Use of eggshell powder as low-cost adsorbent for effective Cr(VI) and Co(II) ion removal

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ABSTRACT

In this work, eggshell powder was used as a low-cost adsorbent for the removal Cr(VI) and Co(II) ions from aqueous solutions as a function of contact time, adsorbent concentration, adsorbate concentration, pH and temperature. Eggshell powder was characterized by X-ray diffraction, scanning electron microscopy and N_2 physisorption measurements. The kinetic studies showed that the experimental data of both solid–liquid systems studied were well adjusted to pseudo-second order kinetics and Langmuir isotherm models. The results showed that the metal ion adsorption equilibrium was attained after 300 min of contact time for the Cr(VI) ion and 180 min for the Co(II) ion. The Co(II) ion adsorption capacity of eggshell powder was found to be approximately four times greater than the Cr(VI) ion. From the Langmuir isotherms, the maximum adsorption capacities of 0.6815 and 2.2888 mg/g were found for Cr(VI) and Co(II) ion, respectively. The thermodynamic parameters were evaluated and showed that Cr(VI) and Co(II) ion adsorption onto eggshell powder were endothermic and spontaneous processes under the studied conditions. These findings demonstrate the important role of eggshell powder as a readily available and low-cost adsorbent for the efficient removal of Cr(VI) and Co(II) ions present in aqueous media.

Keywords: Eggshell powder; Cr(VI) ions; Co(II) ions; Adsorption kinetics; Adsorption isotherms

1. Introduction

Currently, the water contamination by heavy metals of high toxicity, such as arsenic, barium, cadmium, cobalt, and chromium, among others, has been an environmental issue of special interest, because these heavy metals are very persistent and can accumulate in soil and water, as has been widely documented [1–4]. Furthermore, it can be seen that the concentrations of these contaminants have increased considerably, due to their excessive use in industrial processes. It is worth noting that the discharge of the effluents to the environment is carried out without previous treatment [5,6]. Specifically, hexavalent chromium (Cr(VI)) compounds are currently being used in a wide variety of commercial processes and the unregulated disposal of the chromium-containing effluents has led to the contamination of soil, sediment, surface and ground waters [7–11].

On the other hand, exposure to cobalt is of widespread concern. It is well known that cobalt is a toxic contaminant that may contribute to the appearance of a plethora of diseases and disorders when accumulated in living tissues; exposure to this metal produces respiratory illnesses in humans, including lung cancer, asthma and alveolitis. With regards to Co(II) carcinogenicity, there are few studies compared with those that deal with the carcinogenicity of Cr(VI) [12–16]. Nonetheless, Cr(VI) and Co(II) ions should be removed from bodies of water in order to reduce the hazardous effects of these toxic metals to human health [17]. In this

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regard, adsorption processes are considered to be the most promising approaches to remove heavy metals from water through the use of solid adsorbents, which present a large surface areas, porous structure, high adsorption capacity and selectivity [18–28]. Recent studies have shown that the use of non-living biomaterials has been gaining interest because these compounds require minimum care, maintenance and can be obtained more cheaply than other inorganic materials [29–33]. In this sense, eggshell has been identified as a promising biomaterial for environmental purposes, because it has a high affinity for the adsorption of many polluting agents of nuclear and environmental interest. Also, this bioadsorbent is widely available as a poultry waste product and has shown greater advantages in terms of cost, reliability and performance than other known biomaterials [34,35].

Thus, the purpose of this study was to investigate the Cr(VI) and Co(II) ions adsorption capacity of a low cost and highly available waste biomaterial (eggshell powder) in aqueous solutions, in order to evaluate their potential application in the removal of heavy metals. These studies were dedicated to the preparation process, physicochemical characterization of the prepared powder and to the broad description of heavy metal ion adsorption processes. Additionally, the kinetic, equilibrium and thermodynamic parameters of these adsorption processes were analyzed and discussed, making use of the current knowledge on kinetics and isotherm models available in specialized literature.

2. Materials and methods

2.1. Materials and chemicals

All chemical reagents used in this study were of analytical grade, purchased from different companies and used without further purification: 1,5-diphenylcarbazide (Sigma-Aldrich, St. Louis, Missouri, USA ACS reagent, 100 wt.% purity), $NaHCO_3$ (J.T. Baker, New Jersey, USA ACS reagent, 99 wt.% purity) H_2SO_4 (Reasoll, México city, México ACS reagent, 98 wt.% purity), H_2O_2 (Baker ACS reagent, 100 wt.% purity), $K_2Cr_2O_7$ (Baker ACS reagent, 100 wt.% purity), $Co(NO_3)_2 \cdot 6H_2O$ (Baker ACS reagent, 100 wt.% purity), HCl (Baker ACS reagent, 38.0 wt.% purity) and NaOH (Baker ACS reagent, 100.0 wt.% purity). Distilled water was used to prepare all solutions.

2.2. Adsorbent preparation

The solid adsorbent, in powder form, was prepared directly from white eggshell (ES), laid by hen. The dirt and impurities attached were removed by several successive washes with abundant distilled water. Subsequently, the powder was oven-dried at 353 K for 1 h, and finally milled in an agate mortar and sieved in a 60-mesh screen, obtaining homogeneous 0.25 mm particles.

2.3. Adsorbate preparation

The stock solutions of Cr(VI) and Co(II) ions were prepared by dissolving a known quantity of $K_2Cr_2O_7$ and $Co(NO_3)_2 \cdot 6H_2O$ salts in distilled water, respectively. From these solutions, the desired standard concentrations of the

Cr(VI) and Co(II) ions were prepared by serial dilution. The Cr(VI) and Co(II) ion calibration curves were obtained from standard concentrations, ranging from 10 to 60 mg/L, and from 5 to 50 mg/L, respectively. These standard concentrations were prepared under the same procedures and a minimum of six points for each measurement was considered, in order to obtain a good data correlation ($R^2 = 1$). The obtained line equations were employed to determine the unknown concentration of Cr(VI) or Co(II) ions in the sample, at absorbances of 540 and 511 nm, respectively.

2.4. Batch adsorption experiments

Batch adsorption experiments were conducted in separate glass vials in which 0.1 g of ES powder was mixed with 10 mL of aqueous solution containing Cr(VI) or Co(II) ions at concentrations of 10 and 50 mg/L, respectively. The mixtures were kept in constant agitation at 120 rpm and at different time intervals for the kinetic study in a bath with controlled temperature (293 ± 1 K). After agitation, the solutions were separated from the solid phase by centrifugation at 3,000 rpm for 5 min; subsequently, an aliquot of 5 mL was taken for Cr(VI) and 1 mL for Co(II). In all the experiments, the amount of studied contaminant was quantified by UV-Vis spectrophotometry, using a spectrophotometer (Shimadzu model 265, Tokyo, Japan) and performed through the 1,5-diphenylcarbazide method for chromium [36] and the sodium bicarbonate method for cobalt [37]. Finally, the quantity of Cr(VI) and Co(II) ions adsorbed in mg per gram of adsorbent (at equilibrium) was calculated by using the following equation [38,39].

$$q_e = \frac{C_0 - C_f}{m} \times V \tag{1}$$

where m is the mass of adsorbent (g), V is the volume of solution (L), C_0 is the initial metal concentration (mg/L) and C_f is the metal concentration at equilibrium (mg/L). On the other hand, the Cr(VI) and Co(II) ion removal percentages (%) were determined from the difference between the initial and final concentration of both chromium and cobalt ions present in aqueous solution, before and after contact; the following equation was used:

$$\text{Percentage } (\%) \text{ removal} = \frac{C_0 - C_f}{C_0} \times 100 \tag{2}$$

2.5. Equilibrium isotherm experiments

Equilibrium isotherm experiments for Cr(VI) and Co(II) ions were performed by mixing metallic aqueous solutions at different concentrations (2.5–20 mg/L and 10–80 mg/L, respectively) with 0.1 g of adsorbent at 293 ± 1 K, considering the optimum time and pH of each metal in order to ensure the attainment of equilibrium and efficient adsorption.

2.6. Adsorbent characterization

Prepared dry ES powder was characterized by different techniques, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray

spectroscopy (EDXS) and N_2 physisorption measurements. The XRD pattern was recorded on a X-ray diffractometer (Siemens D-500, Madison WI) using CuKα radiation for crystalline phase detection between 5° and 70° in 2θ. The "Joint Committee on Powder Diffraction Standard (JCPDS) files" software was used to identify the compound phase. The morphology of the ES powder sample was determined through the SEM method, using a SEM (JEOL-JMS-5900 LV, Tokyo, Japan). The semi-quantitative microanalysis was carried out using the EDXS technique, through a (JEOL-JMS 5900, Tokyo, Japan) equipment. Finally, the Brunauer–Emmett–Teller (BET) specific surface area, mean pore diameter, total pore volume, and the adsorption–desorption isotherm of the prepared solid material was determined by N_2-physisoption measurements at 77 K with a Belsorp Max (Japan INC, Osaka, Japan) equipment; the sample was previously heated at 573 K for 2 h before the measurements were carried out. The general experimental process scheme is shown in Fig. 1.

3. Results and discussion

3.1. Characterization

3.1.1. XRD analysis

The XRD pattern of the ES powder (Fig. 2) shows a single product with a high degree of crystallinity. The intensity of the diffraction peaks was mainly observed between 29 and 50 in 2θ values, with an important broad reflexion centered at 29.5 in 2θ degree. From these results, it is revealed that the eggshell is predominantly composed of calcium carbonate since, according to the JCPDS file No. 01-085-1108 and the well-defined reflexions, the peaks correspond to a pure calcite phase ($CaCO_3$).

3.1.2. SEM-EDXS analysis

The ES powder morphology observed through the SEM study is shown in Fig. 3. This sample reveals the presence of fine, elongated, amorphous particles with irregular surfaces, and a high degree of packing, with homogeneous and uniform components distribution, and particle sizes between 1 and 5 μm. The microelemental analysis by EDXS, using an aluminum support, revealed that the ES powder was mainly constituted by carbon, oxygen and calcium elements, with very small amounts of Mg, P and S (Fig. 3).

3.1.3. N_2-physisorption measurements

N_2-physisorption measurements revealed that the ES powder has a BET specific surface area of 10.9 m^2/g, a total pore volume of 0.047 cm^3/g, –and a mean pore diameter of 16.71 nm. The N_2 adsorption–desorption isotherm obtained for the ES sample shows an isotherm type IV with very narrow H3 hysteresis loops (Fig. 4), according to the International
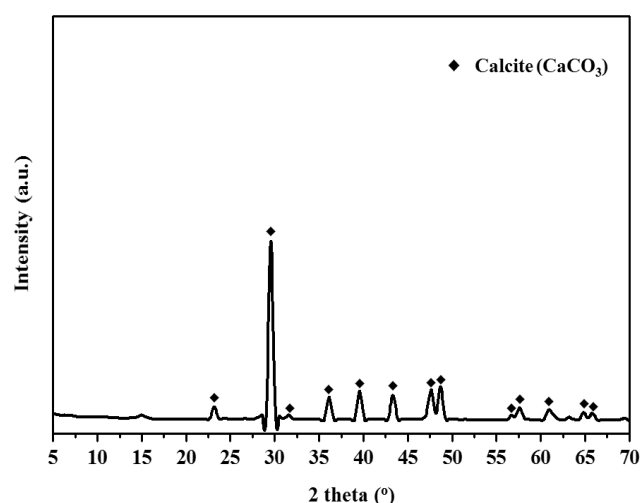
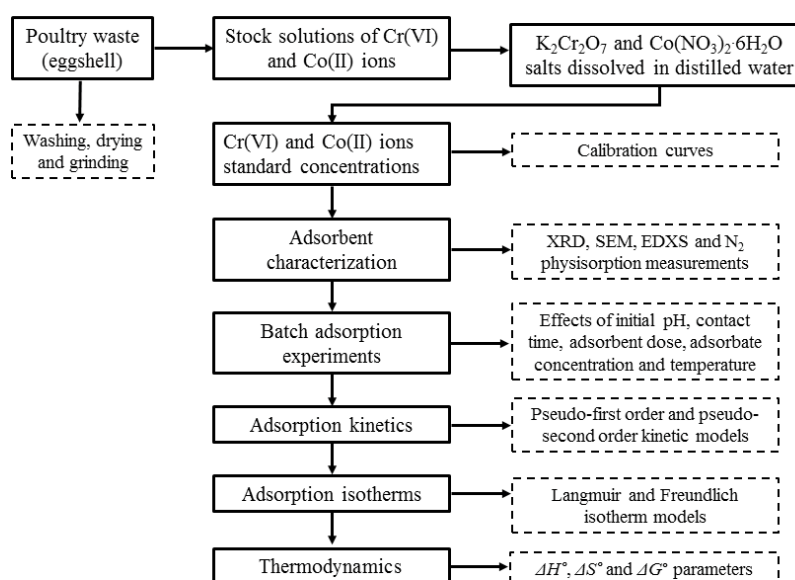Fig. 2. X-ray diffraction pattern of ES powder.
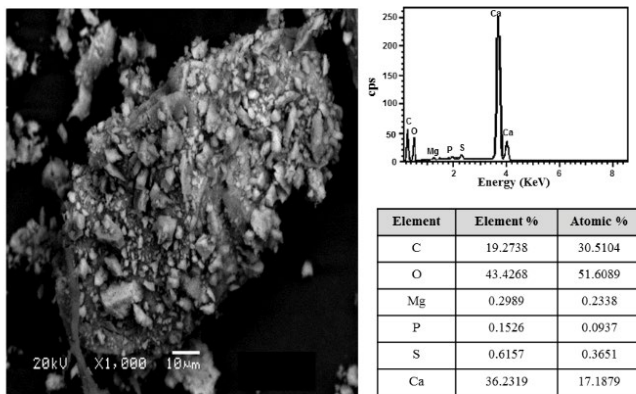
Fig. 1. General experimental process scheme.

Fig. 3. SEM image and EDXS study of ES powder.

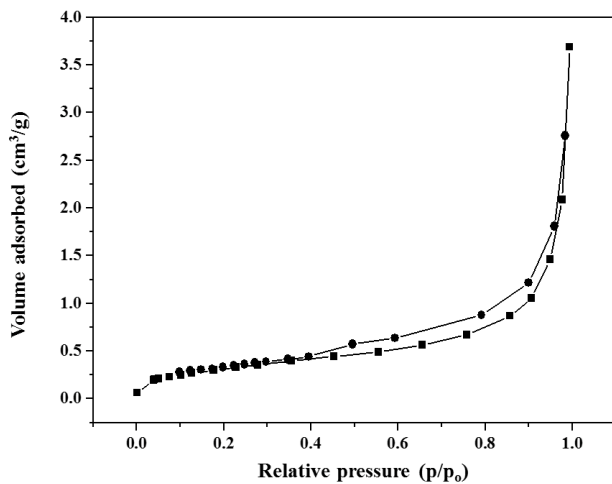| Element	Element %	Atomic %
C	19.2738	30.5104
O	43.4268	51.6089
Mg	0.2989	0.2338
P	0.1526	0.0937
S	0.6157	0.3651
Ca	36.2319	17.1879

Fig. 4. N_2 adsorption–desorption isotherm of ES sample.

Fig. 5. pH effect on Cr(VI) and Co(II) ion adsorption on ES adsorbent.

Union of Pure and Applied Chemistry (IUPAC) classification, which is usually associated with mesoporous solids.

3.2. Adsorption experiments

3.2.1. Initial pH effect

One of the most important factors in adsorption studies is the solution's pH effect; according to Calvete et al., [40], the chemical species of heavy metal may present different ranges of suitable pH for the adsorption depending on the used adsorbing material. For this reason, the adsorption of Cr(VI) and Co(II) ions, as a function of initial hydrogen ion concentration, was determined for solution pH values ranging from 2.0 to 8.0, which were adjusted to the desired value using either 1.0 M HCl or 1.0 M NaOH solutions. A maximum adsorption was found to be around pH 2 ± 0.1 (0.7480 mg/g) and 8.0 (1.6798 mg/g) for Cr(VI) and Co(II) ions, respectively (Fig. 5). Cr(VI) in a weak acid, dissociates itself into $HCrO_4^-$, H_2CrO_4 and CrO_4^{2-} ions, so that the protonation of water attached to the surface of the adsorbent is facilitated when put into contact with water, thus promoting a positively charged surface by inducing an electrostatic attraction of negative Cr(VI) ions (anions) present in aqueous
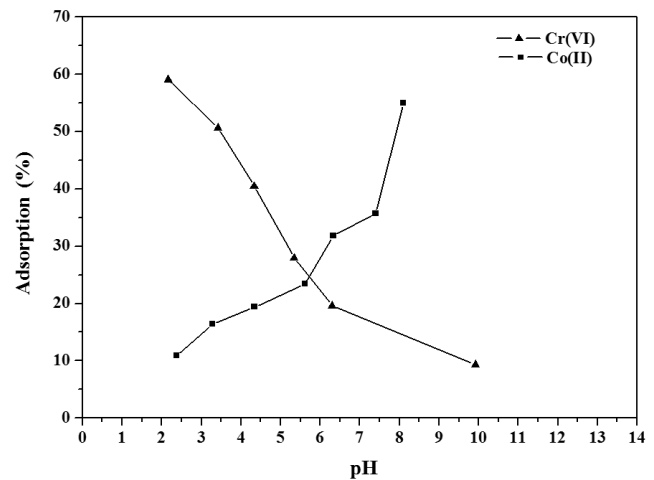
solution. In addition, our results are consistent with those reported by Tewari et al. [41], showing that Cr(VI) chemical species are efficiently removed at a pH range between 2.0 and 3.0; these results are also in accordance with Zhou et al. [42], which found that the rice straw prepared by pyrolysis at 573 K in acidic conditions (with hydrochloric acid) adsorbed 89.9% of Cr(VI) ions. It was also noted that Co(II) ions presented an efficient adsorption capacity in an alkaline medium, as shown in Fig. 5. However, it is important to note that at a high pH values (>8), Co(II) precipitation is possible. Nevertheless, at low pH values, unfavorable adsorption of Co(II) ions was obtained, due to the presence of a higher concentration of H^+ ions in the solution (the surface of the ES is positively charged) which results in a competition between Co(II) ions for the active adsorption sites [43].

3.2.2. Contact time effect

The contact time effect on the removal efficiency for Cr(VI) and Co(II) ions using a known quantity of ES sample and a known concentration of heavy metal solutions is shown in Fig. 6. As can be seen, the adsorption rate of Cr(VI) and Co(II) ions were rapid in the first 180 min, and then reached the point of equilibrium within the first 300 min for Cr(VI) and 180 min for Co(II), respectively. It was observed that the achieved efficiency removal of metal ions at the equilibrium point was q_e = 0.4608 and 1.9439 mg/g of Cr(VI) and Co(II), respectively. Furthermore, the increase, in contact time did not lead to a significant adsorption of ions by the ES powder, since the plateau curves were defined after the mentioned times, due to the saturation of the active sites of the ES sample.

3.2.3. Adsorbent dose effect

To evaluate the adsorbent dose effect on the adsorption processes of Cr(VI) and Co(II) ions, equilibrium experiments were carried out by placing different amounts of ES powder, in the range of 0.01–0.4 g, into the test solution while maintaining pH = 2 ± 0.1 or 6 ± 0.3; t = 300 min or 180 min,

for Cr(VI) and Co(II) ions, respectively. Fig. 7 presents the variation of removal percentage for Cr(VI) and Co(II) ions vs. adsorbent dose, which indicates that the adsorption capacity gradually increased with sorbent amount (0.01–0.1 g) and the percentage of removal metal ions, reached a maximum of 52.01% and 29.20% for Cr(VI) and Co(II), respectively, while adsorption capacity remains almost constant in the range of 0.15–0.4 g. The results could be attributed to the fact that, with the increase in the dosage of adsorbent (ES), the metal ions have interchangeable sites available, resulting in a higher adsorption [44].

3.2.4. Adsorbate concentration effect

In this work, different concentrations of Cr(VI) and Co(II) ions were used in order to find the optimal concentration of adsorbate to be used in the adsorption experiments. The influence of initial concentration is shown in Fig. 8. The maximum adsorption efficiency reached was 85.64%

and 61.97% at concentration of 2.5 and 15 mg/L, for Cr(VI) and Co(II), respectively. However, at higher concentrations, the available sites of ES adsorption become fewer; thus, the high removal percentage of metal ions is favored by low concentrations; this behavior was also seen in the work of Putra et al. [45].

3.2.5. Temperature effect

The influence of temperature (293–333 K) over the adsorption of Cr(VI) and Co(II) ions by ES was studied. As shown in Table 1, at a higher temperature, the metal ions adsorption is clearly increased because the mobility of metal ions also increases, leading to a greater ability to interact with the active sites of the ES powder, which enhances the adsorption capacity of the metal ions with the rise in temperature. This implies that, for the initial concentration of Cr(VI) and Co(II) ions, the adsorption is endothermic in nature.

3.3. Adsorption kinetic study

In order to investigate the adsorption process kinetics, the pseudo-first order and the pseudo-second order models were used to analyze the experimental data of Cr(VI) and Co(II) ions adsorption by ES powder as a function of contact time.

3.3.1. Pseudo-first order kinetic model

Fig. 9 shows the plot of ln $(q_e - q_t)$ vs. t, which gives the linear relationship from which the first-order adsorption
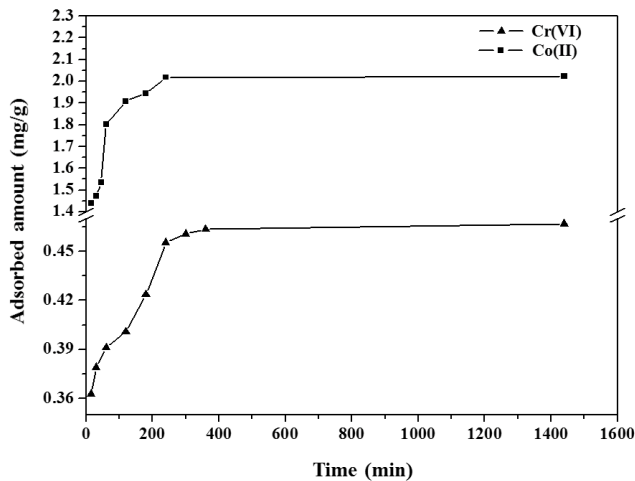
Fig. 6. Contact time effect of Cr(VI) and Co(II) ion adsorption behavior on ES powder.
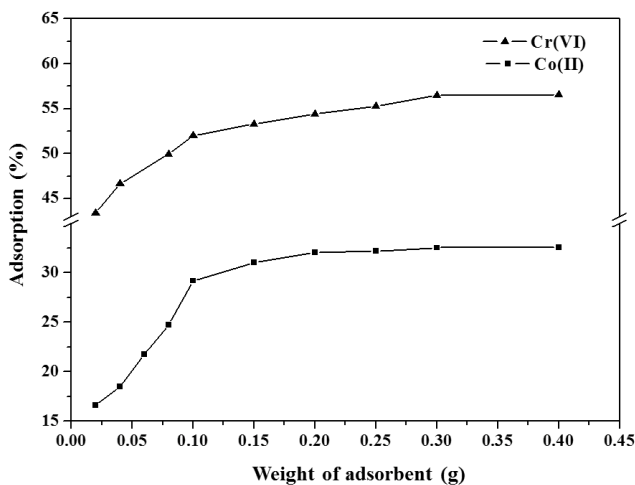
Fig. 7. Adsorbent dose effect on Cr(VI) and Co(II) ion adsorption on ES powder.
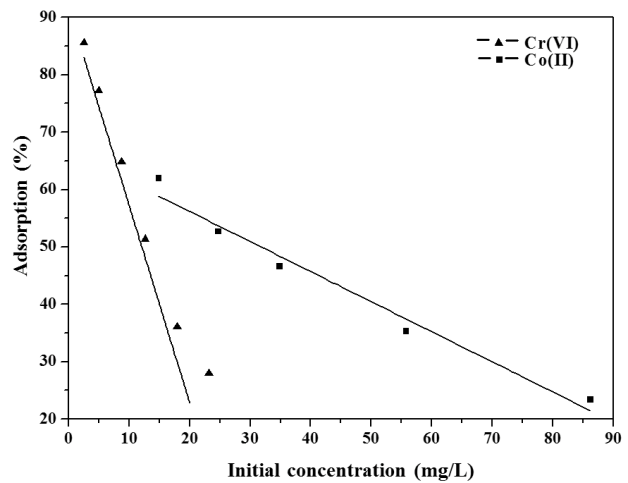
Fig. 8. Adsorbate concentration effect of Cr(VI) and Co(II) ion adsorption capacity on ES powder.

Table 1
Temperature effect on Cr(VI) and Co(II) ion adsorption capacity (%) on ES powder

Metallic ions	T (K)				
	293	303	313	323	333
Cr(VI)	63.22	68.77	74.02	79.44	86.15
Co(II)	29.88	35.58	39.46	43.33	46.02

Fig. 9. Pseudo-first order kinetic plots for Cr(VI) and Co(II) ion adsorption on ES powder.

Table 2
Kinetic parameters for Cr(VI) and Co(II) ion adsorption on ES powder

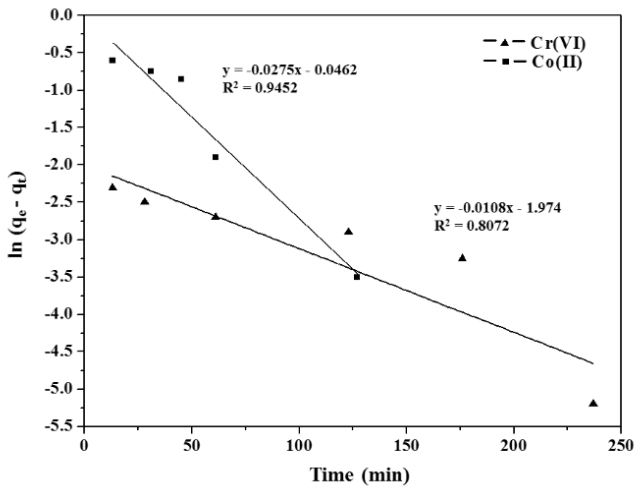| Metallic ions	Constants		
	K (g/mg min)	q_e (mg/g)	R^2
Pseudo-first order model			
Cr(VI)	–0.0108	0.1389	0.8072
Co(II)	–0.0275	0.9549	0.9452
Pseudo-second order model			
Cr(VI)	0.1994	0.4706	0.9998
Co(II)	0.0571	2.0371	0.9999

Fig. 10. Pseudo-second order kinetic plots for Cr(VI) and Co(II) ion adsorption on ES powder.

rate constant k_1 and the adsorption capacity at equilibrium at any given time q_t can be determined. The resulting parameters from the slope and intercept of this plot are shown in Table 2, where it can be seen that the theoretical values of (q_e, R^2) were far higher for the Co(II) ions when compared with those of Cr(VI) ions. However, no high values of regression coefficients (R^2) are noticed for the pseudo-first-order kinetic model; thus, this model is probably not the most appropriate for describing the kinetics of Cr(VI) and Co(II) ion with regard to ES powder.

3.3.2. Pseudo-second order kinetic model

Fig. 10 shows that the plot of t/q_t vs. t is a straight line with a slope of $1/q_e$ and an intercept $1/kq_e$. Using the value of q_e from the slope, the value of k_2 was determined from the intercept. The calculated value of k_2, q_e and their corresponding regression coefficient (R^2) values are presented in Table 2. The regression coefficients were found to be linear with 0.9998 and 0.9999 values for Cr(VI) and Co(II) ions, respectively, which confirms that the adsorption kinetics of Cr(VI) and Co(II) ions follows a pseudo-second order process and is thus a suitable model to describe these studied solid–liquid systems. Therefore, it can be concluded that the adsorption of Cr(VI) and Co(II) ions by ES powder can be better explained by the pseudo-second order kinetic model than by the pseudo-first order kinetic model, indicating that the adsorption processes may be preferably carried out through a chemisorption process. Specifically, the kinetics of the Cr(VI) ion adsorption are in agreement with the results obtained for hexavalent chromium with bio-composite mango kernel (*Mangifera indica*) [46].

3.4. Adsorption isotherms

The equilibrium between the liquid and the solid phases is well described by adsorption isotherms. Experimental isotherm data were fitted into Freundlich and Langmuir classic adsorption isotherm models. For the equilibrium concentration of adsorbate C_e and amount of metal ions adsorbed at equilibrium q_e, the following linear forms of Freundlich (Eq. (3)) and Langmuir (Eq. (4)) isotherms were studied [47,48]. The result of equilibrium isotherms for sorption of Cr(VI) and Co(II) ions on ES powder is shown in Figs. 11 and 12.

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{3}$$

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \tag{4}$$

where C_e is the equilibrium concentration of Cr(VI) and Co(II) ions in solution (mg/L), q_e is the amount of Cr(VI) and Co(II) ions adsorbed per unit weight of adsorbent at equilibrium (mg/g), q_{max} is the monolayer adsorption capacity (mg/g), and K_L is the Langmuir constant and is related with the energy of the adsorption (L/mg), K_F (mg/g)(L/mg)$^{1/n}$ and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

Fig. 10 is a plot of $\ln q_e$ vs. $\ln C_e$ allows to determine the constant K_F and the adsorption intensity n. K_F represents
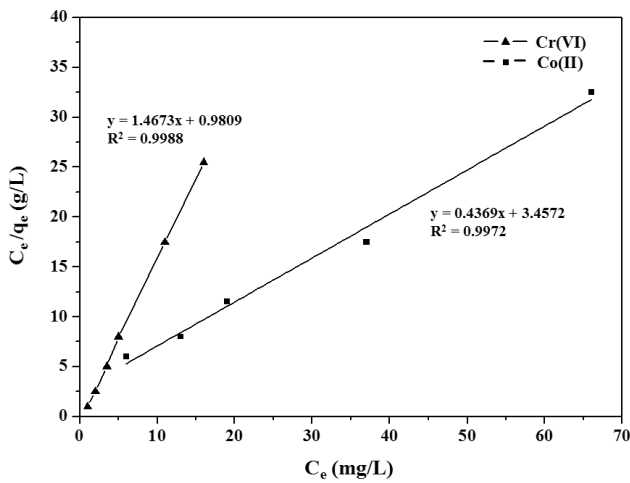
Fig. 11. Langmuir isotherms for Cr(VI) and Co(II) ion adsorption on ES powder.
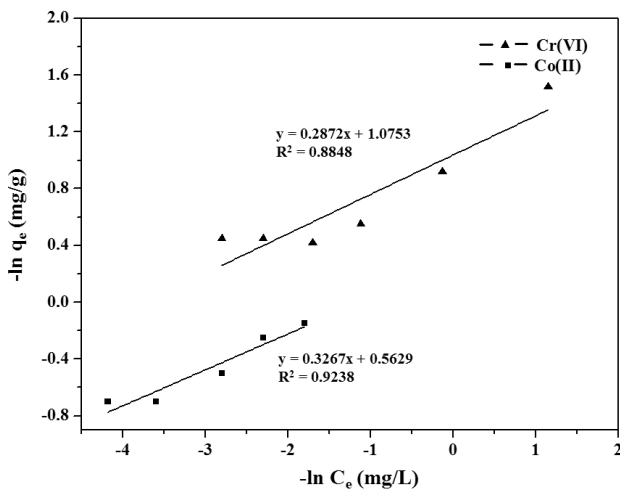

Fig. 12. Freundlich isotherms for Cr(VI) and Co(II) ion adsorption on ES powder.

the quantity of Cr(VI) and Co(II) ions adsorbed onto the ES powder for an equilibrium concentration. When $1/n > 1$, the change in adsorbed concentration is greater than the change in the solute concentration.

The Freundlich model is suitable for use with a heterogeneous surface, but can only describe the adsorption data over a restricted range. The Langmuir and Freundlich isotherm models give straight lines, intercepts and slopes, which were used to determine the values of Langmuir and Freundlich parameters, as given in Table 3.

It is concluded that the values were better adjusted to the Langmuir model, indicating that the values of maximum adsorption correspond to a saturated monolayer of adsorbate molecules over the ES surface with constant energy, and no transmission of adsorbate occurs in the plane of the adsorbent surface. The observed K_L value shows that the adsorbent prefers to bond acidic ions. In addition, if the values of n are between 1 and 10, that indicate a good adsorption. Therefore,

Table 3
Langmuir and Freundlich isotherm parameters of Cr(VI) and Co(II) ion adsorption on ES powder

Parameters	Metallic ions	
	Cr(VI)	Co(II)
Langmuir		
q_{max} (mg/g)	0.6815	2.2888
K_L (L/mg)	1.4958	0.1263
R^2	0.9988	0.9972
Freundlich		
N	3.4818	3.0609
K_F (mg/g) (L/mg)$^{1/n}$	2.9308	1.7557
R^2	0.8849	0.9238

for the adsorption of Cr(VI) and Co(II) ions, n values greater than 3 indicates that the adsorption is favorable in the ES powder [49].

The Cr(VI) and Co(II) ions adsorption capacities of some previously reported biomaterials studied for these metallic ions, including eggshell powder, are given in Table 4. It is difficult to compare these obtained results because the adsorption capacities seen to be affected by the combination of multiple factors that correspond to the different physicochemical characteristics of both the solution and the solid adsorbent studied [50–54].

3.5. Thermodynamics

Thermodynamic parameters such as change in free energy $\Delta G°$ (kJ/mol), enthalpy $\Delta H°$ (kJ/mol) and entropy $\Delta S°$ (kJ/K mol) were determined using the following equations:

$$\Delta G° = -RT \ln K_0 \tag{5}$$

$$K_0 = \frac{C_s}{C_l} \tag{6}$$

$$\log K_0 = \frac{\Delta S°}{2.303R} - \frac{\Delta H°}{2.303RT} \tag{7}$$

where K_o is the equilibrium constant, C_s is the solid phase concentration at equilibrium (mg/L), C_l is the liquid phase concentration at equilibrium (mg/L), T is the temperature expressed in Kelvin, and R is the gas constant.

The enthalpy change ($\Delta H°$), entropy change ($\Delta S°$) and free energy change ($\Delta G°$) values obtained are presented in Table 5. The positive values of $\Delta H°$ show the endothermic nature of adsorption process [55] and the enhancement of adsorption capacity of the metal ions at higher temperatures (Table 5), which can be explained by the nature of the adsorbent and adsorbate. The increase of adsorption with increased temperature indicates that the adsorption of heavy metal ions by adsorbents may involve not only physical but also chemical adsorption; thus, an increase in active sites occurs due to bond rupture [56], which can be also attributed to the enlargement of pore size and activation of

Table 4
Cr(VI) and Co(II) ions adsorption capacities (mg/g) of some previously reported biomaterials

Adsorbents	Cr(VI) ion (mg/g)	Co(II) ion (mg/g)	Reference
Coconut coir	6.30		[50]
Barley straw ash		6.61	[51]
Activated coconut shell carbon	2.20		[52]
Activated bagasse carbon	0.19		[53]
Alginate–chitosan hybrid gel		3.20	[54]
Eggshell powder	0.68	2.28	This work

Table 5
Thermodynamic parameters for Cr(VI) and Co(II) ion adsorption on ES powder

Metallic ions	Parameters		
	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol K)	$\Delta G°$ (kJ/mol)
Cr(VI)	6.18	3.64×10^{-2}	–4.49
Co(II)	8.66	3.89×10^{-2}	–2.66

the adsorbent surface [57]. In addition, the values of $\Delta H°$ are within the range of 1–93 kJ/mol for Cr(VI) and Co(II) ions, indicating that physisorption is more favorable for the adsorption of metal ions. These results were confirming with the low value of $\Delta H° = 6.18$ and 8.66 kJ/mol for Cr(VI) and Co(II), respectively, which suggests that the metallic ions were physisorbed onto the ES adsorbent. The positive values of $\Delta S°$ exhibit the increased disorder and randomness at the solid–solution interface of Cr(VI) and Co(II) ions on the active sites of the ES powder. The negative values of $\Delta G°$ indicate that the adsorption of Cr(VI) and Co(II) ions on the ES powder is highly feasible and spontaneous [58].

4. Conclusion

Porous eggshell powder was successfully prepared and the results indicated that ES material is a promising, new low-cost adsorbent for the efficient removal of Cr(VI) and Co(II) ions from aqueous solutions. The results show a better Co(II) ions adsorption capacity by ES than Cr(VI) ions present in aqueous solution. The kinetics results showed that the Cr(VI) and Co(II) ion adsorption data of the ES powder are well described by the pseudo-second order kinetic model and that the processes are greatly influenced by the initial pH imposed, with optimal pH values of 2 and 8, corresponding to the predominance of CrO_4^{2-} and Co^{2+} chemical species, respectively. The obtained results showed that the adsorption equilibrium data of both studied metallic ions in the ES powder were well adjusted to the Langmuir isotherm model-type monolayer. The thermodynamic studies indicated that the metal ion adsorption onto ES powder was spontaneous, endothermic and through physical reactions by ion exchange. These findings demonstrate the important role of ES powder as a readily available poultry waste biomaterial and low-cost adsorbent capable of efficient removal of Cr(VI) and Co(II) ions present in aqueous media.

References

[1] S. Huang, J. Tu, W. Yin, M. Hua, X. Wu, W. Xu, Y. Yang, H. Wang, Y. Su, Contamination assessment and source identification of heavy metals in river sediments in Nantong, Eastern China, Int. J. Environ. Res., 12 (2018) 373–389.

[2] M. Abbas, M. Adil, S. Ehtisham-ul-Haque, B. Munir, M. Yameen, A. Ghaffar, G.A. Shar, M.A. Tahir, M. Iqbal, *Vibrio fischeri* bioluminescence inhibition assay for ecotoxicity assessment: a review, Sci. Total Environ., 626 (2018) 1295–1309.

[3] M. Iqbal, M. Abbas, J. Nisar, A. Nazir, A.Z. Qamar, Bioassays based on higher plants as excellent dosimeters for ecotoxicity monitoring: a review, Chem. Int., 5 (2019) 1–80.

[4] G.N. Iwuoha, A. Akinseye, Toxicological symptoms and leachates quality in Elelenwo, Rivers State, Nigeria, Chem. Int., 5 (2019) 198–205.

[5] MdS. Bhuyan, M.A. Bakar, A. Akhtar, M.B. Hossain, M.M. Ali, MdS. Islam, Heavy metal contamination in surface water and sediment of the Meghna river, Bangladesh, Environ. Nanotechnol. Monit. Manage., 8 (2017) 273–279.

[6] Y. Du, F. Lian, L. Zhu, Biosorption of divalent Pb, Cd and Zn on aragonite and calcite mollusk shells, Environ. Pollut., 159 (2011) 1763–1768.

[7] A.U. Rajapaksha, Md.S. Alam, N. Chen, D.S. Alessi, A.D. Igalavithana, D.C.W. Tsang, Y.S. Ok, Removal of hexavalent chromium in aqueous solutions using biochar: chemical and spectroscopic investigations, Sci. Total Environ., 625 (2018) 1567–1573.

[8] A.M. Yusof, N.A.N.N. Malek, Removal of Cr(VI) and As(V) from aqueous solutions by HDTMA-modified zeolite Y, J. Hazard. Mater., 162 (2009) 1019–1024.

[9] A. Rajendran, Applicability of an ionic liquid in the removal of chromium from tannery effluents: a green chemical approach, Afr. J. Pure Appl. Chem., 4 (2010) 100–103.

[10] H.N. Bhatti, A.W. Nasir, M.A. Hanif, Efficacy of *Daucus Carota* L. Waste biomass for the removal of chromium from aqueous solutions, Desalination, 253 (2010) 78–87.

[11] X. Guo, F. Zhang, Q. Peng, S. Xu, X. Lei, D.G. Evans, X. Duan, Layered double hydroxide/eggshell membrane: an inorganic biocomposite membrane as an efficient adsorbent for Cr(VI) removal, Chem. Eng. J., 166 (2011) 81–87.

[12] J.M. Mur, J.J. Moulin, M.P. Charruyer-Seinerra, J. Lafitte, A cohort mortality study among cobalt and sodium workers in an electrochemical plant, Am. J. Ind. Med., 11 (1987) 75–81.

[13] F. Van Goethem, D. Lison, M. Kirsch-Volders, Comparative evaluation of the in vitro micronucleus test and the alkaline single cell gel electrophoresis assay for the detection of DNA damaging agent: genotoxic effects of cobalt powder, tungsten carbide and cobalt-tungsten carbide, Mutat. Res., 392 (1997) 31–43.

[14] M. Behl, M.D. Stout, R.A. Herbert, J.A. Dill, G.L. Baker, B.K. Hayden, J.H. Roycroft, J.R. Bucher, M.J. Hooth, Comparative toxicity and carcinogenicity of soluble and insoluble cobalt compounds, Toxicology, 333 (2015) 195–205.

[15] D. Lison, R. Lauwerys, Cobalt bioavailability from hard metal particles. Further evidence that cobalt alone is not responsible for the toxicity of hard metal particles, Arch. Toxicol., 68 (1994) 528–531.

[16] Y. Wang, Q. Liu, L. Shu, M. Miao, Y. Liu, Q. Kong, Removal of Cr(VI) from aqueous solution using Fe-modified activated carbon prepared from luffa sponge: kinetic, thermo-dynamic, and isotherm studies, Desal. Wat. Treat., 57 (2016) 29467–29478.

[17] D. Bulgariu, L. Bulgariu, Equilibrium and kinetics studies of heavy metal ions biosorption on green algae waste biomass, Bioresour. Technol., 103 (2012) 489–493.

[18] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: a review, J. Hazard. Mater., 177 (2010) 70–80.

[19] R.A. Mohamed, J. Shamsuddin, C.F. Ishak, A. Arifin, Q.P. Ali, Adsorption-desorption characteristics of zinc and copper in oxisol and ultisol amended with sewage sludge, J. Chem. Soc. Pak., 40 (2018) 842–855.

[20] B. Lee, Y. Kim, H. Lee, J. Yi, Synthesis of functionalized porous silicas via templating method as heavy metal ion adsorbents: the introduction of surface hydrophilicity onto the surface of adsorbents, Microporous Mesoporous Mater., 50 (2001) 77–90.

[21] S. Alvarez-García, J.J. Ramírez-García, F. Granados-Correa, J.C. Sánchez-Meza, Determination of kinetic, isotherm, and thermodynamic parameters of the methamidophos adsorption onto cationic surfactant-modified zeolitic materials, Water Air Soil Pollut., 229 (2018) 347.

[22] Y. Tao, H. Kanoh, L. Abrams, K. Kaneko, Mesopore-modified zeolites: preparation, characterization, and applications, Chem. Rev., 106 (2006) 896–910.

[23] S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, Chem. Eng. J., 156 (2010) 11–24.

[24] R.T. Yang, A.J. Hernández-Maldonado, F.H. Yang, Desulfuri-zation of transportation fuels with zeolites under ambient conditions, Science, 30 (2003) 79–81.

[25] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Bioresour. Technol., 97 (2006) 1061–1085.

[26] M.L. Foo, R. Matsuda, S. Kitagawa, Functional hybrid porous coordination polymers, Chem. Mater., 26 (2014) 310–322.

[27] A. Dabrowski, P. Podkoscielny, Z. Hubicki, M. Barczak, Adsorption of phenolic compounds by activated carbon-a critical review, Chemosphere, 58 (2005) 1049–1070.

[28] H.N. Bhatti, J. Hayat, M. Iqbal, S. Noreen, S. Nawaz, Biocomposite application for the phosphate ions removal in aqueous medium, J. Mater. Res. Technol., 7 (2018) 300–307.

[29] M. Masomi, A.A. Ghoreyshi, G.D. Najafpour, A.R.B. Mohamed, Dynamic adsorption of phenolic compounds on activated carbon produced from pulp and paper mill sludge: experimental study and modeling by artificial neural network (ANN), Desal. Wat. Treat., 55 (2015) 1453–1466.

[30] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, Carbons, 42 (2004) 83–94.

[31] S. Al-Asheh, F. Banat, D. Al-Rousan, Beneficial reuse of chicken feathers in removal of heavy metals from wastewater, J. Clean. Prod., 11 (2003) 321–326.

[32] K.J. Ruff, D.P. DeVore, M.D. Leu, M.A. Robinson, Eggshell membrane: a possible new natural therapeutic for joint and connective tissue disorders. Results from two open-label human clinical studies, Clin. Interventions Aging, 4 (2009) 235–240.

[33] M.A. Zulfikar, H. Setiyanto, Adsorption of congo red from aqueous solution using powdered eggshell, Int. J. ChemTech Res., 5 (2013) 1532–1540.

[34] M. El Haddad, R. Mamouni, N. Saffaj, S. Lazar, Removal of a cationic dye-basic red 12- from aqueous solution by adsorption onto animal bone meal, J. Assoc. Arab. Univ. Basic Appl. Sci., 12 (2012) 48–54.

[35] S.A. Sayed, S.M. Saleh, E.E. Hasan, Removal of some pollu-ting metals from industrial water using chicken feathers, Desalination, 181 (2005) 243–255.

[36] ASTM D 1687–92., Chromium in Water, Test Method A, 1996.

[37] G. Telep, D.F. Boltz, Ultraviolet spectrometric determination of cobalt with peroxide and bicarbonate, Anal. Chem., 24 (1952) 945–947.

[38] Y. Chen, B. Wang, J. Xin, P. Sun, D. Wu, Adsorption behavior and mechanism of Cr(VI) by modified biochar derived from *Enteromorpha prolifera*, Ecotoxicol. Environ. Saf., 164 (2018) 440–447.

[39] H.N. Bhatti, A. Jabeen, M. Iqbal, S. Noreen, Z. Naseem, Adsorptive behavior of rice bran-based composites for malachite green dye: isotherm, kinetic and thermodynamic studies, J. Mol. Liq., 237 (2017) 322–333.

[40] T. Calvete, E.C. Lima, N.F. Cardoso, J.C. Vaghetti, S.L. Dias, F.A. Pavan, Application of carbon adsorbents prepared from the Brazilian-pine fruit shell for removal of reactive orange 16 from aqueous solution: kinetic, equilibrium, and thermodynamic studies, *J. Environ. Manage.,* 91 (2010) 1695–1706.

[41] N. Tewari, P. Vasudevan, B.K. Guha, Study on biosorption of Cr(VI) by *Mucor hiemalis*, Biochem. Eng. J., 23 (2005) 185–192.

[42] J. Zhou, H. Chen, R.W. Thring, J.M. Arocena, Chemical pretreatment of rice straw biochar: effect on biochar properties and hexavalent chromium adsorption, Int. J. Environ. Res., 13 (2019) 91–105.

[43] Y. Nuhoglu, E. Oguz, Removal of copper (II) from aqueous solutions by biosorption on the cone biomass of *Thuja orientalis*, Process Biochem., 38 (2003) 1627–1631.

[44] A.B. Pérez-Marín, M.I. Aguilar, V.F. Meseguer, J.F. Ortuño, J. Sáez, M. Lloréns, Biosorption of chromium (III) by orange (*Citrus sinensis*) waste: batch and continuous studies, Chem. Eng. J., 155 (2009) 199–206.

[45] W.P. Putra, A. Kamari, S.N.M. Yusoff, C.F. Ishak, A. Mohamed, N. Hashim, I.M. Isa, Biosorption of Cu(II), Pb(II) and Zn(II) ions from aqueous solutions using selected waste materials: adsorption and characterization studies, J. Encapsul. Adsorpt. Sci., 4 (2014) 201–213.

[46] M. Akram, H.N. Bhatti, M. Iqbal, S. Noreen, S. Sadaf, Bio-composite efficiency for Cr(VI) adsorption: kinetic, equilibrium and thermodynamics studies, J. Environ. Chem. Eng., 5 (2017) 400–411.

[47] A. Mannarswamy, S.H. Munson-McGee, R. Steiner, P.K. Ander-sen, D-optimal experimental designs for Freundlich and Langmuir adsorption isotherms, Chemom. Intell. Lab. Syst., 97 (2009) 146–151.

[48] X. Song, Y. Zhang, C. Yan, W. Jiang, C. Chang, The Langmuir monolayer adsorption model of organic matter into effective pores in activated carbon, J. Colloid Interface Sci., 389 (2013) 213–219.

[49] C. Smaranda, M. Gavrilescu, D. Bulgariu, Studies on sorption of congo red from aqueous solution onto soil, Int. J. Environ. Res., 5 (2011) 177–188.

[50] M.H. Gonzalez, G. Labuto, C.B. Pelizaro, E. Menezes, S.G. Lemos, G.B. Sousa, A.R.A. Nogueira, Coconut coir as biosorbent for Cr(VI) removal from laboratory wastewater, J. Hazard. Mater., 159 (2008) 252–256.

[51] M. Arshadi, M.J. Amiri, S. Mousavi, Kinetic, equilibrium and thermodynamic investigations of Ni(II), Cd(II), Cu(II) and Co(II) adsorption on barley straw ash, Water Resour. Ind., 6 (2014) 1–17.

[52] K. Perisamy, K. Srinivasan, P.R. Murugan, Studies on Cr(VI) removal by activated ground nut husk carbón, Ind. J. Environ. Health, 33 (1991) 433–439.

[53] S. Chand, V.K. Agarwal, C. Pavankumar, Removal of hexavalent chromium from wastewater by adsorption, Ind. J. Environ. Health, 36 (1994) 151–158.

[54] T. Gotoh, K. Matsushima, K.I. Kikuchi, Preparation of alginate-chitosan hybrid gel beads and adsorption of divalent metal ions, Chemosphere, 55 (2004) 135–140.

[55] M.W. Amer, A.M. Awwad, Removal of As(V) from aqueous solution by adsorption onto nanocrystalline kaolinite:

equilibrium and thermodynamic aspects of adsorption, Environ. Nanotechnol. Monit. Manage., 9 (2018) 37–41.

[56] G.M. Al-Senani, F.F. Al-Fawzan, Adsorption study of heavy metal ions from aqueous solution by nanoparticle of wild herbs, Egypt. J. Aquat. Res., 44 (2018) 187–194.

[57] S.V. Mohan, N.C. Rao, J. Karthikeyan, Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study, J. Hazard. Mater., 90 (2002) 189–204.

[58] M. Torab-Mostaedi, M. Asadollahzadeh, A. Hemmati, A. Khosravi, Equilibrium, kinetic, and thermodynamic studies for biosorption of cadmium and nickel on grapefruit peel, J. Taiwan Inst. Chem. Eng., 44 (2013) 295–302.