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Removal of heavy metals from simulated water by using eggshell powder

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ABSTRACT

Eggshell powder (ESP) is a cheap, adsorbent material used for removing different heavy metals from water by applying various adsorption methods. In batch adsorption experiments, the potential of ESP for the removal of the cadmium(II) (Cd^{2+}) ion from aqueous solution was investigated. A batch study was utilized as a function of the initial concentration, the ESP amount, the contact time, and the pH of the aqueous solution. Freundlich and Langmuir's linear equations were used to investigate adsorption isotherms. The characterization studies of ESP samples were done using a scanning electron microscope and a Fourier transform infrared spectrometer. The highest Cd^{2+} removal efficiency was found at pH 5.0, an initial ESP dosage of 3.5 g, a temperature at 20°C, a shaking speed at 250 rpm, and a contact time of 60 min. The maximum removal efficiencies coming from the ESP were between 65% and 96% for Cd^{2+} under optimum conditions. The adsorption data were fitted to the Langmuir isotherm. The adsorption capacity and the affinity of the ESP were examined for Cd^{2+}. The Langmuir constants and separation factor (R_L) values indicate that the Cd^{2+} was favorably adsorbed onto the ESP. The maximum adsorption capacities obtained from the Langmuir model for Cd^{2+} were 2.221 mg/g of the ESP. The findings imply that the ESP could be used as an inexpensive, sustainable, and effective adsorbent for Cd^{2+} removal from different aqueous solutions.

Keywords: Adsorption capacity; Cadmium; Eggshells; Simulated water

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1. Introduction

The contamination of water medias, especially with contaminants, is an environmental global issue [1–10]. Cadmium (Cd) is one of the most harmful heavy metal pollutants in the environment because of its toxicity, nondegradability, bioaccumulation, and mobility in natural water and soil ecosystems [11,12]. It has a major cancerogenic impact and could lead to endocrine disorders, as well as nephrosis and bone diseases [13]. Cd contamination comes largely from domestic sewage and the effluents of industries in electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium–nickel batteries, fertilizers, pesticides, pigments and dyes, textile operations, and refining [8,11,14]. The main form of Cd^{2+} in contaminated water is Cd^{2+}, and the remediation technologies available to reduce Cd^{2+} and different heavy metal concentrations in contaminated water systems contain ion exchange, solvent extraction, chemical precipitation, phytoextraction, ultrafiltration, reverse osmosis, electrodialysis, adsorption, etc. [15–22]. The most of these technologies, on the other hand, have limitations in reducing toxic contaminants from contaminated water to safe levels, as they are costly, labor intensive, and time-consuming [23,24]. As compared with the other processes, adsorption was the most promising method because of the low-cost, its simplicity in application and efficiency [25,26]. In the adsorption process, the adsorbent was the key. The adsorption procedure might be a feasible treatment process, since it has important advantages, such as an economical cost and favorable efficiency for removing heavy metals from water and wastewater [27–33].

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So, different natural materials could be mixed to achieve impressive adsorbents whose capacity and applicability are related to the specific ingredients [34–41].

Eggshell is a well-known waste material, obtaining in every day on a massive scale from households, restaurants, the food industry, bakeries, etc. [42]. It is disposed as garbage, leading to another source of pollution. Due to the eggshell porosity and surface properties, it could be effective adsorbents, which could be able to remove heavy metals, phenolic compounds, dyes, and pesticides from wastewater. The use of this kind of adsorbents has a lot of advantages because of the low cost and the availability of eggshells. Furthermore, there is no need for surface activation in the pretreatment [43,44]. In aqueous solution, as a hydrolysis reaction becomes, the system would be more alkaline. Its disposal would be a great concern, and the usage of eggshells as a potential adsorbent is a meaningful endeavor due to its high ion-exchange capacity [45–48]. A literature survey suggests that eggshell was successfully used as an adsorbent in the removal of organic matters and metal ions from industrial effluents. Additionally, to obtain eggshell properties, some technological options were considered to get value-added commercial products from eggshell powder (ESP) [42–51]. This study aims at the applicability of ESP as an adsorbent for Cd^{2+} to eliminate from synthetic solutions. The contact period, pH, amount of the ESP, and their effects, which are considered the most critical parameters creating impacts on the removal of Cd^{2+} from aqueous solutions.

2. Materials and methods

2.1. Simulated effluent preparation

The cadmium-containing medium was obtained from $3CdSO_4{\cdot}8H_2O$ (Sigma-Aldrich Chemie GmbH, Germany). About 2.281 g of $3CdSO_4{\cdot}8H_2O$ was measured and Cd^{2+} wastewater amount of 1,000 mg/L was prepared. Furthermore, an experiment solution of 100 mg/L was created when needs. After the experiment, the effluent wastewater was examined by Perkin Elmer Optima 2100DV model inductively coupled plasma optical emission spectrometry (ICP-OES). Since industry authorities require providing heavy metal discharge standards, diverse industrial wastewater usually includes lower heavy metal concentrations. However, some previous papers indicated that different industry wastewaters include various types of heavy metals, as their effluent concentrations become higher [1–14]. Thus, a cadmium ion concentration of synthetically prepared wastewater was used as 100 mg/L to represent real industrial wastewater.

2.2. Experimental procedure

Cd^{2+} ions search was ended in the adsorption system. The experimental works were finished under the experimental conditions of different operation parameters of a pH of 2–6, a contact time of 1–150 min, and a metal ion concentration of 100 mg/L. The amount of the ESP was 0.05–5 g. ZHICHENG analytic thermal shaker was employed for the batch experiments. The pH experiments were measured with a LABQUEST2 device. The experiments were done by bringing precisely weighted samples of ESP into contact with 100 mL of Cd^{2+} solutions in the sealed 250 mL Erlenmeyer flasks. The suspensions were done in a thermal shaker at a shaking speed of 250 rpm at 20°C in triplicate. After the specified time, suspensions were filtered through a filter study using 0.45 μm pore size membrane filters. The initial pH of the cadmium solution was adjusted to the desired pH by adding 1 mol/L HCl or NaOH solutions. After adsorption, the mixtures were filtered, and the filtrates were examined for Cd content based on an ICP-OES at 261.42 nm.

2.3. Adsorption efficiency

The analyses were done at different conditions for the ESP, the concentration of Cd^{2+} deposited onto ESP surface based on the accompanying numerical phrase:

$$q_e\left(\frac{\text{mg}}{\text{g}}\right) = \frac{\left(C_0 - C_e\right) \times V}{1{,}000 \times w} \tag{1}$$

where q_e indicates the amount of Cd^{2+} deposited on ESP (mg/g), C_e depicts the initial solute concentration in the solution before adsorption (mg/L), C_0 shows the final concentration of solute in the solution after adsorption (mg/L), V depicts the volume of the metal solution (L), and w is the weight of the ESP adsorbent. Adsorption process was quantified by calculating the adsorption percent (E %) as described in Eq. (2) as follows:

$$E\left(\text{adsorption}\right)\left(\%\right) = \frac{\left(C_0 - C_e\right)}{1{,}000 \times C_0} \tag{2}$$

Adsorption experiments were implemented in triplicate and the average concentrations of samples were provided. Also, witness samples were used to control the findings through overall adsorption process. Data performed depicts the mean values from the adsorption analyses, error bars are presented in Figs. 1–3.

2.4. Eggshell properties and preparation

As in Table 1, some properties and the chemical composition of ESP indicate that calcium oxide was the most abundant component [49,52,53]. Eggshell is a biomineralized composite of calcite crystals embedded in an organic

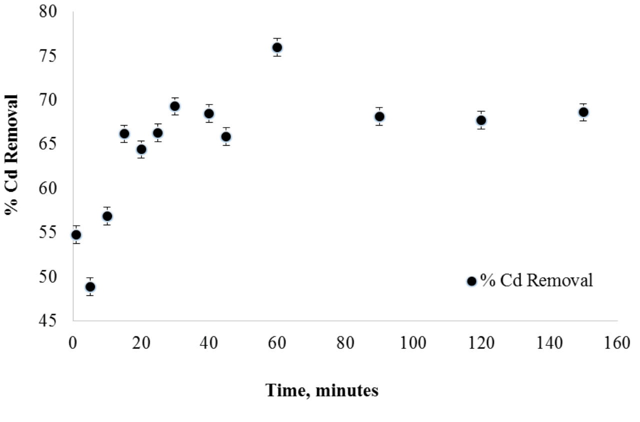

Fig. 1. Effect of adsorption process time on % adsorption of Cd^{2+} using ESP.

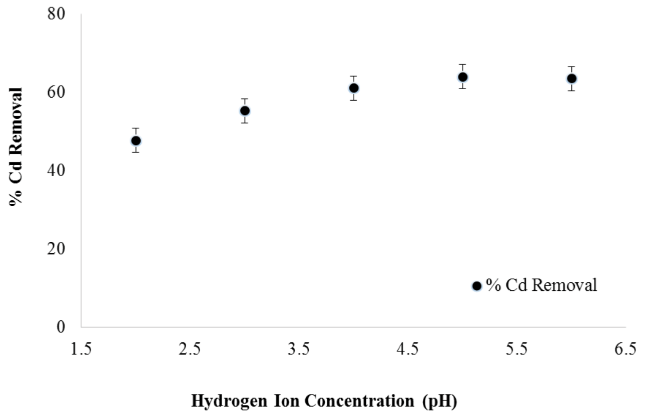

Fig. 2. Effect of solution pH on the removal efficiency of Cd^{2+} using ESP as an adsorbent.

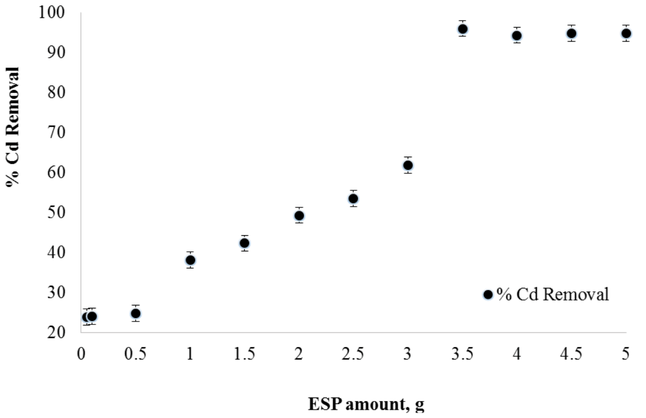

Fig. 3. Effect of adsorbent dose on adsorption of Cd^{2+} by ESP.

framework of protein fibers, which represents about 11% of the total weight of the egg [49,54]. This macroporous structure includes open voids with a similar total volume of 0.006 cm^3/g, as a Brunauer–Emmett–Teller surface area ranges from 0.84 to 1.3 m^2/g [53–56].

The ESP milling was done in a laboratory planetary ball mill Pulverisette 6 (Fritsch, Germany) with slightly different conditions. The common conditions include the following ones: the loading of the mill – 50 balls of 10 mm diameter; the ball charge in the mill – 360 g; the material of the milling chamber – ball tungsten carbide; and the atmosphere-air – laboratory temperature. The differences were in the rotation speed of the planet carrier, the sample mass, the milling time, and the ball-to-powder ratio (see Table 2) [50,51].

2.5. Morphological ESP characterizations

The morphological properties of the natural egg shells samples were examined. The elemental composition was examined by ICP-OES spectrometry. The surface morphology was observed based on a Bruker Evo LS 10 scanning electron microscope (SEM) analysis. Functional groups were characterized by Fourier transform infrared spectrometry (FTIR) using a Bruker Vertex 70 in the range 400–4,000 cm^{-1} [57,58].

Table 1
Some properties and chemical composition of ESP

Parameters	ESP
Moisture (%)	1.0
pH_{ZPC}	5.5 ± 0.1
Electrical conductivity (dS/m)	0.45
Equivalent $CaCO_3$ (g $CaCO_3$/100 $g_{airdired}$)	88 ± 0
Organic matter (%)	6.3 ± 0.1
Total organic carbon/total nitrogen	2.1
Germination index (%)	53.6 ± 3.3
Respiration rate (mg C-CO_2/g C/d)	24 ± 1
Chemical composition	ESP (Wt.%)
C	21.128
Na_2O	0.105
MgO	0.926
P_2O_5	0.415
SO_3	0.326
K_2O	0.054
CaO	76.992

2.6. Determination of zero-point charge (pH_{PZC})

The pH value at the point of zero charge, pH_{PZC}, was decided by the mass titration method [59,60]. Different weighed amounts of activated carbon (0.010–0.600 g) were placed in a series of 50-mL glass bottles and 10 mL of 0.1 M NaCl solution was added to each of them. The bottles were stoppered and left under constant stirring for 48 h, and the pH value of each solution was measured based on a LabQuest model pH meter [61].

3. Results and discussion

3.1. Determination of contact time for ESP adsorbent

The adsorption process time is the key parameter for the selection of the adsorbent for the adsorption process. The batch adsorption experiments were done using a 100 mg/L Cd^{2+} concentration with the function of the adsorption process time and the removal efficiency of ESP; these are shown in Fig. 1. The adsorption of Cd^{2+} has been examined on ESP as a function of time in the range of 1–150 min. The removal efficiency of Cd^{2+} gradually becomes high with higher adsorption process times and reaches equilibrium at around 80 min, at this point the maximum amount of Cd^{2+} is removed from the solution. Fig. 1 indicates that the

Table 2
Different ball milling conditions used for ESP [50,51]

Parameters	ESP
Adsorbent amount (g)	5–250
Ball milling time (min)	0–360
Ball milling (min^{-1})	500
Ball-to-powder ratio	72

adsorption efficiency increased from 48.88% to 75.99% at a contact time of 60 min with a 100 mg/L Cd^{2+} concentration. At this optimum adsorption process time, the clump of the batch experiments was done to make sure that equilibrium was obtained. Furthermore, the adsorption yield enhanced with contact period and reached maximum value (75.99%) in 60 min. In between 90 and 100 min, the adsorption yield was almost unchanged such that it could be considered the equilibrium operation of the Cd^{2+} adsorption. To present that enough contact period was obtained, further adsorption analyses were done for 150 min.

Daraei et al. [42] employ eggshell membrane as a natural adsorbent in the removal of Cr^{+6}. In this paper, the effect of contact time is examined between 0 and 200 min, since 117.52 min are selected for the optimum contact time. Based on natural biomass ash, Xu et al. [62] state that the optimum contact time for reaching the maximum removal efficiency for Cd^{2+} is 90 min. Many different studies in the literature provide results for the optimum contact times. Optimum contact time could be different due to the type of adsorbent used in the operation, the heavy metal scrap that is removed, and other operating conditions. After the effect of contact time on adsorption was examined, the effects of other parameters could be getting based on the optimum contact time.

3.2. Effect of hydrogen ion concentration (pH) on Cd^{2+}

The variation of pH is highly effective in the adsorption process for removal of Cd^{2+} from wastewater based on ESP as an adsorbent. The initial pH of the solution is a significant control parameter for the evaluation of adsorption performances [63]. To get information on the adsorption mechanism, it should determine the point of zero charge (pH_{ZPC}) of the adsorbent, since the point of zero charge depicts the pH value at which the surface charge of an adsorbent equals to zero [64,65]. Thus, cations adsorption on the surface of any adsorbent is favorable at a pH value higher than pH_{ZPC}, while anion adsorption could be favorable at pH value lower than pH_{ZPC}. Here, the value pH_{ZPC} of ESP is 5.5 (Table 2), which shows that adsorption of cadmium happened at the surface of the ESP at $pH < pH_{PZC}$.

The impact of pH on the Cd^{2+} ions is shown in Fig. 2. All the experiments were connected with pH due to the major sensitivity of chemical characteristics of the ESP. The effect of pH on the adsorption of Cd^{2+} at 20°C for constant concentration and the time of adsorption of 70 min is presented in Fig. 2. It was obtained that the pH of the solution varies from 2.0 to 6.0, and the adsorption efficiency becomes very low, since repulsion is between solution and ESP adsorbent. The adsorption efficiency is slowly increasing with the pH (3.0–6.0) of the solution, since the effluent solution is exposed to the negative charges and strongly attracts the Cd^{2+} ions with the adsorbent surface. This subsequently creates a change in the equilibrium conditions and the kinetics of the adsorption process. These studies indicate that the potential of H^+ ions on the ESP surfaces is not metal specific. The maximum efficiency of 64.04% is obtained at pH 5.0. The monitored lower adsorption abilities at the high acid–base balance can be tied with decreasing the adsorption capability of Cd^{2+} ions at high pH. To clarify the removal of these Cd^{2+} ions, a system of changed binary-electrical coat implied by Zulfikar et al. [66] has been used. According to this paper, the sucked particles link to surface of ESP immediately and an external cover in which adsorbed particles or ions have a slack regulation. It is known that ESP includes $CaCO_3$ as the important material. In the aqueous solutions, calcium salts incur change of location reaction and this reaction results in a simple hydrolysis that is also monitored in this analysis [66,67]. When the ESP is blended with the aqueous media, calcium may partly dissolve and spread Ca^{2+}, HCO_3^-, CO_3^{-2}, and OH^{-1} ions, through the following reaction [46,66–68]:

$$CaCO_3 + H_2O \longleftrightarrow Ca^{2+} + HCO_3^- + OH^- + CO_3^{-2} \tag{3}$$

Cd^{2+} ions may be sucked onto the surfaces of the ESP and led to a reverse effect. The effect of pH on the adsorption yield was correlated with the chemical form of Cd^{2+} ions [Cd^{2+}, $Cd(OH)^-$, $Cd(OH)_4^{-2}$, $Cd(OH)^{-3}$] in the aqueous solution [69]. The concentration of the hydrolyzed cadmium species is correlated with the cadmium concentration and the solution pH [69]. Furthermore, at low pH (5.0), H^+ ions are also present in the synthetic solution, based on the surface of the ESP a positive load, leading to electrostatic effect to happen between the ESP and the Cd^{2+}. Moreover, at high pH (≥6), more H^+ ions are presented in the aqueous solution and are adsorbed onto ESP surface, so the superficial load is minus [66]. This will lead to lower the electrostatic pull between the ESP surface and Cd^{2+} ions due to the less positive or more negative surface charge. This fells the adsorption rate of Cd^{2+} ions. These results on the pH value are also parallel to ones in a number of studies that use acidic pH [42,43,62].

3.3. Changing the ESP amount

Fig. 3 suggests the achieved result in changing the studied ESP amount in the uptake of cadmium ions from simulated water. Different amounts of the ESP were added separately to 100 mL solution with initial ion concentrations of 100 mg/L, pH = 3 at 20°C. The results indicate that, with an application of a small amount of ESP, cadmium can be quantitatively removed from simulated water. It was observed that the Cd^{2+} removal yield of the ESP was a function of the ESP amounts in the aquatic solution. The amount of Cd^{2+} adsorbed increased from about 23.82% to 95.93% with higher the ESP amount from 0.05 to 5 g. The maximum adsorption efficiency of Cd^{2+} in to the ESP was obtained as 95.93% at the dose of 3.5 g ESP. It can be argued thus: while the ESP amount increased, more and more surface area is available, and metal ions will be exposed to more active sites for binding [70,71].

3.4. Types of isotherm

The Freundlich and Langmuir isotherms have been broadly used to define the relationship between Cd^{2+} in synthetic water and ESP. The Freundlich model is a numerical expression that depends on adsorption on a complex changeable surface. The linear form of the Freundlich equation is defined in Eq. (4) as follows [62,72,73]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where C_e is the equilibrium concentration of Cd^{2+} (mg/L), q_e is the amount of Cd^{2+} adsorbed per unit weight of adsorbed at equilibrium (mg/g), n is the Freundlich constant, K_f is the adsorption capacity (mg/g). K_f and n can be determined from a linear plot of log q_e against log C_e. The Langmuir isotherm model is used for adsorption in monolayer surface with a finite number of identical sites. The linear form of the Langmuir equation is obtained in Eq. (5) as follows [62,73,74]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Q^b} \tag{5}$$

where C_e is the equilibrium concentration of Cd^{2+} (mg/L), q_e depicts the amount of Cd^{2+} adsorbed per unit weight of adsorbed at equilibrium (mg/g), b shows the Langmuir constant (L/mg), and Q is the maximum adsorption at monolayer (mg/g). The calculated results of the Freundlich and Langmuir isotherm constants are presented in Table 3. As shown in Table 3, the adsorption of Cd^{2+} onto ESP correlated well with the Langmuir isotherm model. The adsorption capacities (Q) estimated from the Langmuir isotherm model for Cd^{2+} were 2.221 mg/g for ESP.

The interaction of metal ions and biosorbents was further examined by separation factor (R_L). R_L equals to a dimensionless constant separation factor, as an equilibrium parameter derived from the Langmuir model. The R_L was described by Hall et al. [75] and is shown in Eq. (6) as follows:

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

As defined in Hall et al. [75], the R_L values imply that the isotherm is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$). The R_L value for Cd^{2+} adsorption onto ESP is in the range of 0–1, indicating that the adsorption of Cd^{2+} was favorable. The R_L value in the direction of the data was decided as 0.103 in the study. Also, the results coming from isothermal, kinetic, and thermodynamic studies in the literature are supported by the statistical models (Hill model, etc.). The statistical physics is also used to relate the microscopic properties of molecules to the macroscopic properties of the materials. The studies are for solid–liquid and solid–gas adsorptions. One of the advantages of implementing this model is to give a physicochemical meaning to the parameters involved in the model. It could be estimated parameters, such as the number of heavy metals and other contaminants, the number of anchorage, steric hindrance,

Table 3
Langmuir and Freundlich isotherm constants for Cd(II) adsorption by ESP

Adsorbent	Metal ion	Freundlich			Langmuir		
		K_f (mg/g)	n	R^2	q_e (mg/g)	b (L/mg)	R^2
ESP	Cd^{2+}	12.100	1.905	0.876	2.221	0.096	0.991

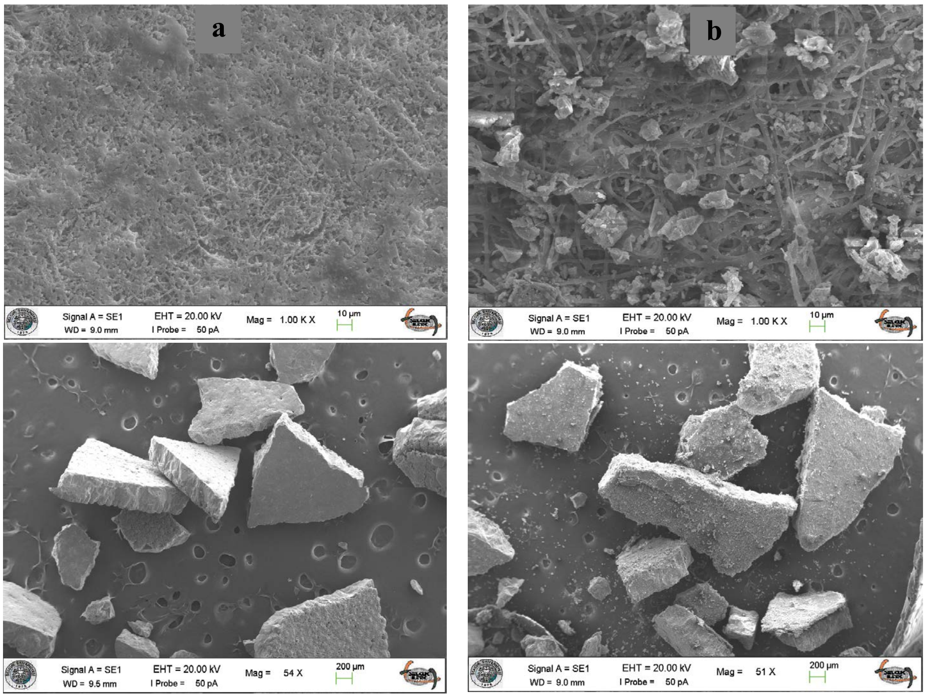

Fig. 4. SEM images of ESP before adsorption (a) and after adsorption (b) of Cd^{2+}.

and molar adsorption energy adsorbed for each area [76–81]. The effect of temperature was not clearly obtained in this study. For this reason, the temperature was chosen to be 20°C as it was in many studies (data not shown).

3.5. Characterization studies for ESP

SEM, an important characterization technique, can be used for investigating the surface morphology of materials such as porosity, particle shape, and appropriate size distribution. In this paper, the surface morphology of the ESP before and after Cd^{2+} ion adsorption was observed based on SEM analysis. There are some significant differences in the surface morphology of the ESP with the formation of discrete aggregates on their surfaces following Cd^{2+} ion adsorption. The SEM images of ESP before and after metal uptake at (51× and 1,000×) magnification are defined in Fig. 4. As shown in Fig. 4(a), ES indicated a dense and porous surface texture. The interaction of ESP with Cd^{2+} created the formation of cube-like deposits on its surface (Fig. 4(b)).

The FTIR spectra of ESP before and after adsorption are shown in Fig. 5. The broad adsorption band near 2,340 cm^{-1} is due to the three stretching C–N and C–C peaks. The band near 1,638 cm^{-1} is correlated with the C=N stretching. Additionally, the peak at 1,107 cm^{-1} is responsive for the C–N stretching, and 900 cm^{-1} is indicative of acid–OH groups. The peak at 768 cm^{-1} corresponds to the stretching and bending vibration of the N–H groups. At around 675 cm^{-1}, the band can be assigned to =C–H bending. From the FTIR study, the formation of new absorption bands, the change in absorption intensity, and the shift in wave number of functional groups could be related to the interaction of metal ions with active sites of biosorbents. The metal ions are bound to the active sites of the biosorbents through either electrostatic attraction or complexation mechanism (see Fig. 5). The electrostatic attraction was between metal ion and carbonate groups [42,58]. The characteristics of carbonate at the aforementioned wave numbers have been further examined in Putra et al. [58] and Xu et al. [62].

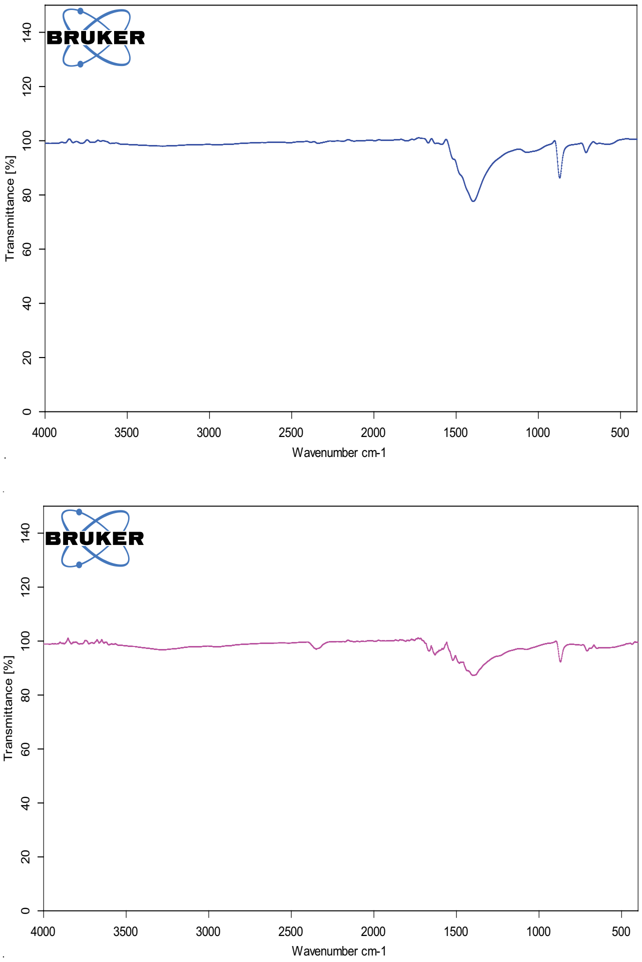

Fig. 5. FTIR spectrum of ESP before adsorption (blue) and after adsorption of (pink) Cd^{2+}.

4. Conclusions

This paper examines the adsorption of Cd^{2+} ions by ESP from simulated water. This experimental study data suggested that the ESP might feasibly be successfully as an adsorbent of Cd^{2+} from aqueous solution. The operating parameters like the solution pH, the ESP dose, and the contact time were effective in the adsorption efficiency of Cd^{2+} ions. The optimum pH value for the experimental study occurred at 5.0 in the adsorption system. The maximum removal efficiencies by the ESP were done between 65% and 96% for Cd^{2+} under optimum conditions (pH = 5.0, contact time = 60 min, ESP amount = 3.5 g, shaking speed = 250 rpm, and 20°C). Experimental equilibrium data presented the best fit with the Langmuir isotherm model, showing monolayer sorption on a homogenous surface (maximum monolayer sorption capacity was 2.221 mg/g at 20°C). Therefore, it may be argued that ESP could be used as a practical, effective, low-cost, high-capacity adsorption; and abundant source for removing Cd^{2+}.

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