Biosorption of hexavalent chromium from aqueous solution by pristine and CaCl_2 -modified erythromycin production residues

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Abstract

In this study, the adsorptive removal of hexavalent chromium [Cr(VI)] from aqueous solutions by the pristine and salt-treated CaCl_2 -erythromycin production residue (EPRs and SEPRs) were investigated. Batch experiments were carried out to determine the effect of contact time, sorbent dosage, pH, initial Cr concentration, and temperature on Cr(VI) sorption by EPRs and SEPRs. The highest adsorptive removal capacities were achieved at the pH equal to 1.0, and the maximum adsorption capacities for EPRs and SEPRs at optimized conditions were 21.74 and 35.24 mg g^{-1} , respectively. Moreover, thermodynamic results indicated that Cr sorption by EPR/SEPRs was feasible, spontaneous and endothermic under the given conditions. Langmuir model fitted well with the experimental data. The pseudo-second order could better describe the adsorptive removal kinetics and the process involving rate-controlling step is much complex involving both boundary layer and intra-particle diffusion processes. Furthermore, adsorption-coupled-reduction process was believed as the main mechanism of Cr(VI) removal by EPRs and SEPRs. Both adsorbents could be considered as promising low-cost biosorbent for the removal of Cr(VI) from aqueous systems.

Introduction

Excessive accumulation of inorganic pollutants such as potential toxic metals in the environment may cause serious environmental problems due to its non-biodegradable nature, toxicity, and bioaccumulation properties (Xiao et al. 2018). Chromium (Cr) is a common metallic element in wastewater released from various industries, like electroplating, leather tanning, metal finishing, battery and textiles, etc. (Miretzky et al. 2010; Behera SK et al. 2020). Although chromium can exist in different oxidation states (from -2 to $+6$). Cr is mostly persisted in either hexavalent [Cr(VI)] or trivalent [Cr(III)] in natural aqueous environment based on its Eh-pH conditions (Miretzky et al. 2010; Hlihor et al. 2017). However, Cr in such two oxidation states is distinct in the toxicity and mobility. Specifically, Cr(III) is essential to animals/plants at low dosage and demonstrates lower mobility, whereas Cr(VI) demonstrates higher toxicity and mobility and is carcinogenic and mutagenic to living organisms (Montazerrahmati et al. 2011; Pavesi et al. 2020). Accordingly, Cr(VI) was regarded as the permissive control pollutants in aqueous solution and the maximum Cr(VI) threshold for drinking water is set at 0.05 mg g^{-1} according to the World Health Organization (WHO) and the US Environmental Protection Agency (WHO, 2004; USEPA, 2011). However, in most effluent from industries, Cr(VI) contents generally ranged from 15 to 300 mg L^{-1} , which would pose significant risks to the aqueous environment (Xiao et al. 2018; Hlihor et al. 2017). Considering its harmful effects on human health and ecosystem, detoxification of Cr(VI) containing wastewater is of great importance (Li et al. 2018).

So far, various treatment approaches such as sorption, ionic exchange, precipitation, ultrafiltration, and reduction have been applied to the detoxification of Cr(VI) containing wastewater (Miretzky et al. 2010; Rambabu et al. 2021; Kumar et al. 2020). However, they all have specific deficiencies and limitations such as high capital and operational costs, high energy and waste-disposal-problem (Li et al. 2017). By

comparison, biosorption, a technique that uses biomass to remove contaminants, has been proved as a cost-efficient and competitive method for detoxification of wastewater (Li et al. 2018). Theoretically, Cr(VI) anion can positively attach to the surface of adsorbent through the physicochemical process (Li et al. 2018; (Li et al. 2017)). Furthermore, part of the adsorbed Cr(VI) may transform into Cr(III), which occurs through a chemical reaction spontaneously or catalyzed effectively by a chromate reductase (Miretzky et al. 2010; Li et al. 2017). For this reason, various biomass, including bacteria, fungi, algae, plants, and agro-sorbents have been applied for the remediation of Cr(VI) contaminated wastewater (Jobby et al. 2018). For example, Hlihor et al (2017) found both dead and living *Arthrobacter viscosus* biomass can effectively remove Cr(VI) from aqueous solutions with the initial Cr(VI) concentration up to 100 mg L⁻¹ (pH = 1/2). Similarly, Patra et al.(2020) found raw and acid-activated *Pongamia pinnata* shells achieved high Cr(VI) removal efficiencies with the maximum adsorption capacities at up to 96.2((raw biomass), 152(phosphoric acid-activated biomass) and 192(sulphuric acid-activated biomass) mg/g. However, studies are still conducting to explore/develop novel adsorbents for the detoxification of Cr(VI) containing wastewater. Generally, sorbents with more abundant functional groups or higher contents of the dissolvable organic compound were efficient to achieve higher Cr(VI) removal efficiencies (Miretzky et al. 2010; Montazerrahmati et al. 2011; Patra et al. 2020). Therefore, modification of biomass with chemical agents (i.e., acid, alkali, and oxidant) is an effective method for enhancing Cr(VI) removal performance (Patra et al. 2020; Abdolali et al.2015). For example, Foroutan et al. (2018) studied CaCl₂-modified *Sargassum oligocystum* algae biomass for removal of Cr(VI), and the biosorption capacity was 34.46 mg g⁻¹. Additionally, studies have also shown that the modification with calcium chloride can prevent leaching the adsorptive components from adsorbate and increase the stability of the biosorbent (Montanzerrahmati et al. 2011; Yang et al.2008).

Antibiotics have been regarded as one of the most effective drug developed for preventing diseases and promoting growth. With the growing population and misuse of antibiotics, the global annual antibiotic consumption has increased by 35% from 2000 to 2010 (Van Boeckel et al. 2014). Meanwhile, the antibiotic production residues have also significantly increased during the past few years. However, antibiotic production residues have been classified as hazardous solid waste in most countries due to the potential ecological risks associated with residual antibiotic and antibiotic residence genes, and hence the direct re-utilization of such waste is strictly forbidden. Recently, novel techniques such as moderate oxidation drying technology and electron beam have been successfully applied into antibiotic production residues treatment with residual antibiotic reduced to an acceptable level, which makes re-utilization possible. Therefore, the aim of this study is to investigate removal efficiencies of Cr(VI) on the pristine and salt-treated erythromycin production residue (EPRs and SEPRs). Effects of adsorption time, pH, sorbent dosage, initial Cr(VI) concentration, and environmental temperature have been investigated. Furthermore, multiple techniques such as FTIR and SEM were employed to explore the potential mechanisms involved in the Cr(VI) removal by the EPRs and SEPRs. The objectives of the present work are: 1) to evaluate the removal efficiencies of Cr on (un)modified EPRs, 2) to determine the effects of various factors on Cr(VI) removal on different adsorbents, and 3) to explore the mechanisms that governs the removal of Cr(VI) by EPRs and SEPRs.

Materials And Methods

Feedstocks and reagents

The EPRs were obtained from a pharmaceutical factory in Shaanxi Province, China. Generally, the main compositions of EPRs were mycelium, nutritional substance like starch, maize slurry, protein, and amino acid (Xiao et al. 2015). A novel moderate oxidation drying technology and electron beam has been applied for eliminate the potential ecological risks. There were no residual antibiotic and antibiotic residence genes detected in EPRs according to our previous studies (Zhao et al. 2018). After collection, samples were air-dried followed by oven-drying at 65°C for 72 h. Samples were then crushed and sieved to pass through a 0.15 mm nylon sieve, and stored in a desiccator until further experiments.

All chemicals used for analysis were of analytical grade and used without further purification. Acetone (CH_3COCH_3), 1,5-diphenylcarbazide (DPCI), HCl, HNO_3 , H_3PO_4 , H_2SO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, CaCl_2 , and NaOH were obtained from Xinong Chemical Co., Ltd. (China). Stock solutions of Cr(VI) were prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ in 1000 mL of deionized water (DW, 18.2 M Ω). The working solutions were obtained by diluting the stock solution with a different ratio of DW.

Biosorbent preparation and characterization

SEPRs were prepared following methods described by Montazerrahmati et al. (2011) and Abdolali et al. (2015). Briefly, EPRs were added into 1 mol L⁻¹ CaCl_2 at a ratio of 1:20 (w/v). The mixture was then stirred at 200 rpm for 24 h at room temperature. After that, the solid phase was centrifugated and washed with DW until solution pH reached to 7.0 ± 0.1 . Samples were then oven dried at 65°C, ground and stored in a desiccator until further utilization in the sorption experiments.

Elemental composition (i.e., C, H, N, and S) of EPRs and SEPRs were determined by a CE 440 elements analyzer (Agilent, US). The surface morphology of samples was characterized using a scanning electron microscopy (S-4800, Hitachi, S4800). BET surface area (S_{BET}), total pore volume, and pore size distribution of adsorbents were analyzed by a Surface Area and Porosity Analyzer (V-sorb 2800 P, App-One, China). The zeta potential of each sample was characterized using a zeta potential analyzer (Nano ZS90, Zetasizer, England). Additionally, surficial functional groups of samples before and after Cr(VI) sorption were observed using a Tensor 27 Fourier transform infrared (FTIR) spectrometer (Bruker, Germany).

Batch adsorptive removal experiments

The removal of Cr(VI) from aqueous solution using EPRs and SEPRs were examined in a series of batch experiments. Firstly, the effect of biomass dosage on Cr(VI) removal was investigated by adding different amounts of EPRs/SEPRs (i.e., 0.1, 0.2, 0.25, 0.3, 0.4, 0.5, 0.75, 1.0, 1.25 g (dry weight)) in 100 mL

polycarbonate tubes that contained 50 mL of 50 mg L⁻¹ Cr(VI) solution (pH = 4.0). Tubes were then shaken for 4 h at room temperature using a horizontal shaker. Additionally, the effect of solution pH was investigated by adjusting solution pH to be in the range of 1.0 to 9.0 using 0.1 M NaOH/HCl solutions. Moreover, adsorptive removal isothermal experiments were carried out with Cr(VI) concentration ranged from 0 to 500 mg L⁻¹ (pH = 1.0). Besides, adsorptive removal kinetic experiments were carried out in 250 mL flasks with 0.5 g EPRs/SEPRs and an aliquot of 100 mL 50 mg L⁻¹ Cr(VI) solution (pH = 1.0). At each interval of 0, 10, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210, 240, 270, 300, 360 and 480 min, 1 mL of suspension was withdrawn and then filtered using cellulose filter membrane (0.45µm). Furthermore, thermodynamic studies were also conducted to evaluate Cr(VI) removal efficiencies by adjusting temperature into 25°C, 30°C, 40°C, and 50°C.

Cr concentration determination

The total Cr concentration in the filtrate was analyzed by a flame atomic absorption spectrophotometer (FAAS Z-5000, Hitachi, Japan). Simultaneously, the concentrations of Cr(VI) in the filtrate was analyzed by complexing with 1,5-diphenylcarbazide in an acidic medium, using a UV-visible spectrophotometer at 540 nm (Muthusamy et al. 2014). The level of Cr(III) was then calculated by the difference between the total Cr content and the content of Cr(VI) (Xiao et al. 2018).

All the experiments were triplicated, and the efficiency of Cr(VI) removal (%) was calculated from equation (1). Meanwhile, the adsorption capacities of each sample were calculated based on the difference in the total Cr concentration in filtrate before and after adsorption according to the equation (2)

$$\text{Removal (\%)} = (C_0 - C_e) \times 100 / C_0 \quad (1)$$

$$q_e = (C_0 - C_e) \times V / m \quad (2)$$

where C_0 and C_e are the initial and the final concentration (obtained by FAAS) of the Cr(VI) in solution (mg L⁻¹), respectively. V is the volume of solution (L) and m is the sorbent mass (g).

Model simulation of Cr(VI) biosorption

Widely applied Langmuir model (eq. 3) and the Freundlich model (eq. 4) in linearized forms were used to fit the equilibrium data (Wang 2017; Li et al. 2017).

$$q_e = K_c q_m C_e / (1 + K_c C_e) \quad (3)$$

$$\ln q_e = \ln K_f + 1/n \times \ln C_e \quad (4)$$

Where q_m (mg g⁻¹) is the maximum adsorption capacity and K_c (L mol⁻¹) is the Langmuir constant, C_e is the equilibrium concentration of Cr(VI) in the solution (mg L⁻¹), q_e is the adsorption capacity of Cr(VI) at

equilibrium (mg g^{-1}), K_f (L mg^{-1}) is a Langmuir binding constant related to the energy of adsorption.

To investigate the controlling mechanism of biosorption process, the pseudo-first-order (eq.5) and the pseudo-second-order (eq.6) kinetic models in linearized forms were used to analyze the sorption process (Li et al. 2019).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (6)$$

where, q_e and q_t (mg g^{-1}) are the biosorption capacity at equilibrium and at time t , respectively. k_1 (min^{-1}) and k_2 ($\text{g (mg} \cdot \text{min)}^{-1}$) are the rate constants of pseudo-first-order and pseudo-second-order adsorption, respectively.

Moreover, thermodynamic parameters associated with chemical reactions in isothermal processes, such as changes in Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were estimated according to the following Equations (Li et al. 2017; Hlihor et al. 2017). The equilibrium constant K_c (L mol^{-1}) derived from the Langmuir modeling of isotherm data, T is the sorption temperature (K) and R is the ideal gas constant ($8.314 \text{ J (mol} \cdot \text{K)}^{-1}$).

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

$$\Delta H^\circ = RT_1 T_2 (T_2 - T_1) \ln \frac{K_c T_2}{K_c T_1} \quad (8)$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T \quad (9)$$

Results And Discussion

Characterization of the biosorbent

The physical properties of EPRs and SEPRs, including the average pore diameter (APD), the BET surface area (S_{BET}), and the total pore volume (TPV) are presented in Table 1. As can be seen, the surface area of the antibiotic residue was enhanced after CaCl_2 treatment. More specifically, the S_{BET} increased from $0.39 \text{ m}^2 \text{ g}^{-1}$ (EPRs) to $3.70 \text{ m}^2 \text{ g}^{-1}$ (SEPRs). However, a slight reduction in TPV and APD was observed in SEPRs, which was probably due to the blockage of inner interior pore structure with the introduction of CaCl_2 salt. Furthermore, the nitrogen adsorption-desorption isotherms of the EPRs and SEPRs samples showed a type-IV isotherm with an obvious H1-type hysteresis loop (Fig. S1 in the Supplementary materials), indicating the existing of mesoporous cylindrical structure in the adsorbents.

Table 1
Physical chemical properties of the EPRs and SEPRs samples

Sample	S_{BET} (m^2/g)	TPV (cm^3/g)	APD (nm)	C (%)	H (%)	N (%)	S (%)	Zeta Potential (mv)	pH_{zpc}
EPRs	0.39	0.0042	42.65	30.92	5.15	4.96	1.41	-0.354	4.3
SEPRs	3.70	0.0222	33.05	25.80	4.65	2.72	0.64	-25.6	5.4

Effect of adsorbent dosage on Cr(VI) sorption

The percentage of Cr(VI) removed as a function of adsorbent dosage for both EPRs and SEPRs is illustrated in Fig. 1. The Cr removal rates steadily increased with the increasing of adsorbent dosage for both EPRs and SEPRs. Moreover, SEPRs were superior to EPRs to achieve higher Cr(VI) remove rates. A complete removal of Cr(VI) was obtained at an adsorbent dosage of 40 g L^{-1} for SEPRs. By comparison, 90% of Cr(VI) was removed under this condition among EPRs treatments. Enhanced Cr(VI) removal with increasing dosage was consistent with previous studies can be explained with the abundance of binding sites available for Cr(VI) sorption (Muthusamy et al. 2014; Rambabu et al. 2020; Hlihor et al. 2017). Considering the high Cr(VI) removal efficiencies and marginal effect, biosorbent dosage of 20 g L^{-1} was selected and applied in further experiments.

[Fig. 1]

Effect of solution pH on Cr(VI) removal

Solution pH is one of the factors that significantly affect the removal of contaminants since a rising aqueous solution pH affects both the surficial chemical properties of adsorbents as well as the speciation of Cr(VI) ions in solution (Miretzky et al. 2010, Rambabu et al. 2020). As presented in Fig. 2, the removal of Cr(VI) gradually decreased from over 90% and 80% to approximately 50% with rising pH from 1.0 to 9.0 for SEPRs and EPRs, respectively. This finding was consistent with previous studies, in which the Cr(VI) removal was significantly reduced from 100% to less than 20% when solution pH increased from 1.0 to 3.0 (Blázquez et al. 2009). On one hand, a low solution pH renders sorbent surface to be positively charged, which facilitated Cr(VI) removal by electronic attraction. Additionally, Cr(VI) ions were dominantly existed as HCrO_4^- under low pH, which had higher affinity to adsorbents (Pradhan et al. 2019). On the other hand, Cr(VI) ions can be easily reduced into Cr(III) in the presence of electron donor under the acid condition, which can further bind with surface functional groups or form stable precipitation under slightly acidic or neutral conditions (Miretzky et al. 2010). For this reason, the highest Cr(III) contents in solutions were observed at the initial pH at 3.0, and a significantly higher percent of Cr(III) in the aqueous solution was observed in treatments with EPRs than that in treatment with SEPRs (p

< 0.05). Considering the high chromium removal efficiencies, solution was adjusted at 1.0 in the following experiments.

[Fig. 2]

Biosorption isotherms

The removal efficiencies of Cr(VI) with rising initial Cr(VI) ion concentrations that ranged from 10 to 500 mg L⁻¹ at pH 1.0 for EPRs and SEPRs are presented in Fig. 3a. As it can be seen, the removal of Cr(VI) decreased with rising initial Cr(VI) concentration, especially when the concentration was over 100 mg L⁻¹. However, less than 30% of the Cr(VI) was removed from solution at an initial Cr(VI) concentration of 500 mg L⁻¹. Langmuir and Freundlich equations were employed to simulate experiment data, and the results are presented in Table 2. Generally, the Langmuir isotherm model assumes monolayer coverage of adsorbate on the surface of adsorbent, while the Freundlich isotherm model is based on multilayer adsorption with the interaction between adsorbed molecules (Li et al. 2017). It is from Table 2, that the Langmuir isotherm model best fitted to the sorption data with high *r*² values, suggesting that monolayer surface coverage played an important role in Cr(VI) sorption on EPRs and SEPRs. Additionally, SEPRs demonstrated maximum absorption capacities than EPRs, with the values of 21.74 and 35.24 mg g⁻¹ for EPRs and SEPRs, respectively. Furthermore, the *n* value of EPRs and SEPRs are all within the range from 1 and 10, which indicates Cr(VI) adsorption on both sorbents were favorable sorption processes (Dsilva et al. 2016).

Table 2
Isotherm parameters onto different adsorbents at different temperatures

Adsorption	Temperation (K)	Langmuir constant			Freundlich constant		
		Kc (L/mol)	q _m (mg/g)	<i>r</i> ²	n	K _f (L/mg)	<i>r</i> ²
EPRs	298	3273	21.74	0.999	2.36	0.798	0.857
	303	3253	23.18	0.999	2.35	0.817	0.860
	313	3257	24.55	0.999	2.34	0.830	0.862
	323	3416	25.78	0.998	2.35	0.864	0.863
SEPRs	298	3685	35.24	0.999	2.42	0.915	0.838
	303	3395	36.58	0.999	2.35	0.951	0.826
	313	4540	37.85	0.999	2.35	0.966	0.837
	323	4085	38.98	0.999	2.36	0.993	0.838

[Fig. 3]

Effect of contact time on Cr(VI) sorption

The effect of prolonged contact time on Cr(VI) removal is given in Fig. 3b. It can be seen that Cr(VI) removal was rapid in the first 30–40 min. After that, biosorption rates were gradually reduced with increasing contact time, and an equilibrium was reached at about 150 min. Notably, approximately 50% of Cr(VI) was removed by EPRs during the first 60 min, and the value was over 80% for SEPRs. A similar trend has been reported in the literature, such as the employment of sugarcane bagasse waste biomass (Ullah et al. 2013), *Cystoseira indica* (Basha et al.2008), microalgae *Scenedesmus* sp. (Pradhan et al.2019), dead and living *Arthrobacter viscosus* biomass (Hlihor et al. 2017).

Generally, Cr(VI) removal by sorbent can be divided into two stages: 1) an initial rapid uptake correlated with surface adsorption on the cell walls, and 2) a subsequent slow uptake via membrane transport of the metal ions on the cytoplasm of the cells, which continued until the equilibrium is reached (Ullah et al. 2013; Basha et al. 2008). In order to evaluate the kinetic mechanism that controls the biosorption process, the pseudo-first-order and pseudo-second-order models were used to test the experimental data of Cr(VI) biosorbent by EPRs and SEPRs. The fitted curves of the pseudo-first-order kinetic and the pseudo-second-order kinetic are plotted in Fig. 3c and d, respectively. The constants for EPRs and SEPRs along with the correlation coefficients (r^2) are showed in Table 3. As shown in Table 3, the correlation coefficient (r^2) for the pseudo-second-order equation is high and the calculated $q_{eq,cal}$ values (20.12, 34.18 mg g⁻¹) were consistent with experimental $q_{eq,exp}$ obtained from isotherms simulation. This suggests that the biosorption of Cr(VI) was more appropriately by the pseudo-second-order. Similarly, Dsilva et al. (2016) reported that the pseudo-second-order kinetic model represented the data better than the pseudo-first-order model for biosorption of Cr(VI) by free and immobilized dead *Sargassum* sp. Similar phenomenon has been observed in the adsorption of Cr(VI) onto native and immobilized sugarcane bagasse waste biomass (Ullah et al. 2013).

Table 3
Kinetic parameters for the sorption of Cr(VI) on the EPRs and SEPRs

Biomass	First-order model		Second-order model				
	$q_{e,exp}$ (mg/g)	$k_1 \times 10^{-3}$ (min ⁻¹)	$q_{e,cal}$ (mg/g)	r^2	$k_2 \times 10^{-3}$ (g/mg/ min)	$q_{e,cal}$ (mg/g)	r^2
EPRs	20.21	7.83	18.46	0.853	65.87	20.12	0.999
SEPRs	34.25	36.66	30.56	0.881	19.87	34.18	0.999

Furthermore, the changes of Cr(VI) and Cr(III) concentrations in solution during Cr(VI) sorption are illustrated in Fig. 3b. With the prolonged sorption experiment, Cr(III) contents in solutions steadily increased, and stabilized after 4 h at approximately 4 and 9 mg L⁻¹ for EPRs and SEPRs, respectively.

Thermodynamic analysis

Solution temperature is also an important parameter affecting metal sorption behaviors. Sorption isotherm data obtained at different temperatures were used to calculate the thermodynamic parameters using Eqs. (7) - (9), and the results were presents in Fig. 4 and Table 4. It showed the negative value of ΔG° at different experiment conditions, indicating that the sorption process was feasible and spontaneous in nature. Additionally, ΔG° values reduced with an increase in temperature, suggesting that a higher temperature condition facilitate Cr(VI) adsorption on EPRs and SEPRs. Moreover, the positive value of ΔH° shows that sorption process is endothermic in nature. Since the values of the activation energy are below 40 kJ mol^{-1} (Módenes et al. 2017), the sorption process may be physisorption mechanism. A positive value of ΔS° described that the increased randomness at the solid-liquid interface during the adsorption of Cr by the antibiotic residues. Similar results were also reported by other types of adsorbents, including treated waste newspaper (Dehghani et al. 2016).

Table 4
The adsorption thermodynamic parameters of the Cr(VI) on EPRs and SEPRs

Temperature (K)		ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/ mol.K)
EPRs	298	-20.05	1.37	0.0719
	303	-20.37		
	313	-21.05		
	323	-21.85		
SEPRs	298	-20.37	3.51	0.0799
	303	-20.68		
	313	-21.49		
	323	-22.33		

[Fig. 4]

Cr(VI) removal mechanism analysis

Morphological features and surface characteristics of bio-sorbent before and after Cr(VI) adsorption were obtained from scanning electron microscopy (SEM). The image in Fig. 5a and c showed that antibiotic residues particle is mostly irregular in shape and has a porous surface, which would facilitate metal ions diffusion/penetration into the inner parts of adsorbents [10]. After sorption, the pores and surfaces of adsorbent became smooth (Fig. 5b and d), which could be due to retaining of Cr(VI) on adsorbent surface.

[Fig. 5]

[Fig. 6]

Fourier transform infrared spectroscopy (FT-IR) spectra of EPRs and SEPRs before and after sorption are shown in Fig. 6. The strong and broadband around 3347cm^{-1} ($3334\text{--}3434\text{ cm}^{-1}$) indicated the existence of bound hydroxyl group (--OH stretching) (Pradhan et al.2019; Dsilva et al.2016). The weak bands at 2924 cm^{-1} and 2852 cm^{-1} indicated the --CH stretching of the groups --CH_2 and --CH_3 (Rambabu et al.2021; Long et al. 2017). The peaks at 1657 cm^{-1} and 1454 cm^{-1} indicated the stretching vibration of C=O groups (Pradhan et al.2019; Iqbal et al.2009). The peak at 1043 cm^{-1} may correspond to a C--O group (Saha et al. 2013). Some shifts were found in contrast to the biosorbent after adsorption. Those changes include a shift in the band from 3336 to 3347 cm^{-1} in EPRs and 3400 to 3408 cm^{-1} in SEPRs, and the bands at 1622 , 1455cm^{-1} to 1657 , 1454cm^{-1} in SEPRs, and a shift of band from 1654 , 1453 cm^{-1} to 1657 , 1453 cm^{-1} in EPRs. Moreover, the peak at 2925 , 2924 cm^{-1} in EPRs and SEPRs was moved to 2924 and 2923 cm^{-1} , respectively. These changes suggested that the --OH , C=O , and C--O groups could be predominant contributors in Cr(VI) uptake (Rambabu et al.2020; Dsilva et al. 2016).

Conclusion

Both EPRs and SEPRs have proved as promising biosorbent for Cr(VI) removal from aqueous solutions, and the maximum adsorption capacities for EPRs and SEPRs were 21.74 and 35.24 mg g^{-1} , respectively. Solution pH significantly affected Cr(VI) removal by EPRs and SEPRs, and a rising solution pH reduced Cr(VI) removal. The optimum pH for Cr(VI) detoxification was 1.0 , under this conditions, 78.61% and 90.13% of the initial Cr(VI) were removed by EPRs and SEPRs respectively. Higher adsorbent dosage facilitated the removal of Cr(VI) and Cr(VI) removal was an endothermic and spontaneous chemical reaction. Spectroscopic analysis revealed that --OH and C=O groups are mainly involved in Cr(VI) adsorption, and the mechanism of Cr(VI) removal by EPRs and SEPRs was adsorption-coupled-reduction.

Declarations

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Contributions

Xining Sun: study design, study concept, data collection, statistical analyses, visualization, acquired funding, writing of the first draft. Dongsheng Li: performed experiments. Zengqiang Zhang: supervision, writing—review and editing. All authors read and approved the final manuscript.

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Ethics declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Competing interests

The authors declare no competing interests.

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Data Availability

All relevant data generated or analyzed during this study were included in this published article.

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Figures

Figure 1

Effect of adsorbent dosage on Cr(VI) removal by EPRs and SEPRs.

Figure 2

Effect of initial solution pH on Cr(VI) removal by EPRs and SEPRs, and Cr(III) concentration in solutions after sorption.

Figure 3

Effect of initial Cr(VI) concentration (a) and adsorption time (b, c, d) on Cr(VI) removal by EPRs and SEPRs

Figure 4

Effect of temperature on Cr(VI) removal by EPRs (a) and SEPRs (b), and the plot of ΔG° versus T (c).

Figure 5

Scanning electron microscopic picture of pure (a and c) and chromium loaded (b and d) antibiotic residues (a. EPRs; b. Cr-loaded EPRs; C. SEPR; D. Cr-loaded SEPRs)

Figure 6

FTIR spectra of adsorbent before and after Cr(VI) adsorption (a: EPRs; b: SEPRs)

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