsorption process. After the adsorption process (Fig. 1b), some pores on the eggshell surface are covered by cobalt ions, which indicates that the adsorption process is done successfully.

Also, BET analysis was performed to determine the surface attributes of eggshell nanoparticles. Accordingly, the BET specific surface area, Langmuir specific surface area, pore volume, and pore diameter of particles were 21.96 m<sup>2</sup> g<sup>-1</sup>, 26.74 m<sup>2</sup> g<sup>-1</sup>, 0.035 cm<sup>3</sup> g<sup>-1</sup>, and 12 nm, respectively, which demonstrates that eggshell nanoparticles have mesoporous structure due to its pore diameter, which is between 2 to 50 nm [23].

Moreover, the evaluate the average particle size of eggshell, DLS analysis was employed and the outcomes are revealed in Fig. 2. As demonstrated, the mean size of particles is around 27 nm, which shows that the eggshell sorbent is on a nanosize scale.



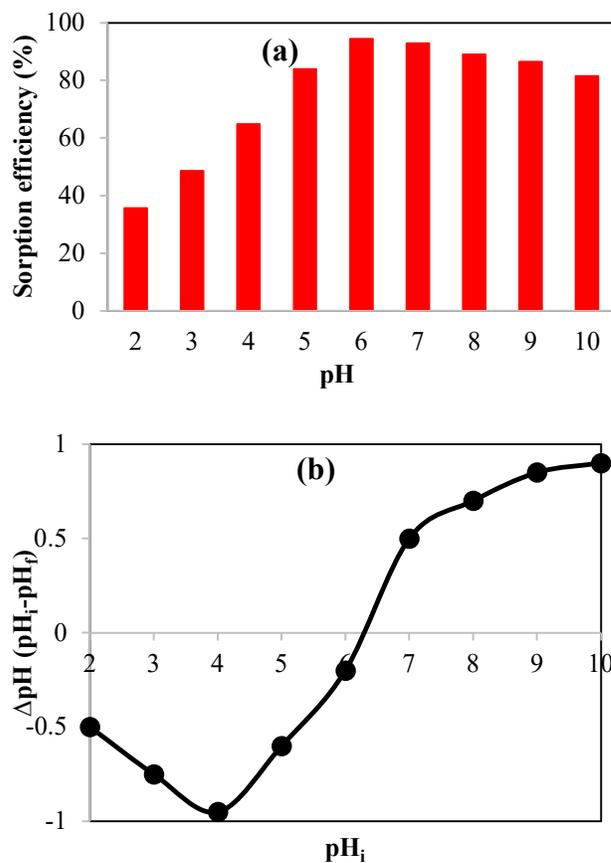
**Fig. 1.** SEM analysis from the surface of eggshell nanoparticles before (a) and after (b) sorption of cobalt ions.



**Fig. 2.** DLS data for determining the average particle size of eggshell.

### The Influence of Diverse Variables on Sorption

Many factors influenced the sorption efficiency of Co(II) ions from aqueous solutions, including pH, stirring speed, time, sorbent dosage, and Co(II) ion concentration. pH is a critical factor in the sorption of all pollutants as the sorption efficiency in the solution highly depends on  $H^+$  and  $OH^-$  concentrations [24]. Investigating the influence of pH on the cobalt ion sorption using eggshell nanoparticles in the domain of 2-10 is seen in Fig. 3a.

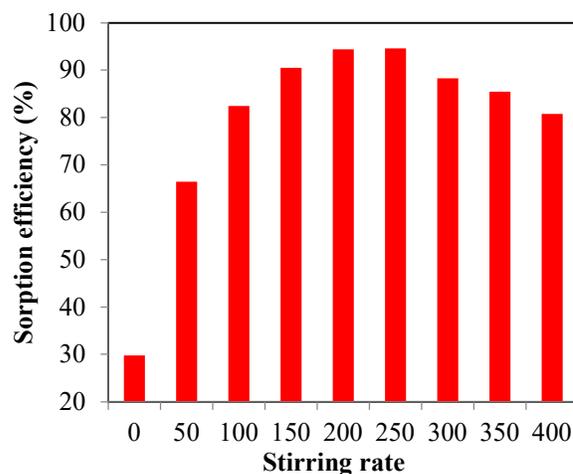


**Fig. 3.** The effect of pH on the sorption efficiency of cobalt ions utilizing eggshell nanoparticles (a) and determination of  $pH_{zpc}$  (b) (Conditions: temperature = 30 °C, cobalt ion concentration = 10 mg l<sup>-1</sup>, eggshell dosage = 3 g l<sup>-1</sup>, stirring speed = 200 rpm, time = 40 min).

According to the results, the uptake efficiency of cobalt ions enhances with rising pH from 2 to 6 and then dwindles. The highest removal efficiency of Co(II) in pH 6 was 94.36%. At low pH amounts, the concentration of  $H^+$  is high and these ions compete with cobalt ions to place on the active sites of eggshell nanoparticles. Therefore, the sorption efficiency at low pHs is low. Because of the high concentration of  $H^+$  ions at low pH amounts (pH = 2) and the easier sorption of these ions compared to metal ions, the minimum sorption efficiency of Co(II) ions occurs. With enhancing pH from 6 to 10, the concentration of  $H^+$  ions in the solution is reduced, while the concentration of  $OH^-$  ions is enhanced. At high pH, hydroxide ions form a complex with cobalt ions and cause precipitation of cobalt ions, thus prevent cobalt ions from being placed on the active sites of eggshell nanoparticles. However, the concentration of both  $H^+$  and  $OH^-$  ions in the solution is low at pH around 7, and Co(II) ions are placed easily on the active sites of eggshell nanoparticles. Similar results were obtained in previous studies [25-26]. Therefore, the highest sorption efficiency was attained at pH 6. In addition, the surface charge of eggshell nanoparticles plays a crucial role in the interaction between the binding sites of pollutant molecules and the sorbent surface. To this end, the zero-point charge ( $pH_{zpc}$ ) of the adsorbent was determined. Figure 3b shows the results of  $pH_{zpc}$  for eggshell nanoparticles in the sorption of Co(II) ions. According to Fig. 3b, the  $pH_{zpc}$  of eggshell nanoparticles is 6.2, which means that the net surface charge of eggshell nanoparticles becomes positive at pH below 6.2 and negative above this value [27].

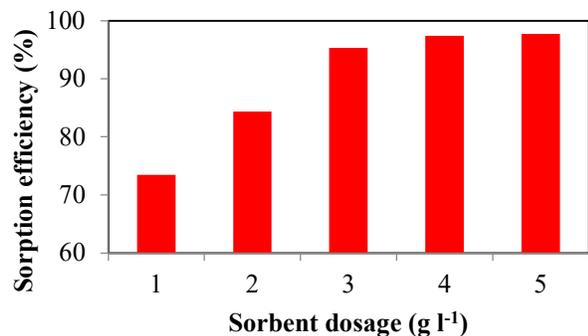
Another factor that has huge influence on cobalt ion adsorption is mixing rate [28], and this factor was investigated in the range of 0-400 rpm under operating conditions including temperature of 30 °C, time of 40 min, pH 6, cobalt ion concentration of 10 mg l<sup>-1</sup>, and eggshell dosage of 3 g l<sup>-1</sup>. To do these experiments, a magnet stirrer was employed. According to Fig. 4, the removal efficiency of Co(II) ions enhances with rising stirring rate from 0 to 200 rpm, because by increasing the rate of mixing, the possibility of contact between the active sites on the eggshell surface and the cobalt ions in the solution increases. Mixing the solution reduces the boundary layer and thus reduces the resistance of cobalt ions transfer, which results in an increase in the ion transfer rate [29]. At a higher stirring rate, the

sorption efficiency declined. Therefore, the highest sorption efficiency (94.36%) was attained at 200 rpm.



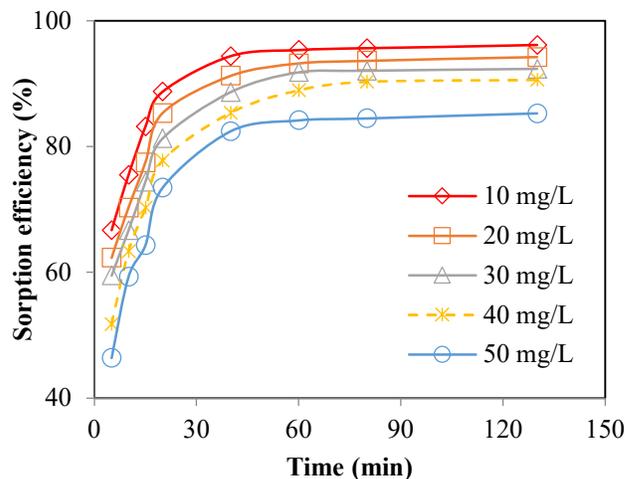
**Fig. 4.** Impact of stirring rate on the sorption efficiency of cobalt ions utilizing eggshell nanoparticles (Conditions: temperature = 30 °C, cobalt ion concentration = 10 mg l<sup>-1</sup>, eggshell dosage = 3 g l<sup>-1</sup>, pH = 6, time = 40 min).

The concentration of the adsorbent also plays a crucial role in the sorption efficiency because this parameter determines the sorption capacity and the amount of pollutant adsorbed on the sorbent surface [22]. In this research, the influence of sorbent dosage (1-5 g l<sup>-1</sup>) was studied on the sorption of cobalt ions, while other conditions such as temperature (30 °C), stirring rate (200 rpm), cobalt ion concentration (10 mg l<sup>-1</sup>), pH (6), and time (40 min) were kept constant. As illustrated in Fig. 5, the uptake efficiency of cobalt ions enhances from 73.44 to 97.43% with enhancing eggshell concentration from 1 to 4 g l<sup>-1</sup>. The number of active sites increases with enhancing the amount of adsorbent, and more cobalt ions can be adsorbed on the eggshell surface. Nonetheless, no change is seen in the sorption efficiency with an increment in the sorbent dosage above 4 g l<sup>-1</sup>, which is due to the saturation of the sorbent's active sites [29]. Therefore, the sorbent concentration of 4 g l<sup>-1</sup> was considered the optimal quantity.



**Fig. 5.** Impact of sorbent concentration on the sorption efficiency of cobalt ions utilizing eggshell nanoparticles (Conditions: temperature = 30 °C, cobalt ion concentration = 10 mg l<sup>-1</sup>, pH = 6, stirring speed = 200 rpm, time = 40 min).

Furthermore, the impact of cobalt ion concentration in different contact times was studied on the sorption efficiency, and the output is observed in Fig. 6. In this study, various concentrations of Co(II) ions from 10 to 50 mg l<sup>-1</sup> at different times (5-130 min) were studied, while other parameters, such as pH 6, temperature of 30 °C, eggshell concentration of 4 g l<sup>-1</sup>, and stirring rate of 200 rpm, were considered constant. Fig. 6 demonstrates that the sorption efficiency increases with rising contact time and cobalt ion concentration because by increasing the concentration of cobalt ion, the necessary force for mass transfer between solid and liquid phases is well provided. At low Co(II) concentrations, the proportion of Co(II) ions to the active sites of eggshell nanoparticles is low and all Co(II) ions are adsorbed on the adsorbent surface, while at high Co(II) concentrations, there are fewer active sites for adsorption. Owing to the saturation of the active sites at high ion concentrations, many Co(II) ions are not adsorbed, which decreases the sorption efficiency [25]. Also, the rate of sorption of cobalt ions by eggshell nanoparticles was faster in the early times, which is caused by the absorption of cobalt ions by the active sites of the sorbent. The equilibrium time for the uptake of Co(II) ions in the solution by eggshell nanoparticles was determined to be 60 min, and after the mentioned time, the sorption percentage increased slowly, which indicates that the active sites of eggshell nanoparticles are occupied by cobalt ions as well as sorption through the penetration of ions into adsorbent layers.



**Fig. 6.** Impact of cobalt ion concentration at different contact times on the sorption efficiency in the existence of eggshell nanoparticles (Conditions: temperature = 30 °C, eggshell dosage = 4 g l<sup>-1</sup>, and stirring speed = 200 rpm, pH = 6).

### Equilibrium and Kinetic Studies

Equilibrium isotherms show the relationship between adsorbent particles and contaminants in a solution. The adsorption mechanism of pollutants is usually determined by these isotherms [30]. Freundlich and Langmuir isotherm models are two well-known models to describe the equilibrium behavior of the adsorption process. These two models were employed in this research in order to describe the isotherm behavior of Co(II) ion sorption using eggshell nanoparticles. In the Langmuir model, it is assumed that there are only interactions between active sites of the adsorbent and contaminant molecules, so the sorption process is only done single layer [31]. The linear form of this model is defined as follows:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{k_L C_e q_{max}} \quad (3)$$

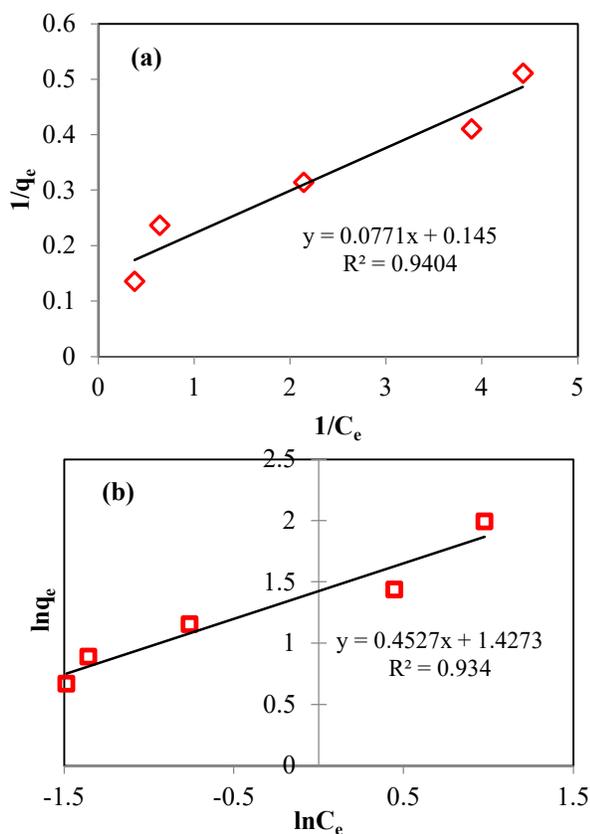
Where,  $C_e$ ,  $q_e$ ,  $q_{max}$ , and  $k_L$  are equilibrium concentration of metal ions (mg l<sup>-1</sup>), sorption capacity (mg g<sup>-1</sup>), maximum sorption capacity (mg g<sup>-1</sup>), and Langmuir model constant, respectively.

Another important isotherm model is Freundlich, which can be utilized for describing the sorption potential of organic and inorganic pollutants using sorbent. In this model, it is assumed that the sorption of metal ions occurs on the non-

uniform and heterogeneous surfaces of the sorbent [32]. The linear form of this model is defined as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

In this relationship,  $K_F$  and  $n$  are both the constants of the Freundlich model, which depend on the sorption capacity and potential of the sorbent [33]. In this study, the Langmuir and Freundlich models were employed to describe the equilibrium behavior of the Co(II) ions sorption. By utilizing these isotherms, the sorption capacity is determined. To investigate the equilibrium sorption behavior of eggshell nanoparticles, several tests were done and the outcomes are revealed in Fig. 7 as well as Table 1.



**Fig. 7.** Langmuir (a) and Freundlich (b) isotherm diagrams for investigating the equilibrium behavior of eggshell nanoparticles in Co(II) ion removal (Conditions: temperature = 30 °C, cobalt ion concentration = 10 mg l<sup>-1</sup>, stirring speed = 200 rpm, pH = 6, time = 60 min).

**Table 1.** Constants and Parameters of Langmuir and Freundlich Models for Co(II) Removal by Eggshell Nanoparticles

Isotherm	Variables	Amount
Langmuir	$q_{\max}$ (mg g <sup>-1</sup> )	6.896
	$K_L$ (l mg <sup>-1</sup> )	1.88
	$R_L$	0.05
	$R^2$	0.9404
Freundlich	$n$	2.208
	$K_F$ (mg g <sup>-1</sup> )	4.167
	$R^2$	0.934

Owing to a higher amount of  $R^2$ , the sorption of Co(II) ions utilizing eggshell nanoparticles follows the Langmuir model, which means that the sorption of Co(II) ions using eggshell nanoparticles is monolayer on the homogeneous surface of the adsorbent [22]. Also, the small amount of  $R_L$  (*i.e.*, 0.05) demonstrates that the adsorption of cobalt ions using eggshell nanoparticles is favorable. Moreover, the maximum adsorption capacity of cobalt ions using eggshells is 6.896 mg g<sup>-1</sup>. Furthermore, the amount of  $n$  (2.208) using the Freundlich model shows that the uptake of cobalt ions using eggshell nanoparticles is physical and favorable [34]. In addition, the amounts of sorption energy (*i.e.*,  $K_L$ ) and  $K_F$  were 1.88 l mg<sup>-1</sup> and 4.167 mg g<sup>-1</sup>, respectively, which are suitable amounts [35].

Another investigation done in this work was studying the kinetic behavior of the sorption process. This behavior depends on the physical and chemical attributes of the adsorbent. In this study, the pseudo-first-order (PFO), pseudo-second-order (PSO), and intraparticle diffusion kinetic models are employed for describing the kinetic behavior of the sorption of Co(II) metal ions. The PFO model is one of the equations that has been extensively utilized for describing the kinetic behavior of the adsorbent in many studies. In the PFO model, it is assumed that the rate of change of solute removal with time is directly proportional to the changes in saturation concentration and amount of sorbate removal with time [36]. The linear form of PFO is expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (5)$$

Here,  $q_t$  ( $\text{mg g}^{-1}$ ) and  $k$  ( $1 \text{ min}^{-1}$ ) are the sorption capacity at time  $t$  and the sorption constant rate, respectively. Another important kinetic model is PSO, which is expressed as follows [37]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e} \quad (6)$$

Where  $K_2$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) is the rate constant of the PSO model.

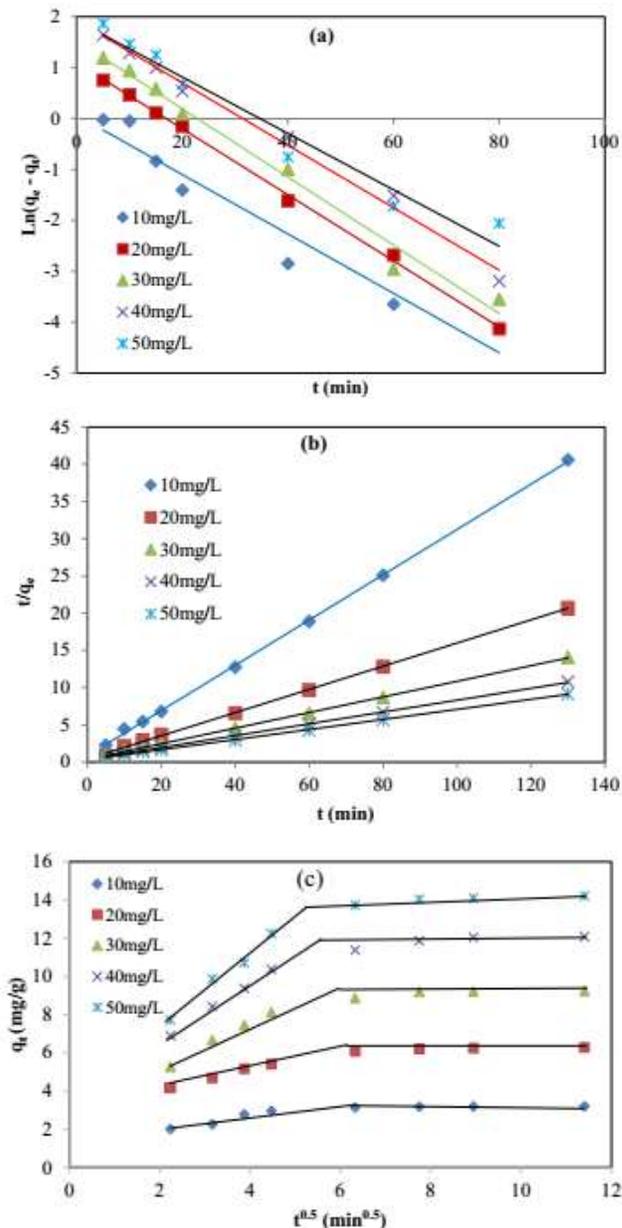
Also, the following relationship is used to describe the intraparticle diffusion kinetic model:

$$q_t = k_i t^{1/2} + I \quad (7)$$

where,  $I$  and  $k_i$  are the equilibrium constant ( $\text{mg g}^{-1}$ ) and the intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{ min}^{1/2}$ ), respectively. These parameters are calculated from the intercept and slope of  $q_t$  against  $t^{1/2}$ , respectively. If the plot of  $q_t$  vs.  $t^{1/2}$  is a straight line, intraparticle diffusion can be considered a limiting step in the adsorption process. Also, if the plot of  $q_t$  vs.  $t^{1/2}$  is not a straight line, the liquid film diffusion will be dominant in the sorption process [38].

The kinetic behavior of the sorption process of cobalt ions utilizing eggshell nanoparticles was studied by three well-known models namely PFO, PSO, and intraparticle diffusion, and the results are shown in Fig. 8 and Table 2. To investigate the kinetic behavior, several experiments were carried out in various cobalt ion concentrations (*i.e.*, 10, 20, 30, 40, and 50  $\text{mg l}^{-1}$ ). The amounts of  $R^2$  show that the PSO model is better fitted with the experimental data compared to PFO and intraparticle diffusion models. Also, the amounts of  $q_{e,cal}$  for the PSO model are closer to the amounts of  $q_{e,exp}$  compared to the PFO model. Therefore, the PSO model is more suitable for describing the kinetic behavior of cobalt ions sorption using eggshell nanoparticles. The results are consistent with previous studies [39]. According to the intraparticle diffusion model (Fig. 8c), there are two stages of adsorption. The first step is carried out at a high rate and is related to film diffusion. In this step, Co(II) ion is transferred from a thin layer to the sorbent surface [40]. The rate of the second stage is slow and the diffusion of Co(II) ions into the sorbent limits the reaction rate. If the film diffusion step is the mass transfer

controlling step, the equilibrium is reached at early times. In conclusion, intraparticle and film diffusion mechanisms are important in the sorption of Co(II) ions using eggshell nanoparticles [41].



**Fig. 8.** Kinetics of cobalt ion sorption using eggshell nanoparticles, including PFO (a), PSO (b), and intraparticle diffusion model (c) (Conditions: temperature = 30 °C, eggshell dosage = 4  $\text{g l}^{-1}$ , stirring speed = 200 rpm, pH = 6).

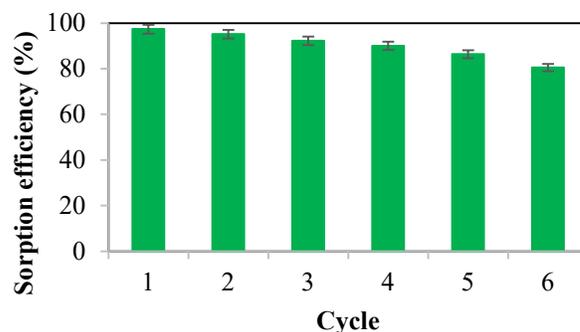
**Table 2.** Parameters of PFO and PSO Kinetic Models for Cobalt Ion Sorption Using Eggshell Nanoparticles

Kinetic models	Variable	Cobalt ion concentration (mg l <sup>-1</sup> )				
		10	20	30	40	50
PFO	q <sub>e cal</sub> (mg g <sup>-1</sup> )	1.0713	2.995	4.623	6.902	6.8517
	K <sub>1</sub> (min <sup>-1</sup> )	0.0584	0.0649	0.067	0.0614	0.0554
	q <sub>e exp</sub> (mg g <sup>-1</sup> )	3.203	6.2806	9.232	12.077	14.206
	R <sup>2</sup>	0.9449	0.9984	0.9845	0.9913	0.9596
PSO	q <sub>e cal</sub> (mg g <sup>-1</sup> )	3.286	6.418	9.532	12.562	14.79
	K <sub>2</sub>	0.112	0.0599	0.03	0.0184	0.0154
	h	1.209	2.467	2.725	2.9	3.368
	R <sup>2</sup>	0.9996	0.9993	0.9997	0.9998	0.9995
Intraparticle diffusion	K <sub>i,1</sub> (mg g <sup>-1</sup> min <sup>-1/2</sup> )	0.292	0.468	0.860	1.088	1.449
	I <sub>1</sub> (mg g <sup>-1</sup> )	1.452	3.226	3.819	4.924	5.045
	R <sup>2</sup>	0.864	0.977	0.909	0.934	0.947
	K <sub>i,2</sub> (mg g <sup>-1</sup> min <sup>-1/2</sup> )	0.011	0.036	0.063	0.127	0.115
	I <sub>2</sub> (mg g <sup>-1</sup> )	3.086	5.896	8.576	10.744	13.281
	R <sup>2</sup>	0.912	0.826	0.795	0.835	0.926

### Reusability

The reusability of adsorbents is a critical factor to evaluate the feasible applicability of adsorbents in the industry [42]. In this research, the reusability of eggshell nanoparticles in cobalt ion removal was surveyed in 6 reuse cycles, and the outcomes are revealed in Fig. 9. After each cycle, the sorbent surface was washed with a mix of water and HNO<sub>3</sub> to delete impurities and cobalt ions, and then the eggshell was reused in the next step. Also, the experiments were done under optimal conditions. According to the results, the sorption efficiency reduces from 97.43% to 90.1% after 4 cycles (*i.e.*, 7.5% reduction in efficiency), which reveals that eggshell has significant stability. Kavand and colleagues investigated the reusability of activated carbon in the removal of Pb(II), Cd(II), and Ni(II) ions in four successive cycles. They employed HNO<sub>3</sub> to clean and remove impurities from the sorbent surface after each stage. After 4 reuse cycles, the reduction in the sorption efficiency of Pb(II) and Cd(II) was around 7%, while an 8.5% reduction was observed in the removal efficiency of Ni(II) ions. These outcomes reveal that the reusability of activated carbon is comparable with the

eggshell used in this work [43]. In another study, Hamed and Borai investigated the reusability of cobalt imprinted polymer in the sorption of Co(II) ions. After 5 successive cycles, the sorption efficiency reduced by 9%, which shows a lower reusability than our study [44].



**Fig. 9.** The reusability of eggshell nanoparticles in 6 cycles (Conditions: temperature = 30 °C, eggshell dosage = 4 g l<sup>-1</sup>, cobalt ion concentration = 10 mg l<sup>-1</sup>, stirring speed = 200 rpm, pH = 6, time = 60 min).

**Table 3.** The Removal Percentage of some Important Chemical and Physical Features of the Wastewater through Adsorption onto the Eggshell Nanoparticle

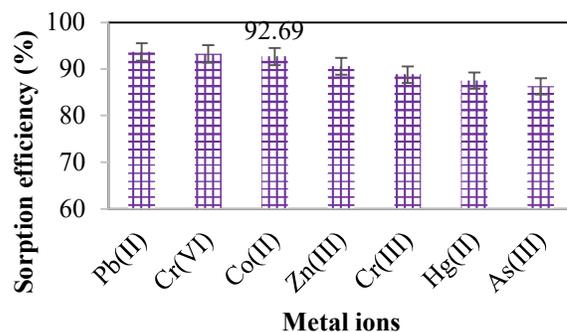
Parameter	Before treatment	After treatment by nano-biochar	Removal percentage (%)
Co(II) ion (mg l <sup>-1</sup> )	4.7	0.8	83
Hg(II) ion (mg l <sup>-1</sup> )	1.1	Non-detectable	100
Turbidity (NTU)	19.5	12.3	37
COD (mg l <sup>-1</sup> )	322.50	137.65	57.3
BOD <sub>5</sub> (mg l <sup>-1</sup> )	185.50	86.95	53.1
pH	7.4	7.1	-

### Real Wastewater

The potential of eggshell nanoparticles in the treatment of a real sample of wastewater was studied and the results are presented in Table 3. As shown, several important features such as BOD<sub>5</sub>, COD, metal ions, pH, and turbidity before and after sorption using eggshells were measured and compared. As reported, eggshell nanoparticles were able to eliminate Co(II) and Hg(II) ions with high efficiency from the effluent. In addition, the concentration of other pollutants such as COD, turbidity, and BOD<sub>5</sub> was reduced significantly after adding eggshell nanoparticles. Also, the pH of the wastewater after adding the eggshell nanoparticle changed from 7.4 to 7.1, which is due to the removal of contaminants from the wastewater. Overall, due to the high removal efficiency, eggshell nanoparticles are proposed as an attractive sorbent for industrial wastewater purification.

### Impact of Interfering Ions

Figure 10 demonstrates the sorption efficiency of these ions onto the sorbent. As shown, Pb(II) and As(III) with sorption efficiency of 93.65 and 86.3% have the highest and lowest sorption percentages among all other metal ions, respectively, so that Pb(II) ions have the maximum interfering impact among other ions on the sorption of cobalt ions by eggshell nanoparticles. Also, the sorption efficiency of Co(II) ions is 92.69%. The sorption efficiency of other ions such as Cr(VI), Cr(III), Zn(II), and Hg(II) is 93.25, 90.6, 88.8, and 87.55%, respectively.



**Fig. 10.** The influence of interference ions on the sorption efficiency of Co(II) ions onto the eggshell surface under optimal conditions (Conditions: temperature = 30 °C, eggshell dosage = 4 g l<sup>-1</sup>, stirring speed = 200 rpm, pH = 6, time = 60 min).

### CONCLUSION

In this study, cobalt heavy metal ions were removed using eggshell nanoparticles. DLS, BET, and SEM analyzes were utilized to evaluate particle size, specific surface area, and morphological features of eggshell particles. The results revealed that the average particle size of eggshell is about 24 nm, the eggshell is highly porous, and its specific surface area is significant, therefore, the sorbent is suitable for the sorption of metal ions. Also, the utmost uptake efficiency of cobalt ions utilizing eggshell nanoparticles under optimal conditions (*i.e.*, stirring rate of 200 rpm, 4 g l<sup>-1</sup> eggshell dose, time of 60 min, Co(II) ion concentration of 20 mg l<sup>-1</sup>, temperature of 30 °C, and pH 6) was 97.43%. In this survey,

the isotherm and kinetic behavior of Co(II) ions sorption was investigated and the outcomes revealed that the Langmuir isotherm and PSO kinetic models could describe better the sorption behavior of Co(II) ions using eggshell nanoparticles. Also, the equilibrium study showed that the sorption of Co(II) ions using eggshell nanoparticles is favorable and physical. In addition, the reusability study of eggshell in Co(II) ion removal showed that eggshell nanoparticles have high reusability after 4 reuse steps so their sorption efficiency reduced by only 7.5%. Moreover, eggshell nanoparticles could remove BOD<sub>5</sub>, COD, Hg(II), and Co(II) ions from a real wastewater with removal percentages of 53.1, 57.3, 100, and 83%, respectively, which indicates the remarkable capability of eggshell nanoparticles. Furthermore, the impact of interfering ions, such as Zn(II), Pb(II), Cr(III) and Cr(VI), Hg(II), and As(III), was studied on the sorption performance of Co(II) ions by eggshell nanoparticles, and the results revealed that Pb(II) and As(III) had the highest and lowest sorption efficiency, respectively. Based on the results, eggshell nanoparticles are suggested as an efficient adsorbent for the removal of Co(II) ions from industrial wastewater.

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## REFERENCES

- [1] Qasem, N. A.; Mohammed, R. H.; Lawal, D. U., Removal of heavy metal ions from wastewater: A comprehensive and critical review. *Npj Clean Water* **2021**, *4*, 36. <https://doi.org/10.1038/s41545-021-00127-0>.
- [2] Odumbe, E.; Murunga, S.; Ndiiri, J., Heavy Metals in Wastewater Effluent: Causes, Effects, and Removal Technologies. *Trace Metals in the Environment*. **2023**. <https://doi.org/10.5772/intechopen.1001452>.
- [3] Hua, Q.; Guo, H.; Wang, D.; Huang, Y.; Cao, Y.; Peng, W.; Fan, G., A new strategy for selective recovery of low concentration cobalt ions from wastewater: Based on selective chelating precipitation-flotation process. *J. Taiwan Inst. Chem. Eng.* **2022**, *141*, 104605. <https://doi.org/10.1016/j.jtice.2022.104605>.
- [4] Al-Shahrani, S. S., Treatment of wastewater contaminated with cobalt using Saudi activated bentonite. *Alex. Eng. J.* **2014**, *53* (1), 205-211. <https://doi.org/10.1016/j.aej.2013.10.006>.
- [5] Amoo, K. O.; Amoo, T. E.; Olafadehan, O. A.; Alagbe, E. E.; Adesina, A. J.; Bamigboye, M. O.; Olowookere, B. D.; Ajayi, K. D., Adsorption of cobalt(II) ions from aqueous solution using cow bone and its derivatives: Kinetics, equilibrium and thermodynamic comparative studies. *Results Eng.* **2023**, *20*, 101635. <https://doi.org/10.1016/j.rineng.2023.101635>.
- [6] Lin, S.; Pan, X.; Meng, D.; Zhang, T., Electric conversion treatment of cobalt-containing wastewater. *Water Sci. Technol.* **2021**, *83* (8), 1973-1986. <https://doi.org/10.2166/wst.2021.101>.
- [7] Al-Jlil, S. A., Adsorption of cobalt ions from waste water on activated Saudi clays. *Appl. Water Sci.* **2017**, *7*, 383-391. <https://doi.org/10.1007/s13201-014-0253-z>.
- [8] Dev, V. V.; Nair, K. K.; Baburaj, G.; Krishnan, K. A., Pushing the boundaries of heavy metal adsorption: A commentary on strategies to improve adsorption efficiency and modulate process mechanisms. *Colloid Interface Sci. Commun.* **2022**, *49*, 100626. <https://doi.org/10.1016/j.colcom.2022.100626>.
- [9] Mine, Y.; Oberle, C.; Kassaiy, Y., Eggshell matrix proteins as defense mechanism of avian eggs. *J. Agric. Food Chem.* **2003**, *51*, 249-253. <https://doi.org/10.1021/jf020597x>.
- [10] Esmaeili, H.; Foroutan, R., Adsorptive behavior of methylene blue onto sawdust of sour lemon, date palm, and eucalyptus as agricultural wastes. *J. Dispers. Sci. Technol.* **2019**, *40* (7), 990-999. <https://doi.org/10.1080/01932691.2018.1489828>.
- [11] Sanka, P. M.; Rwiza, M. J.; Mtei, K. M., Removal of selected heavy metal ions from industrial wastewater using rice and corn husk biochar. *Water Air Soil Pollut.* **2020**, *231*, 1-13. <https://doi.org/10.1007/s11270-020-04624-9>.
- [12] Zeng, G.; He, Y.; Liang, D.; Wang, F.; Luo, Y.; Yang, H.; Wang, Q.; Wang, J.; Gao, P.; Wen, X.; Yu, C., Adsorption of heavy metal ions copper, cadmium and nickel by *Microcystis aeruginosa*. *Int. J. Environ. Res. Public Health* **2022**, *19* (21), 13867. <https://doi.org/10.3390/ijerph192113867>.

- <https://doi.org/10.3390/ijerph192113867>.
- [13] Uddin, M. T.; Islam, M. A.; Mahmud, S.; Rukanuzzaman, M., Adsorptive Removal of Methylene Blue by Tea Waste. *J. Hazard. Mater.* **2009**, *164*, 53-60. <https://doi.org/10.1016/j.jhazmat.2008.07.131>.
- [14] Michael-Igolima, U.; Abbey, S. J.; Ifelebuegu, A. O.; Eyo, E. U., Modified orange peel waste as a sustainable material for adsorption of contaminants. *Materials* **2023**, *16* (3), 1092. <https://doi.org/10.3390/ma16031092>.
- [15] Karimi, F.; Rahimi, G.; Kolahchi, Z.; Nezhad, A. K. J., Using industrial sewage sludge-derived biochar to immobilize selected heavy metals in a contaminated calcareous soil. *Waste. Bio. Valor.* **2020**, *11* (6), 2825-2836. <https://doi.org/10.1007/s12649-018-00563-z>.
- [16] Yao, Y.; Zhang, J.; Zhang, R.; Shi, Y.; An, P.; Hu, X.; Wan, Y., Optimization of preparation of calcium acetate from eggshell by Response Surface Methodology (RSM). *Food Sci. Technol.* **2022**, *42*, 114421. <https://doi.org/10.1590/fst.114421>.
- [17] Chen, W.; Wu, Y.; Xie, Z.; Li, Y.; Tang, W.; Yu, J., Calcium hydroxide recycled from waste eggshell resources for the effective recovery of fluoride from wastewater. *RSC Adv.* **2022**, *12* (43), 28264-28278. <https://doi.org/10.1039/D2RA05209A>.
- [18] Lanzón, M.; Madrid-Mendoza, J. A.; Navarro-Moreno, D.; García-Vera, V. E., Use of eggshell waste: A green and effective method for the synthesis of pure calcium hydroxide suspensions. *Constr. Build. Mater.* **2023**, *377*, 131106. <https://doi.org/10.1016/j.conbuildmat.2023.131106>.
- [19] Dinh, L. X.; Van Tung, N.; Lien, N. T.; Minh, P. T.; Le, T. H., The Adsorption Kinetic and Isotherm Studies of Metal Ions ( $\text{Co}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cs}^{+}$ ) on  $\text{Fe}_3\text{O}_4$  Nanoparticle of Radioactive Importance. *Results Chem.* **2023**, 101095. <https://doi.org/10.1016/j.rechem.2023.101095>.
- [20] Al-Saedi, S. I.; Areej, A.; Qamar, M. T.; Alhujaily, A.; Iqbal, S.; Alotaibi, M. T.; Aslam, M.; Qayyum, M. A.; Bahadur, A.; Awwad, N. S.; Jazaa, Y., Isotherm and kinetic studies for the adsorption of methylene blue onto a novel  $\text{Mn}_3\text{O}_4\text{-Bi}_2\text{O}_3$  composite and their antifungal performance. *Front. Environ. Sci.* **2023**, *11*, 1156475. <https://doi.org/10.3389/fenvs.2023.1156475>.
- [21] Huang, X.; Dong, K.; Liu, L.; Luo, X.; Yang, R.; Song, H.; Li, S.; Huang, Q., Physicochemical and structural characteristics of nano eggshell calcium prepared by wet ball milling. *LWT* **2020**, *131*, 109721. <https://doi.org/10.1016/j.lwt.2020.109721>.
- [22] Khaleghi, H.; Jaafarzadeh, N.; Esmacili, H.; Ramavandi, B., Alginate@  $\text{Fe}_3\text{O}_4$ @ Bentonite nanocomposite for formaldehyde removal from synthetic and real effluent: optimization by central composite design. *Environ. Sci. Pollut. Res.* **2023**, *30* (11), 29566-29580. <https://doi.org/10.1007/s11356-022-24189-w>.
- [23] Zhang, W.; Liu, H.; Qiu, X.; Zuo, F.; Wang, B., Mesoporous silica nanoparticles as a drug delivery mechanism. *Open Life Sci.* **2024**, *19* (1), 20220867. <https://doi.org/10.1515/biol-2022-0867>.
- [24] Aljar, M. A. A.; Rashdan, S.; Almutawah, A.; El-Fattah, A. A., Synthesis and characterization of biodegradable poly (vinyl alcohol)-chitosan/cellulose hydrogel beads for efficient removal of Pb(II), Cd(II), Zn(II), and Co(II) from water. *Gels* **2023**, *9* (4), 328. <https://doi.org/10.3390/gels9040328>.
- [25] Maleki, F.; Gholami, M.; Torkaman, R.; Torab-Mostaedi, M.; Asadollahzadeh, M., Multivariate optimization of removing of cobalt(II) with an efficient aminated-GMA polypropylene adsorbent by induced-grafted polymerization under simultaneous gamma-ray irradiation. *Sci. Rep.* **2021**, *11* (1), 18317. <https://doi.org/10.1038/s41598-021-97826-y>.
- [26] Pourshojaei, Y.; Nasiri, A., Cobalt separation from water and food samples based on penicillamine ionic liquid and dispersive liquid-liquid microextraction before determination by AT-FAAS. *Anal. Methods Environ. Chem. J.* **2021**, *4* (03), 21-32. <https://doi.org/10.24200/AMECJ.V4.I03.148>.
- [27] Annane, K.; Lemlikchi, W.; Tingry, S., Efficiency of eggshell as a low-cost adsorbent for removal of cadmium: Kinetic and isotherm studies. *Biomass Conv. Bioref.* **2023**, *13* (7), 6163-6174. <https://doi.org/10.1007/s13399-021-01619-2>.
- [28] Wojnicki, M.; Socha, R. P.; Luty-Błocho, M.; Fitzner, K., Kinetic studies of the removal of Pt(IV) chloride complex ions from acidic aqueous solutions using activated carbon. *React. Kinet. Mech. Catal.* **2017**, *120*, 715-734. <https://doi.org/10.1007/s11144-017-1151-9>.
- [29] Batouti, M. E.; Ahmed, A. M. M.; Ibrahim, N. A.; Mohamed, N., Adsorption of Co(II) on nanobentonite

- surface: kinetic and equilibrium studies. *Indian J. Chem. Technol.* **2017**, *24*, 461-470. <https://doi.org/10.56042/ijct.v24i5.10452>.
- [30] Ekeoma, B. C.; Sambudi, N. S.; Ndukwe, C. O., Activated empty palm fruit bunch for the adsorption of heavy metal ions: kinetics and thermodynamics. *Phys. Chem. Res.* **2022**, *10* (4), 505-518. <https://doi.org/10.22036/PCR.2022.319988.2002>.
- [31] Revellame, E. D.; Fortela, D. L.; Sharp, W.; Hernandez, R.; Zappi, M. E., Adsorption kinetic modeling using pseudo-first order and pseudo-second order rate laws: a review. *Clean Eng. Technol.* **2020**, *1*, 100032. <https://doi.org/10.1016/j.clet.2020.100032>.
- [32] Khayyun, T. S.; Mseer, A. H., Comparison of the experimental results with the Langmuir and Freundlich models for copper removal on limestone adsorbent. *Appl. Water Sci.* **2019**, *9* (8), 170. <https://doi.org/10.1007/s13201-019-1061-2>.
- [33] Salim, N. A. A.; Puteh, M. H.; Khamidun, M. H.; Fulazzaky, M. A.; Abdullah, N. H.; Yusoff, A. R. M.; Zaini, M. A. A.; Ahmad, N.; Lazim, Z. M.; Nuid, M., Interpretation of isotherm models for adsorption of ammonium onto granular activated carbon. *Biointerface Res. Appl. Chem.* **2021**, *11* (2), 9227-9241. <https://doi.org/10.1016/j.cej.2012.02.080>.
- [34] Khaleghi, H.; Esmacili, H.; Jaafarzadeh, N.; Ramavandi, B., Date seed activated carbon decorated with CaO and Fe<sub>3</sub>O<sub>4</sub> nanoparticles as a reusable sorbent for removal of formaldehyde. *Korean J. Chem. Eng.* **2022**, *39* (1), 146-160. <https://doi.org/10.1007/s11814-021-0972-4>.
- [35] Boushehrian, M. M.; Esmacili, H.; Foroutan, R., Ultrasonic assisted synthesis of Kaolin/CuFe<sub>2</sub>O<sub>4</sub> nanocomposite for removing cationic dyes from aqueous media. *J. Environ. Chem. Eng.* **2020**, *8* (4), 103869. <https://doi.org/10.1016/j.jece.2020.103869>.
- [36] Sheela, T.; Nayaka, Y. A., Kinetics and thermodynamics of cadmium and lead ions adsorption on NiO nanoparticles. *Chem. Eng. J.* **2012**, *191*, 123-131. <https://doi.org/10.1016/j.cej.2012.02.080>.
- [37] Al-Harby, N. F.; Albahly, E. F.; Mohamed, N. A., Kinetics, isotherm and thermodynamic studies for efficient adsorption of Congo Red dye from aqueous solution onto novel cyanoguanidine-modified chitosan adsorbent. *Polymers* **2021**, *13* (24), 4446. <https://doi.org/10.3390/polym13244446>.
- [38] Vitela-Rodriguez, A. V.; Rangel-Mendez, J. R., Arsenic removal by modified activated carbons with iron hydro (oxide) nanoparticles. *J. Environ. Manage.* **2013**, *114*, 225-231. <https://doi.org/10.1016/j.jenvman.2012.10.004>.
- [39] Aboli, E.; Jafari, D.; Esmacili, H., Heavy metal ions (lead, cobalt, and nickel) biosorption from aqueous solution onto activated carbon prepared from Citrus limetta leaves. *Carbon Lett.* **2020**, *30*, 683-698. <https://doi.org/10.1007/s42823-020-00141-1>.
- [40] Foroutan, R.; Mohammadi, R.; Razeghi, J.; Ramavandi, B., Performance of algal activated carbon/Fe<sub>3</sub>O<sub>4</sub> magnetic composite for cationic dyes removal from aqueous solutions. *Algal Res.* **2019**, *40*, 101509. <https://doi.org/10.1016/j.algal.2019.101509>.
- [41] Vitela-Rodriguez, A. V.; Rangel-Mendez, J. R., Arsenic removal by modified activated carbons with iron hydro (oxide) nanoparticles. *J. Environ. Manage.* **2013**, *114*, 225. <https://doi.org/10.1016/j.jenvman.2012.10.004>.
- [42] Tamjidi, S.; Ameri, A.; Esmacili, H., A review of the application of fungi as an effective and attractive bio-adsorbent for biosorption of heavy metals from wastewater. *Environ. Monit. Assess.* **2023**, *195* (1), 91. <https://doi.org/10.1007/s10661-022-10687-4>.
- [43] Kavand, M.; Kaghazchi, T.; Soleimani, M., Optimization of parameters for competitive adsorption of heavy metal ions (Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>) onto activated carbon. *Korean J. Chem. Eng.* **2014**, *31*, 692-700. <https://doi.org/10.1007/s11814-013-0280-8>.
- [44] Hamed, M. G.; Borai, E. H., Ultrasound assistance synthesis of optimized ion imprinted polymer for efficient and selective removal of cobalt ions from waste streams. *J. Polym. Res.* **2023**, *30* (11), 428. <https://doi.org/10.1007/s10965-023-03816-1>.