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Chemically modified hydroxyethylcellulose: a high capacity sorbent for removal of As(III) and As(V) from aqueous solution

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ABSTRACT

Hydroxyethylcellulose succinate (HEC-Suc) was utilized for the removal of As(III) and As(V) from aqueous solution. HEC-Suc was characterized by FTIR and scanning electron microscope–energy dispersive spectroscopic analysis (SEM–EDS) before and after arsenic uptake. Effect of initial arsenic concentration, sorbent dose, pH, contact time and temperature on the uptake of arsenic was studied. Isothermal equilibrium sorption data were subjected to Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherm models which provided better fit suggesting monolayer formation on the sorbent surface. The maximum sorption capacity was 151.5 and 204.10 mg g^{-1} for As(III) and As(V), respectively, as calculated by Langmuir model. Values of mean sorption energy (E) calculated by D–R model suggested that chemisorption appeared to be the mechanism of removal of both As(III) and As(V). Negative values for thermodynamic parameters ($\Delta G°$ and $\Delta H°$) revealed the feasible, spontaneous and exothermic nature of sorption process. Contact time experiment data were subjected to pseudo-second order, pseudo-first order, intraparticle diffusion and Elovich models. Pseudo-second order model provided the best fit to the experimental data. HEC-Suc appeared an efficient and super-sorbent in removing As(III) and As(V) from aqueous solution as compared with other sorbents already used for the removal of arsenic. Regeneration studies were also carried out.

Keywords: Arsenic; Chemisorption; Modified cellulose; Thermodynamic parameters; Regeneration

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1. Introduction

According to WHO and EPA, maximum permissible limit of arsenic in drinking water is 10 μg/L [1], whereas 100 times more than the maximum allowed concentration of arsenic is found in many parts of the world. Therefore, the poisoning of arsenic present in water has emerged as a great public concern as its concentration is increasing day by day in water sources by combination of natural routes (weathering of rocks and volcanic eruption) and anthropogenic activities [2,3]. Among anthropogenic activities, timber industry is responsible for about 70% production of total arsenic due to copper chrome arsenate used for timber treatment while 22% of the world arsenic production is coming out of fertilizers, insecticides and herbicides. As(III) and As(V) forms of As are highly toxic and greater cellular uptake of As(III) makes it 60 times more toxic than As(V) [4].

Arsenic is known to cause failure of multisystem organs along with several other diseases which are not curable or difficult to treat and many of them cause permanent damage to the body, that is, black foot disease, teratogenic to animals, diffused and spotted melanosis and keratosis, nonpitting edema, Bowen's disease, gangrene and cancers of skin, liver and lungs [5–7].

High cost, low arsenic removal capacity, generation of toxic sludge or other waste products and energy requirements are the disadvantages associated with traditional

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arsenic removal methods. Likewise, most of the traditional sorbents involve the use of agricultural waste materials having several disadvantages which include presence of several kinds of functional groups, less sorption capacity and lack of selectivity [8–10]. Therefore, it is utmost need to develop sorbents having single kind of functionalities, selective and enhanced arsenic uptake capacity.

Cellulose is a biopolymer having hydroxyl (OH) groups but has low affinity for heavy metal due to strong intermolecular hydrogen bonding [11]. To get maximum arsenic removal efficiency, chemical modification of cellulose is required. Among chemically modified cellulose materials, hydroxyethylcellulose is a versatile material and getting attention of researchers working in various fields. In HEC, OH groups are away from the main polymeric backbone chain and are less sterically hindered therefore easily available for chemical modification such as esterification. This makes HEC, a suitable material to be succinylated. Succinylated polysaccharides are nowadays being widely evaluated for toxic metal uptake after their conversion to sodic form [12–14]. To the best of our knowledge, HEC-Suc (in non-sodic form) has not been reported for the removal of any form of arsenic.

The present work aims to investigate HEC-Suc (non-sodic form) for the removal of arsenic from aqueous solution. The effects of various factors such as initial arsenic concentration, pH, sorbent dosage, contact time and temperature on sorption of arsenic are systematically examined. The sorption capacity of HEC-Suc was calculated and compared with other sorbents already used for the removal of arsenic. Further equilibrium, isothermal, kinetic and thermodynamic studies have also been carried out.

2. Experimental setup

2.1. Reagent and materials

Hydroxyethylcellulose (Natrosol hydroxyethylcellulose, HE10K, Belgium), arsenic trioxide (As_2O_3), sodium arsenate ($Na_2HAsO_4·7H_2O$), HNO_3 and NaOH were obtained from Sigma-Aldrich (St. Louis, MO, USA). HEC was dried in an oven at 110°C for a period of 2 h before use. All the chemicals used in the study were of analytical grade and used without further purification. Deionized double-distilled water was used for the preparation of solution. As(V) was reduced to As(III) by adding 2 mL of (35%–37%) HCl and 2 mL of 20% (w/v) KI to 20 mL of the standard or sample solution and left for about 15 min [15].

2.2. Synthesis and characterization of HEC-Suc conjugate

Esterification of HEC with succinic anhydride to get HEC-Suc was carried out in presence of 4-dimethylaminopyridine as per the method reported by us [12] and same material was used in present study.

FTIR spectra were recorded using IRPrestige-21 (Shimadzu, Japan). The pH corresponding to the point of zero charge, that is, pH_{ZPC}, of the sorbent HEC-Suc was calculated by a reported method [16] and found to be 4.2. The pH_{ZPC} of any sorbents helps to predict the charge on the surface of sorbent by changing pH. Above and below pH_{ZPC}, the surface of the sorbent has negative charge and positive charge, respectively. Scanning electron microscope (SEM; Nova, NanoSEM 450) equipped with a low energy Everhart-Thornley detector was used to obtain images of the sorbent HEC-Suc before and after arsenic uptake, and energy dispersive X-ray (EDX, Oxford Instruments, Oxon, UK) was used to conduct energy dispersive spectroscopic analysis (EDS).

2.3. Sorption studies

Stock solution (1,000 mL) of As(III) and As(V) were prepared by dissolving appropriate amounts of arsenic trioxide (As_2O_3) and sodium arsenate ($Na_2HAsO_4·7H_2O$) in deionized double-distilled water. All other solutions required for batch experiments were prepared by diluting these stock solutions. Batch experiments were carried out in Erlenmeyer flasks (250 mL). This was done by adding optimized amount of sorbent in 100 mL of aqueous arsenic solution (As(III) and As(V)) of desired arsenic ion concentration, initial pH and temperature. 0.1 M HCl and 0.1 M NaOH solutions were added to arsenic ion solution to get solution of desired initial pH. The flasks were gently agitated using a shaking thermostat machine (Orbital Shaking Incubator, PA-42/250R, PAMICO Technologies, Faisalabad, Pakistan) at 150 rpm for a desired time. The content of flask was separated from sorbent and analyzed for remaining arsenic concentration by using flame atomic absorption spectrophotometer AA 6300 (Shimadzu, Japan) fitted with acetylene-nitrous oxide at a wavelength 193.7 nm. The sample solutions were diluted to get the results within the calibration range. All the experiments were performed in triplicates and the concurrent values were taken to present results. The amount of arsenic removed per unit mass of the sorbent, q_e (mg g^{-1}) and percentage arsenic uptake were calculated by Eqs. (1) and (2):

$$q_e = \frac{C_i - C_e}{w} \times V \tag{1}$$

$$\text{Percentage uptake} = \frac{C_i - C_f}{C_i} \times 100 \tag{2}$$

where C_i and C_e are the initial and equilibrium As(III) and As(V) concentration in mg/L, respectively. V (L) and w (g) volume of solution and weight of sorbent, respectively.

Effect of variation of initial arsenic ion concentration and contact time was studied with an initial arsenic concentration of 30–100 mg/L for both As(III) and As(V) and sorbent dosage of 50 g/100 mL, respectively; pH was kept at 7.0 for As(III) and at 4.0 for As(V) and shaking time of 1 h at 298 K. Effect of sorbent dosage (10–80 mg) on arsenic uptake was studied by using 100 mL of solution with initial arsenic concentration of 50 mg/L for both As(III) and As(V) and at temperature of 298 K at pH 7.0 for As(III) and at 4.0 for As(V) and shaking time of 1 h. Effect of initial pH (2–10) on arsenic uptake was studied by using 100 mL of solution with initial arsenic concentration of 50 mg/L for both As(III) and As(V) and sorbent dosage of 40 mg/100 mL and 30 mg/100 mL for As(III) and As(V), respectively, at temperature of 298 K and shaking time of 1 h. Effect of contact time was studied with an initial arsenic concentration of 50 mg/L for both As(III) and As(V) and sorbent dosage of 40 g/100 mL and 30 g/100 mL for As(III) and As(V), respectively; pH was kept at 7 for As(III) and at

4 for As(V) and contact time was varied from 5 to 120 min at 298 K. The effect of temperature on arsenic uptake was studied in the range 298–343 K at initial arsenic concentrations of 50 mg/L for both As(III) and As(V) and sorbent dosage of 40 mg/100 mL and 30 mg/100 mL for As(III) and As(V), respectively, at pH 7.0 for As(III) and 4.0 for As(V).

2.4. Desorption experiments

Recovery of the sorbent and its use for sorption of arsenic after regeneration is an important factor which is taken into consideration during wastewater treatment procedures. To carry out regeneration studies of the sorbent, HEC-Suc after arsenic uptake was stirred with 0.1 M NaOH solution (100 mL) for a period of 8 h. After equilibrium was attained, suspension was filtered and the recovered sorbent was washed with distilled water and air-dried while the filtrate was analyzed for desorbed arsenic. This regenerated sorbent was again used for arsenic uptake under optimal conditions. These sorption–regeneration studies were repeated five times.

3. Results and discussions

3.1. Synthesis and characterization of sorbent

HEC-Suc was synthesized by esterification of HEC with succinic anhydride in the presence of catalyst 4-dimethylaminopyridine as per reported method [12]. HEC-Suc was found completely insoluble in water. This provided the basis for its use for the treatment of wastewater containing arsenic.

Fig. 1 shows the FTIR (KBr) spectra of HEC-Suc and As-loaded HEC-Suc (HEC-Suc-As). The signals at 1,735 cm^{-1} is showing presence of ester carbonyl groups in HEC-Suc which was shifted to lower wavenumber 1,720 cm^{-1} in HEC-Suc-As. Such type of shifting of peak to lower wavenumber after arsenic loading can be evidenced from literature [17]. However, the band appearance at 1,564 cm^{-1} in the spectrum of HEC-Suc-As is for carboxylate anion illustrating successful loading of arsenic. Further the absorption of arsenic to oxygen bond appeared intense at 569 cm^{-1}.

The pH$_{ZPC}$ of HEC-Suc was calculated to predict change in charge on the surface of the sorbent with change in pH and was found to be 4.2. The pH$_{ZPC}$ value less than 7.0 is an evidence of successful esterification and presence of weak acidic character due to carboxylic acid groups on the surface of the sorbent.

SEM–EDS plots of the sorbent before (HEC-Suc) and after arsenic uptake (HEC-Suc-As) are depicted in Fig. 2. Presence of As on the surface of the sorbent after arsenic uptake is evidenced from the EDS plot of HEC-Suc-As.

3.2. Sorption studies

3.2.1. Effect of the initial arsenic concentration

Fig. 3 shows that sorption capacity of both As(III) and As(V) on the surface of the sorbent increases with increase in initial concentration of the arsenic ion reaching to an optimum level of 50 mg/L for both As(III) and As(V) and after

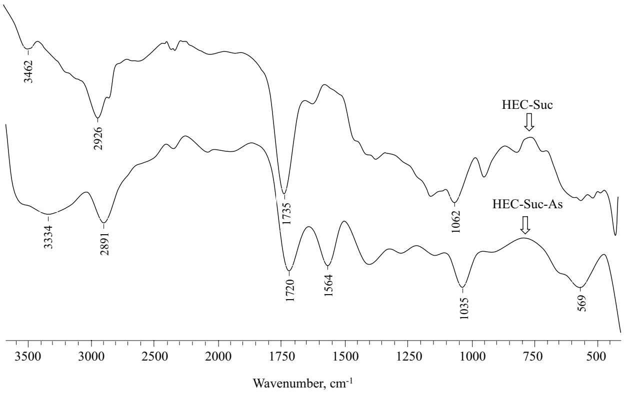

Fig. 1. FTIR (KBr, transmittance) spectra of HEC-Suc and HEC-Suc-As.

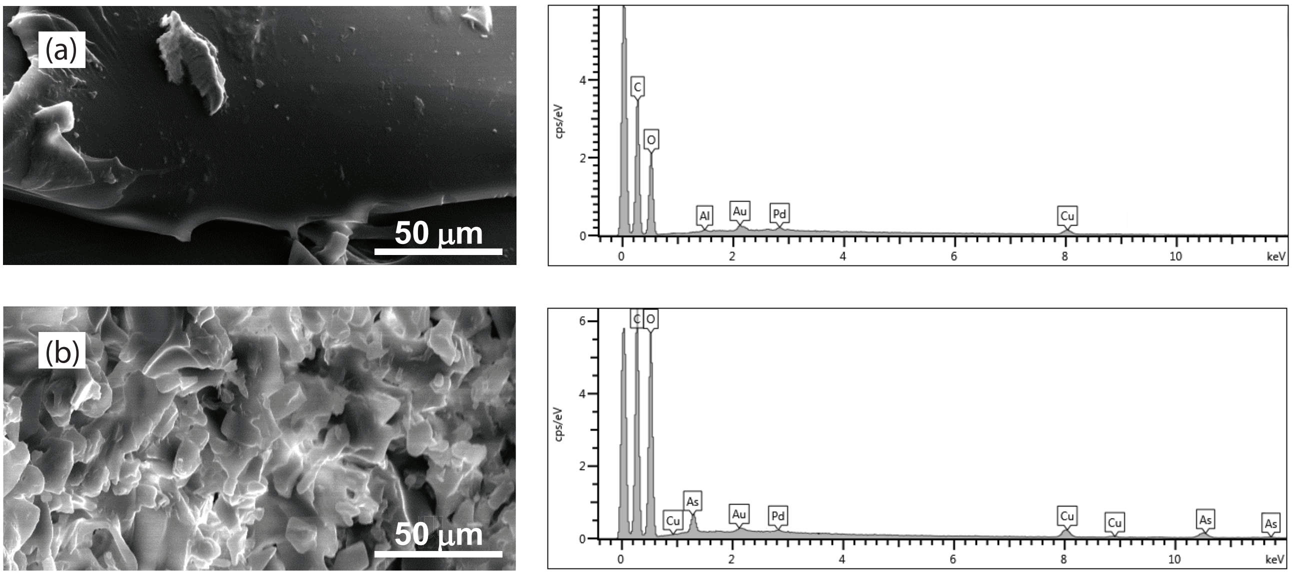

Fig. 2. SEM–EDS of HEC-Suc (a), and As(III) adsorbed on HEC-Suc (b).

that sorption capacity becomes constant. The reason behind might be high ratio of sorptive surface area to the sorbent amount which provides greater chance for removal of arsenic ions. As the concentration is raised to optimal concentrations of arsenic ions, binding sites on the surface of sorbent become more quickly saturated due to which sorption capacity of the sorbent becomes constant.

3.2.2. Effect of the sorbent dosage

The effect of sorbent (HEC-Suc) dosage was studied in the range 10–100 mg for both As(III) and As(V). Fig. 4 shows that sorption capacity increases with the increase in sorbent dosage from 10 to 30 mg for As(III) and from 10 to 40 mg for As(V) after which it starts decreasing. Increase in sorption capacity with increase in sorbent dosage is attributed to the availability of more active sorption sites with increasing amount of sorbent. Decrease in sorption capacity at later stages may be due to the fact that there is an unavailability of arsenate and arsenite ions to be bound with the sorbent (HEC-Suc) surface sites.

3.2.3. Effect of pH on As(III) and As(V) uptake

The pH of sorption medium affects charge on the surface of sorbent, degree of ionization and speciation in solution. Moreover, industrial effluent containing wastewater may be acidic or alkaline so it is important to study the effect of pH on sorption of an arsenic ion from aqueous solution. Effect of pH on sorption of arsenic from aqueous solution was studied in the pH range 2–10. In the pH range 2.0–9.0, As(III) exists as H_3AsO_3 while in pH range 10–12 it exists as $H_2AsO_3^-$. Literature reveals that As(V) exists as $H_2AsO_4^-$ in the pH range 3–6 while at pH greater than 8 it exists as $HAsO_4^{-2}$. In the pH range 6–8, both $H_2AsO_4^-$ and $HAsO_4^{-2}$ co-exist. When the pH value is near 2, a small concentration of H_3AsO_4 is also present in solution. Sorption capacity is low in case of As(III) at pH 2 and remains constant as the pH is increased from 2 to 5 and a sudden increase takes place with further increase in pH and reaches a maximum at pH 7. Further increase in pH causes a sharp decrease in sorption capacity (Fig. 5). The reason for low sorption capacity at pH 2–5 is attributed to the fact that in extreme acidic conditions, the surface of the sorbent is highly protonated and does not support As(III) removal. Further increase in pH decreases the degree of protonation of the surface. Maximum sorption capacity of As(III) at pH 7.0 is attributed to the fact that at this pH As(III) exists in the form of neutral species H_3AsO_3. At this pH, As(III) is sorbed on the surface of sorbent in the form of various unspecified reaction products in the sorption process. At pH greater than 8, surface of the sorbent acquires negative charge and it repels the negatively charged species ($H_2AsO_3^-$) resulting decrease in sorption capacity.

Sorption capacity of As(V) increases with increase in pH from 2 to 4, with maximum value at pH 4 then starts decreasing up to pH 10 (Fig. 5). Reason behind might be the presence of neutral species H_3AsO_4 in addition to $H_2AsO_4^-$. The value of pH_{ZPC}, for HEC-Suc, is 4.2 below which its surface acquires positive charge which favors the uptake of As(V) in the form of oxyanion ($H_2AsO_4^-$) due to electrostatic force of attraction between oppositely charged species. Decrease in the sorption

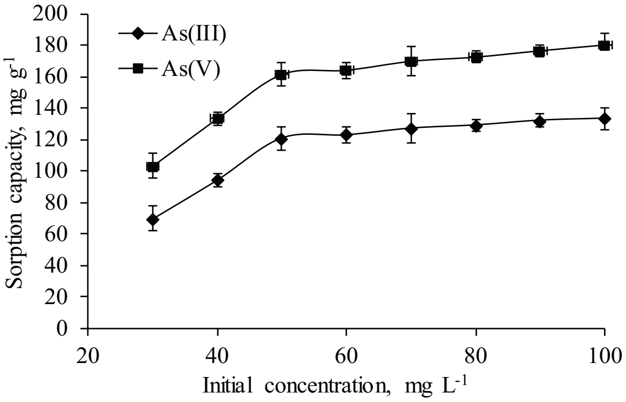

Fig. 3. Sorption capacity of As(III) and As(V) as a function of initial arsenate and arsenite concentration (sorption conditions: sorbent dose = 50 mg in 100 mL arsenic solution, arsenate and arsenite concentration = 30–100 mg L^{-1}, temperature = 298 K, contact time = 1 h, pH was kept at 7.0 for As(III) and at 4.0 for As(V)).

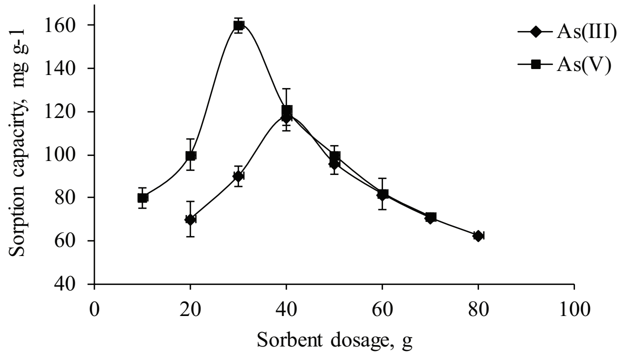

Fig. 4. Sorption capacity of As(III) and As(V) as a function of sorbent dosage (sorption conditions: sorbent dose = 10–100 mg in 100 mL arsenic solution, arsenate and arsenite concentration = 50 mg L^{-1}, temperature = 298 K, contact time = 1 h, pH was kept at 7.0 for As(III) and at 4.0 for As(V)).

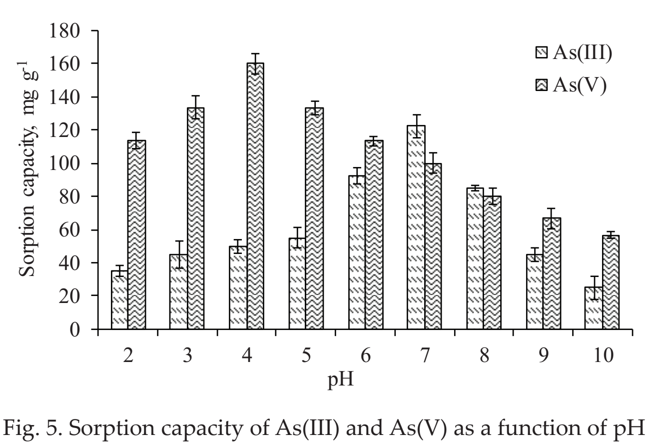

Fig. 5. Sorption capacity of As(III) and As(V) as a function of pH (sorption conditions: sorbent dose = 50 mg in 100 mL arsenic solution, arsenate and arsenite concentration = 50 mg L^{-1}, temperature = 298 K, contact time = 1 h, pH = 2–10).

capacity of As(V) with increase in pH value from 4 onward is attributed to the fact that there is an increase in the force of repulsion between negatively charged surface of the sorbent (at pH > pH_{ZPC}) and oxyanion.

3.2.4. Effect of temperature

To predict the endothermic or exothermic nature of the sorption process the effect of temperature on sorption of As(III) and As(V) by HEC-Suc was studied in the range 298–338 K. Decrease in sorption capacity with increase in temperature for As(III) and As(V) was found to be 12 and 20 mg g^{-1}, respectively (Fig. 6). This decrease in sorption capacity with increase in temperature is due to higher mobility of sorbate species at higher temperature causing decreased sorbate–sorbent interaction and is indicative of exothermic nature of sorption process.

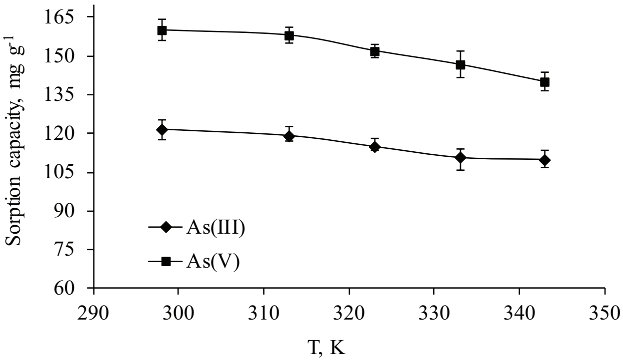

Fig. 6. Sorption capacity of As(III) and As(V) as a function temperature (sorption conditions: sorbent dose = 50 mg in 100 mL arsenic solution, arsenate and arsenite concentration = 50 mg L^{-1}, temperature = 298–343 K, contact time = 1 h, pH was kept at 7.0 for As(III) and at 4.0 for As(V)).

3.2.5. Effect of contact time

Fig. 7 represents the effect of contact time on the uptake of arsenic by HEC-Suc. The time required to attain equilibrium, that is, saturation period for sorption of As(V) and As(III) on HEC-Suc is 30 and 60 min, respectively. Presence of sufficient sorption sites on the surface of the sorbent and involvement of chemisorption process is the reason for rapid uptake of arsenic at early stages of sorption.

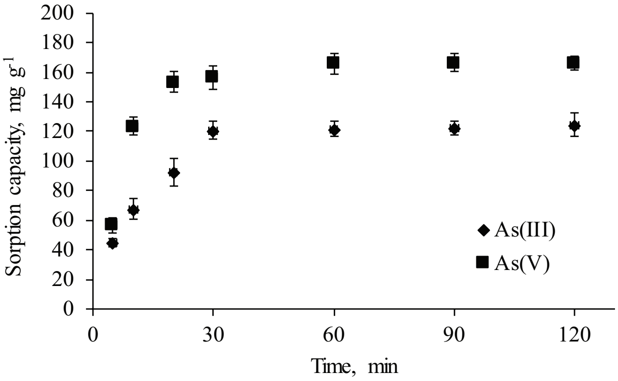

Fig. 7. Sorption capacity of As(III) and As(V) as a function contact time (sorption conditions: sorbent dose = 50 mg in 100 mL arsenic solution, arsenate and arsenite concentration = 50 mg L^{-1}, temperature = 298 K, contact time = 5–120 min, pH was kept at 7.0 for As(III) and at 4.0 for As(V)).

3.2.6. Kinetic modeling

In order to establish mechanism of sorption, the data obtained from contact time experiments were fitted to pseudo-first order, pseudo-second order, intraparticle diffusion and Elovich models.

Linear form of pseudo-first order kinetic model is given by Eq. (3):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (3)$$

Linear form of pseudo-second order kinetic model is given by Eq. (4):

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

where q_e (mg g^{-1}) is amount of arsenic ion sorbed at equilibrium and q_t is amount of arsenic sorbed at time t; k_1 (g mg^{-1} min^{-1}) is the rate constant for pseudo-first order reaction while k_2 is rate constant (g mg^{-1} min^{-1}) for pseudo-second order reaction. Table 1 shows the values of different parameters for pseudo-first order and pseudo-second order kinetic models (k_1, k_2, q_e and R^2). Pseudo-first order model (Fig. 8(a)) did not provide the better fit to experimental data as evident from the less values of correlation coefficient (R^2). So, pseudo-second order kinetic model was fitted to kinetic data. Straight lines with high correlation coefficients were obtained for both As(III) and As(V) (Fig. 8(b)). Fitting of pseudo-second order kinetic model to the experimental data showed involvement of chemisorption mechanism in the rate limiting step.

Intraparticle diffusion study was carried out in order to investigate any possibility of transport of sorbate species into the pores of sorbent, which appears rate controlling step in many studies. Intraparticle diffusion equation is given by Eq. (5):

$$q_t = k_{id}t^{0.5} + C \quad (5)$$

where q_t (mg g^{-1}) is the amount of arsenic ion sorbed at time t, k_{id} (mg g^{-1} $min^{0.5}$) is intraparticle diffusion rate constant and C is intercept. Data from contact time experiments are fitted to this model by plotting a graph between q_t and $t^{0.5}$ (Fig. 8(c)). Straight lines with high values of R^2 are obtained. The values of k_{id} and C are obtained from slope and intercept of these straight lines (Table 1). If these straight lines pass through origin, then intraparticle diffusion is supposed to be the only rate limiting step. However, in case of sorption of As(III) and As(V) by HEC-Suc straight lines do not pass through origin indicating that both chemisorption and intraparticle diffusion contribute to the rate limiting step.

Table 1
Pseudo-first order, pseudo-second order, intraparticle diffusion, Elovich model, Freundlich, Langmuir, D–R, Temkin models and thermodynamic parameters for removal of As(III) and As(V) from aqueous solution using HEC-Suc

Models	Parameters	As(III)	As(V)
Pseudo-second order	q_e (mg g^{-1})	134.18	177.90
	k_2 (g mg^{-1} min^{-1})	0.0009	0.0010
	R^2	0.9969	0.9974
Pseudo-first order	q_e (mg g^{-1})	398.80	437.42
	k_1 (g mg^{-1} min^{-1})	0.0478	0.4389
	R^2	0.5817	0.7317
Intraparticle diffusion	k_{id} (mg g^{-1} min$^{0.5}$)	0.9407	2.2120
	c	114.04	147.40
	R^2	0.8578	0.8377
Elovich model	α (mg (g min)$^{-1}$)	2.3304	5.9101
	β (g mg^{-1})	0.1270	0.2873
	R^2	0.9033	0.8892
Experimental	q_e (mg g^{-1})	140.47	189.09
	$Q_{\max}$ (mg g^{-1})	151.50	204.10
Langmuir parameters	b (mg L^{-1})	0.0778	0.0708
	R^2	0.9994	0.9989
	R_L	0.2044	0.2202
Freundlich parameters	n	1.2758	1.7843
	k_F	4.4782	11.437
	R^2	0.9348	0.9443
D–R constants	β (kJ^2/mol^2)	–0.0078	–0.0048
	X_m (mmol/g)	0.8484	0.0072
	R^2	0.9742	0.9789
	E (kJ mol^{-1})	8.0079	11.321
Temkin constants	A	3.7802	7.9870
	b_T	129.23	90.470
	R^2	0.9873	0.9844
Thermodynamic parameters	$\Delta S°$ (J mol^{-1} K^{-1})	–81.407	–73.278
	$\Delta H°$ (kJ mol^{-1})	–33.169	–29.994
	R^2	0.9773	0.9668
	$\Delta G°$ (kJ mol^{-1})	–8.973	–7.8738

In order to establish whether the arsenic removal occurred through chemisorption or physio-sorption Elovich equation is commonly. The linear form of Elovich equation is given by Eq. (6):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{6}$$

where q_t (mg g^{-1}) is the amount of arsenic ion sorbed at time t, β (g mg^{-1}) represents the extent of surface coverage and activation energy for chemisorption and α (mg (g min)$^{-1}$) is related to the rate of chemisorption at zero coverage. The data obtained from contact time experiments were subjected to Elovich equation and values of ln$t$ were plotted against q_t (Fig. 8(d)). Straight lines with higher values of correlation coefficients were obtained for both As(III) and As(V). Slope and intercept of these straight lines give values of β and α, respectively (Table 1). Fitting of data to Elovich equation suggested the involvement of chemisorption through sharing or exchange of electrons between sorbent and sorbate.

3.2.7. Sorption isotherm

The sorption isotherms are used to describe mechanism for sorption equilibrium during wastewater treatment. Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin sorption isotherm models were selected to fit sorption data from initial arsenic ion concentration experiments. The initial arsenic ion concentration was studied in the range 50–100 mg g^{-1} for both As(III) and As(V).

The Freundlich model describes equilibrium on heterogeneous surfaces. Linear form of the isotherm is represented in Eq. (7):

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \tag{7}$$

The values of Freundlich constants n (sorption intensity) and k_F are calculated from slope and intercept of straight line obtained by plotting logq_e vs. C_e, respectively (Fig. 9(a), Table 1). The values of n are 1.27 for As(III) and 1.78 for As(V) (between 1 and 10) or value of 1/n less than 1 indicate favorable sorption. The low values of R^2 for both As(III) and As(V) show that this isotherm did not fit to experimental data. So, the data were fitted to the Langmuir model which describes that the arsenic uptake occurs on a homogeneous surface by monolayer formation without any interaction between sorbed molecules. Linear form of Langmuir model is given in Eq. (8):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} \times b} \tag{8}$$

The values $Q_{\max}$ (maximum sorption capacity/g of sorbent) and b (Langmuir constant) were calculated from slope and intercept of the straight lines obtained from plots between C_e/q_e against C_e, respectively (Fig. 9(b), Table 1). Straight lines with high values of R^2 were obtained for both As(III) and As(V) which gave an evidence of involvement of chemisorption for these arsenic removal by HEC-Suc. Maximum sorption capacities were found to be 151.5 and 204.10 mg g^{-1} for As(III) and As(V), respectively. Validity of this model to kinetic data is evidence of monolayer formation, that is, chemisorption. The values of separation factor (R_L) for both As(III) and As(V) uptake ranging from 0 and 1 (Table 1) indicate favorable sorption and are calculated by Eq. (9):

$$R_L = \frac{1}{1 + bC_i} \tag{9}$$

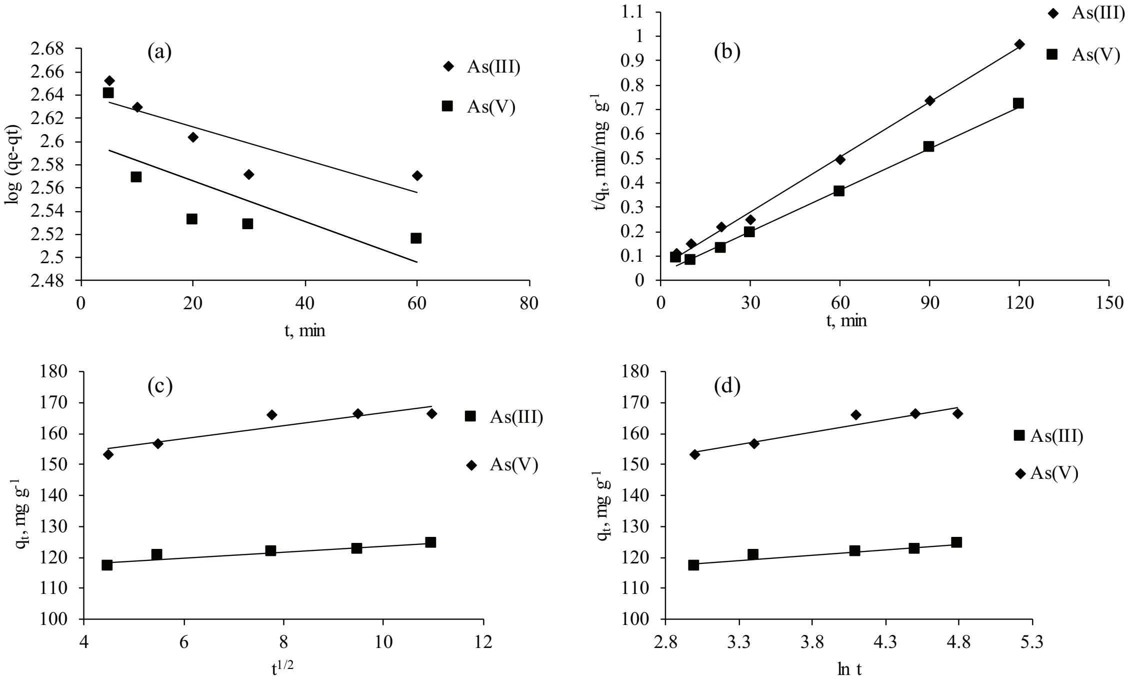

Fig. 8. Pseudo-first order model (a), and pseudo-second order model (b), intraparticle diffusion model (c) and Elovich model (d) for removal of As(III) and As(V) from aqueous solution using HEC-Suc.

where b and C_i are Langmuir constant and initial arsenic ion concentration, respectively.

In order to investigate whether the sorption process is of chemical or physical nature, value of mean sorption energy, E, is calculated from D–R isotherm linear form of which is given by Eqs. (10)–(12):

$$\ln q_e = \ln X_m - \beta\varepsilon^2 \tag{10}$$

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \tag{11}$$

$$E = \frac{1}{\sqrt{-2\beta}} \tag{12}$$

where R is general gas constant, T (K) is absolute temperature, q_e (mg g^{-1}) is the amount of arsenic sorbed by HEC-Suc and C_e (mg L^{-1}) is the concentration at equilibrium. The values of constant β (kJ^2 mol^{-2}) and X_m (mmol g^{-1}) were obtained from slope and intercept of the plot between lnq_e against ε^2 (Fig. 9(c), Table 1). Straight lines with high value of R^2 obtained show validity of this model. Value of mean sorption energy, E (kJ mol^{-1}), calculated from value of β were between 8 and 16 kJ mol^{-1} for both As(III) and As(V) which indicate arsenic uptake occur through chemisorption.

Temkin isotherm considers that heat of adsorption of all the molecules in the layer decreases linearly with surface coverage due to sorbate–sorbate interactions and is given by relation Eq. (13):

$$q_e = B\ln A + B\ln C_e \tag{13}$$

where $B = RT/b_T$, where T (K) is the temperature and R is the ideal gas constant R. b_T is the constant related to heat of sorption and A is the equilibrium binding constant (L min^{-1}) corresponding to the maximum binding energy. Values of b_T and A are calculated from slope and intercept of straight line obtained from plot between q_e and lnC_e (Fig. 9(d), Table 1).

3.2.8. Thermodynamic parameters determination

Thermodynamic parameters such as entropy change ($\Delta S°$), enthalpy change ($\Delta H°$) and Gibbs free energy change ($\Delta G°$) are used to predict exothermic or endothermic, spontaneity and feasibility of sorption process and are calculated from Eqs. (14)–(16):

$$K_c = \frac{C_{\text{ads}}}{C_e} \tag{14}$$

$$\Delta G° = -RT\ln K_c \tag{15}$$

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{16}$$

where K_c is the sorption equilibrium constant, C_{ads} is the amount of arsenic sorbed and C_e is the equilibrium concentration of arsenic ion. The data obtained from effect of temperature on sorption capacity are used to determine thermodynamic parameters. Value of $\Delta S°$ and $\Delta H°$ was obtained from slope and intercept of straight line obtained by plotting lnK_c vs. 1/T, respectively (Fig. 10, Table 1). Negative

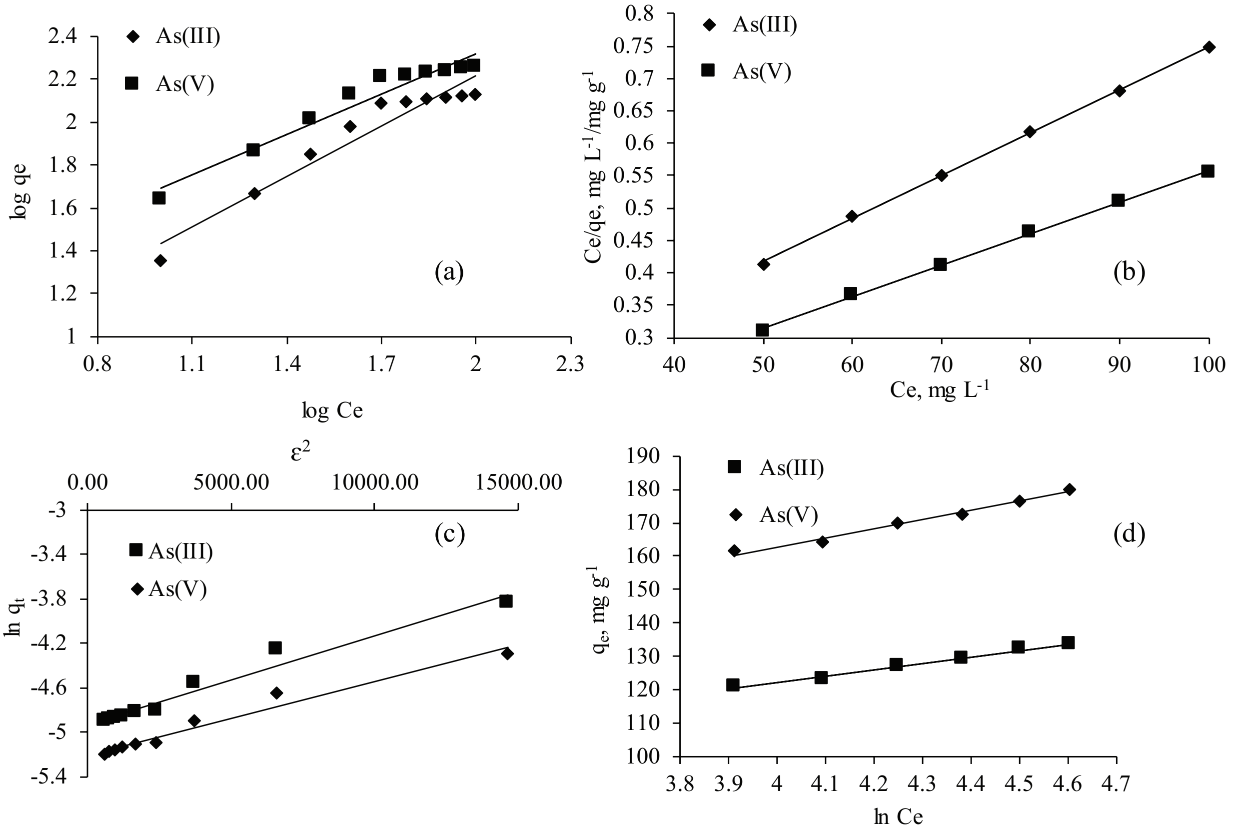

Fig. 9. Freundlich sorption isotherm (a), Langmuir sorption isotherm (b), D–R (c) and Temkin isotherm models for removal of As(III) and As(V) from aqueous solution using HEC-Suc.

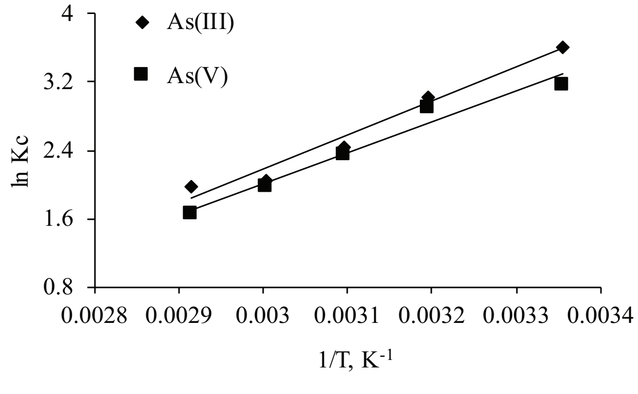

Fig. 10. Effect of temperature on equilibrium constant for removal of As(III) and As(V) from aqueous solution using HEC-Suc.

values of all the three parameters ΔG°, ΔH° and ΔS° indicate spontaneity, feasibility, exothermic nature of sorption process and decrease in randomness at sorbate–sorbent interface, respectively.

3.2.9. Desorption

To make the wastewater treatment process more economical, recovery of the sorbed material and regeneration of the sorbent are important parameters. Successive sorption and regeneration studies were carried out to test the stability and suitability of the sorbent. Sorption conditions maintained during sorption–desorption studies are sorbent dosage of 40 mg/100 mL for As(III) and 30 mg/100 mL for As(V), arsenate and arsenite concentration = 50 mg L^{-1}, temperature = 298 K, pH was kept at 7.0 for As(III) and at 4.0 for As(V). While desorption studies were carried out by stirring 40 mg of As(III)-loaded HEC-Suc in 100 mL of 0.1 M NaOH solution and 30 mg of As(V)-loaded sorbent in 100 mL of 0.1 M NaOH solution for a contact time of 8 h at a temperature of 298 K. The reason for desorption in 0.1 M NaOH can be clearly evidenced from the pH plot for sorption of arsenic by HEC-Suc. Both As(III) and As(V) show least sorption capacity at alkaline pH (pH of 0.1 M NaOH solution). The results are consistent with those observed for effect of pH on arsenic uptake by the sorbent. These sorption–regeneration studies were carried out over five cycles. Decrease in sorption capacity of HEC-Suc after five cycles was not significant for both As(III) (14.2 mg g^{-1}) and As(V) (13.7 mg g^{-1}) suggesting the reusability of the sorbent (Figs. 11 and 12).

Table 2 shows efficiency of HEC-Suc for As(III) and As(V) removal as compared with other sorbents already used for the arsenic removal. Highest value of HEC-Suc for arsenic removal as compared with other sorbents showed that HEC-Suc appeared a super-sorbent and can be a better option for arsenic removal from arsenic contaminated water.

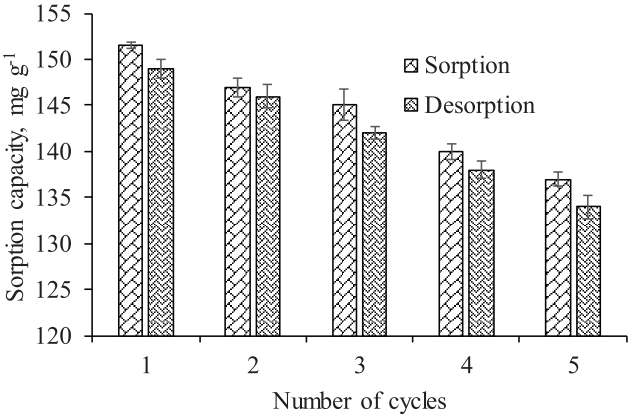

Fig. 11. Adsorption–desorption values for As(III) ions by HEC-Suc from aqueous solution (sorption conditions: sorbent dosage = 40 mg/100 mL for As(III) and 30 mg/100 mL for As(V), arsenate and arsenite concentration = 50 mg L^{-1}, temperature = 298 K, pH = 7.0 for As(III) and at 4.0 for As(V). Desorption conditions: 40 mg As(III)-loaded HEC-Suc/100 mL of 0.1 M NaOH solution contact time = 8 h at a temperature = 298 K).

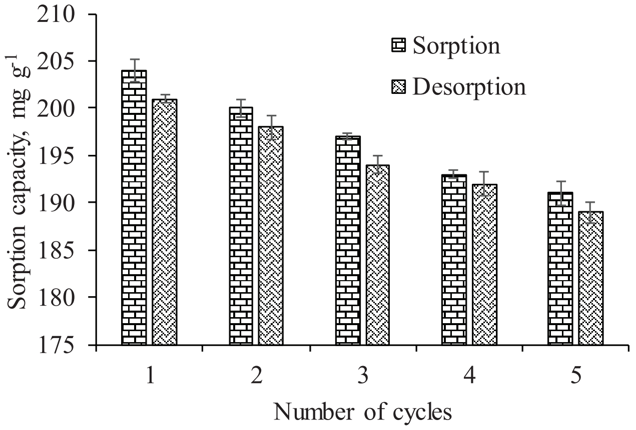

Fig. 12. Adsorption–desorption values for As(V) ions by HEC-Suc from aqueous solution (sorption conditions: sorbent dosage = 40 mg/100 mL for As(III) and 30 mg/100 mL for As(V), arsenate and arsenite concentration = 50 mg L^{-1}, temperature = 298 K, pH = 7.0 for As(III) and at 4.0 for As(V). Desorption conditions: 30 mg As(V)-loaded HEC-Suc/100 mL of 0.1 M NaOH solution contact time = 8 h at a temperature = 298 K).

Table 2
Comparison of sorption capacities of the HEC-Suc with other sorbents for the removal of As(III) and As(V) from aqueous solution

Adsorbent	pH	Initial concentration range	Sorption capacity (mg g^{-1})		Reference
			As(III)	As(V)	
Copper-impregnated coconut husk carbon	6.5		20.35	–	[18]
Coconut husk carbon	12.0	50–600 mg/L	146.30	–	[18]
Rice polish	7.0 for As(III) 4.0 for As(V)	100–1,000 μg/L	0.14	0.15	[15]
Iron-modified activated carbon	7.7–8.0		38.8	51.3	[19]
Fresh biomass	6.0	50–2,500 mg/L	128.1	–	[20]
Immobilized biomass	6.0	50–2,500 mg/L	704.11	–	[20]
Tea fungal biomass	7.20	1.3 for As(III) and 0.9 mg/L for As(V)	1.11	4.94	[21]
Penicillium purpurogenum	5.0	10–750 mg/L	35.6	–	[22]
Orange juice residue	7–11 for As(III) 2–6 for As(V)	–	70.43	67.43	[23]
Phosphorylated orange waste	2–6	–	68.18	68.18	[24]
Orange juice waste	2–6	–	–	70.43	[25]
Molybdate-impregnated chitosan gel beads	–	–	–	200	[26]
Lessonia nigrescens		50–600 mg/L	–	45.2	[27]
Iron oxyhydroxide loaded cellulose beads	7.0	1–100 mmol/L	99.7	33.2	[28]
N-methylglucamine modified cellulose	2.4–4.5	–	–	95%	[29]
Biochar-supported zerovalent iron	–	–	–	23%–95%	[30]
Hydroxyethylcellulose succinate (HEC-Suc)	7.0 for As(III) 4.0 for As(V)	10–100 mg/L	151.5	204.10	Present study

4. Conclusions

Novel material HEC-Suc was found to be super-sorbent for the removal of both As(III) and As(V). Fitting of data to D–R (values of *E* between 8 and 16 kJ mol^{-1}) and Elovich models suggested that removal of arsenic species took place through chemisorption. Fitting of intraparticle diffusion and pseudo-second order kinetic model suggested that rate determining step was diffusion of sorbate species along with chemisorption. Monolayer formation on heterogeneous surface was concluded by fitting of data to Langmuir and

Freundlich isotherm. Negative values of thermodynamic parameters were an evidence of feasible, spontaneous and exothermic nature of sorption process. Removal of As(III) and As(V) was found to be highly pH dependent. NaOH (0.1 M) was found to be capable of regenerating the sorbent with negligible decrease in sorption capacity.

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