Sequential adsorptive removal of phosphate, nitrate and chromate from polluted water using active carbon derived from stems of *Carissa carandas* plant

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Abstract

Sulphuric acid-generated active carbon from stems of *Carissa carandas* plant is investigated successfully as an adsorbent for the sequential removal of phosphate, nitrate and chromate from polluted water. Controlling parameters are investigated and optimized for the maximum removal of the pollutants. At pH: 7, phosphate and nitrate can be simultaneously removed, while at pH: 2, chromate can be sequentially removed from the admixtures of the three pollutants. The active carbon is characterized using Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX). Sorption mechanisms are investigated using various adsorption isotherms and kinetic models. Thermodynamics parameters are evaluated. The data reveal the Langmuir isotherm model of adsorption, pseudo-second-order kinetics and spontaneity of sorption processes. Langmuir individual maximum adsorption capacity is: 72.75 mg/g for chromate; 63.40 mg/g for phosphate; and 49.15 mg/g for nitrate. The active carbon can be regenerated and reused. The method is used for the removal of all three pollutant ions from polluted water. The merit of this investigation is that an active carbon is identified with good adsorption capacities for the successful sequential removal of phosphate, nitrate and chromate ions from polluted water.

Key words: activated carbon, *Carissa carandas* plant, chromate, nitrate, phosphate, water remediation

Highlights

- An active carbon is synthesized from stems of *Carissa carandas* plant.
- Sequential separation of Cr(VI), PO_4^{3-} and NO_3^- from polluted water is effected.
- Simultaneous quantitative separation of nitrate and phosphate is possible at pH: 7.
- Data reveal Langmuir model, pseudo-second-order and spontaneity of sorption process.
- Adsorption capacities are high in comparison with reported values in literature.

Graphical Abstract
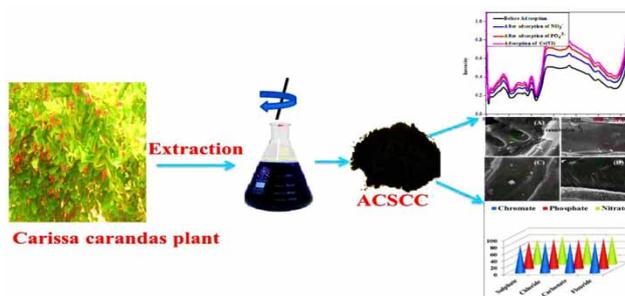
INTRODUCTION

Toxic chemicals discharging into aqueous systems can pose a significant risk to public health and the environment. For instance, heavy metal ions, inorganic phosphorus (P) and nitrogen (N) containing ions that are released due to human activities are hazardous for human survival. The contamination of water bodies with phosphorus and nitrogen containing ions causes the unwanted phenomenon of 'eutrophication', which degrades fresh water and imposes great risk to the ecological systems (Howarth & Marino 2006; Zhang & Gao 2013). Due to increasing water pollution in the past few decades, more attention has been paid to water treatment (Debnath et al. 2016).

The toxicity of chromate, phosphate and nitrate is well known and they are common contaminants in water bodies. The ill- or un-treated discharges from chrome-based industries are the important source of chromate pollution (Bhowmik et al. 2017). Chromate contamination in water causes kidney, skin, liver and ulceration problems in human beings due to its carcinogenicity, teratogenicity and mutagenicity (Karthikeyan et al. 2005; Bhowmik et al. 2017). Nitrate in water originated due to the complete oxidation of nitrogenous matter of organic pollutants and also from agricultural wastes. It causes a dread ailment: *Methamoglobinemia or blue babies* when the concentration of nitrate is more than 50 ppm. Natural weathering of phosphate rocks, agricultural fertilizer wastes and domestic sewages are the important sources of phosphate contamination in water bodies. Nitrate and phosphate cause eutrophication in natural water bodies and thereby decrease the dissolved oxygen (DO) content in water. This results in stress on eco-systems and aquatic life (Zhang & Gao 2013; Rajeswari et al. 2015; Zolgharnein et al. 2017; Zong et al. 2018; Wang et al. 2019). The permissible limits as per WHO are 0.05 mg/L for Cr(VI) (US 1991); 50 ppm for nitrates (Shen et al. 2019), and 50 µg/L for phosphate respectively (Sereshti et al. 2020).

Various methods such as adsorption, ion exchange, membrane separation, electrochemical precipitation, chemical precipitation and photo-reduction are employed for the removal of these ions individually (Bhowmik et al. 2017). Of all these, methods based on 'adsorptive removal' using sorbents derived from the plant materials is interesting the researchers. These methods are simple, effective, and economical (Debnath et al. 2016) and based on abundantly available renewable biosources (Babu et al. 2016; Ravulapalli & Kunta R 2018). The investigations for simultaneous or successive removal of these pollutants using active carbons are few and far between.

In the present investigation, **A**ctive **C**arbon derived from **S**tems of *Carissa Carandas* plant (**ACSCC**) is identified and investigated as an effective adsorbent for the simultaneous and/or successive removal of chromate, nitrate and phosphate from polluted water.

The adsorbents developed are found to be successful in removing nitrate and phosphate simultaneously at pH: 7 and, further, the same active carbon is effective in removing chromate at pH: 2. The present study is a comprehensive investigation of the nature of its sorption by varying various physicochemical parameters, surface morphological studies, adsorption isotherms, kinetics of adsorption and thermodynamic studies. The adsorbent is effectively used for the treatment of polluted lake water samples collected from different sources in Tenali Mandal of Guntur District of Andhra Pradesh, India, and samples collected from effluents of tannery industries in Ethiopia.

MATERIALS AND METHODS

Reagents and chemicals

A.R. grade $K_2Cr_2O_7$, $NaNO_3$ and KH_2PO_4 were purchased from Merck India Pvt. Ltd. Other chemicals were purchased from S.D. Chemicals, India. The solutions were prepared using double-distilled water throughout this research work.

Active carbon generation

Plant

Carissa carandas plant (Figure 1) belongs to the *Apocynaceae* family of the plant kingdom, is grown well in all kinds of soils and is a kind of tolerant drought plant. During the rainy season, it yields fruits that are rich in iron and vitamin C. The fruits are used in making pickles in India. Its stems have thorns. The bio-parts of this plant are used in the preparation of herbal medicines in India.

Figure 1 | *Carissa carandas* plant showing affinity for phosphate, nitrate and chromate.

Active carbon

Stems of *Carissa carandas* plant were cut, washed with deionized water and were dried for two days under sunlight. Stems were immersed in Conc.H_2SO_4 for one day. Then the material was digested in a round bottomed flask with condenser set-up for 2.0 hours until all the material was completely carbonized. Thus generated carbon was filtered, washed with double distilled water to neutrality and dried in an oven at 110 °C for 6 h. The carbon was pulverized and sieved to a particle size less than 75 μm using ASTM meshes. This active carbon was named as: **ACSCC** (**A**ctivated **C**arbon derived from **S**tems of *Carissa Carandas* plant).

Extraction experiments

All chemicals used were of analytical grade. Simulated solutions containing chromate, nitrate, or phosphate and their mixtures were prepared using distilled water. Batch modes of adsorption studies were adopted (Trivedy 1995; Babu *et al.* 2018). Initially, optimum conditions of extractions were established by taking simulated solutions containing only the individual ions. After establishing the conditions, the method was applied to the combinations of synthetic simulated solutions: 'nitrate and phosphate' and 'chromate + nitrate + phosphate'.

Establishment of optimum extraction conditions

For individual ions: Known amounts of chromate, nitrate and phosphate were taken into 250 mL conical flasks and initial pHs were adjusted with diluted HCl or NaOH. The flasks were agitated in an orbital shaker for the desired period at 300 rpm and at temperature of 300 ± 1 °C. After the required periods of equilibration, the solutions were filtered and the filtrates were analysed using spectrophotometric methods as described in the literature (APHA 1985): chromate by diphenylcarbazide method; nitrate by sulphanilamide method; and phosphate by molybdenum blue method. Percentage removals of chromate, NO_3^- and PO_4^{3-} and adsorption capacities of **ACSCC** (q_e) for the said anions

were evaluated by using equations (Krishna *et al.* 2017; Biftu *et al.* 2020).

$$\%\text{removal} = \frac{(C_0 - C_e)}{C_0} \times 100$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V$$

where C_0 and Ce are the initial and final concentrations (mg/L); m = mass of adsorbent (g); V = volume of the solution (L) of chromate, NO_3^- and PO_4^{3-}.

The effect of pH, **ACSCC** dosage, time of contact between **ACSCC** and adsorbates, initial concentration of adsorbate, effect of interfering ions and temperature, on the adsorptivities of **ACSCC** for chromate, NO_3^- and PO_4^{3-}-ions, were investigated adopting the above described batch method. In assessing **ACSCC** adsorptivities for ions, the targeted parameter was gradually varied while all other experimental conditions were kept at optimum levels. The results are presented in the Results and discussion section (Figure 5).

Analysis of mixtures of ions

As is revealed from the results for individual ions (Results and discussion section), at pH: 7, nitrate and phosphate were removed while at pH: 2.0, chromate was removed with the **ACSCC** as an adsorbent. So in this investigation, the simulated mixed solutions of: nitrate + phosphate and chromate + nitrate+ phosphate of different concentrations were treated with the **ACSCC**. In the case of nitrate + phosphate, the extraction studies were made at pH: 7. In the case of chromate + nitrate+ phosphate, in the first instance, nitrate and phosphate, were simultaneously removed and the filtrate obtained was subjected to the removal chromate at pH: 2.

For assessing whether the optimum conditions established for individual ions also hold good for the mixtures, investigations were made with the said mixtures of ions at the optimum conditions established with the individual ions. The results show that the adsorbent dosage is to be increased to 0.25 g/100 mL and time of equilibration to 50 minutes for the simultaneous removal of phosphate + nitrate. For sequential removal of chromate, the conditions remain the same as that of individual chromate ions removal. Except for these minor changes in the parameters, the other extraction conditions are the same for individual ions as well as for the mixtures. The conditions of extractions and results of the adsorptive investigations for the removal of toxic nitrate, phosphate and chromate are presented in Tables 2 and 3.

Characterization of ACSCC

The active carbon was subjected to Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX) investigations to assess the adsorptivities of the ions onto the adsorbent. For this, the spectrum or images of **ACSCC** were noted before and after adsorption of chromate, nitrate and phosphate. The results are presented in Figures (2)–(4).

Applications

The active carbon developed was applied to treat lake waters and effluents from leather industries polluted with phosphate, nitrate and chromate. Lake water samples were collected from Tenali Mandal of Guntur District of Andhra Pradesh, India, where pollution of nitrate and phosphate in water bodies was reported due to intensive agricultural activities and over-utilization of fertilizers. Further, the samples from the effluents of Ethiopia Tannery Companies at Kombolcha City, located in the north part of Ethiopia, were collected as they were causing chromate and nitrate pollution to the water of the Leyole and Worka rivers.

The samples were analysed for the existing concentrations of nitrate, phosphate and chromate. The samples from Tenali Mandal of Guntur District Lakes had nitrate and phosphate while the samples from the effluents of tannery industries in Ethiopia contained nitrate and chromate. Then these samples were subjected to treatment with the procedures developed in this work. The results are presented in Table 7.

RESULT AND DISCUSSION

Characterization studies

Physicochemical parameters

Various physicochemical parameters for **ACSCC** were assessed adopting standard procedures described elsewhere. Particle size, iodine number, apparent density, moisture contents, ash content and Brunauer-Emmett-Teller (BET) surface areas, before and after adsorption of adsorbates, were determined and are presented in Table 1.

Table 1 | Physicochemical properties of adsorbent, ACSCC

S. no.	Parameter	Value	Reference
1	Apparent density (g/mL)	0.35	Namasivayam & Kadirvelu (1994)
2	Moisture content	(%) 6.18	Bureau of Indian Standards (1989)
3	Iodine number	(mg/g) 641	ASTM D(4607)-94 (2006)
4	Ash content	(%) 3.67	Bureau of Indian Standards (1989)
5	Particle size	(μ) 32	El-Hendawy et al. (2001)
6	BET analysis Surface area (m²/g)	Before adsorption: 362.6 After adsorption of: • chromate: 187.3; • phosphate: 202.5 • nitrate: 215.8	Brunauer et al. (1938)

Table 2 | Sequential removal of nitrate, phosphate chromate ions

Sample number	Concentration, mg/L $Cr(VI) + PO_4^{3-} + NO_3^-$			After adsorption mg/L			%Removal			Adsorbent capacity (mg/g)		
	PO_4^{3-}	NO_3^-	Cr(VI)	PO_4^{3-}	NO_3^-	Cr(VI)	PO_4^{3-}	NO_3^-	Cr(VI)	PO_4^{3-}	NO_3^-	Cr(VI)
Sample1	5.0	30.0	5.0	0	3.06	0	100	89.8	100	2.0	10.78	5.0
Sample2	10.0	40.0	7.5	0.86	5.32	0	91.4	86.7	100	3.66	13.87	7.5
Sample3	15.0	50.0	10.0	1.38	8.5	0	90.8	83.0	100	5.45	16.6	10.0
Sample4	20.0	60.0	12.5	2.14	11.16	0.235	89.3	81.4	98.2	7.14	19.54	12.28
Sample5	25.0	70.0	15.0	2.78	13.86	0.525	88.9	80.2	96.5	8.89	22.46	14.48

(Optimum conditions for extraction: pH:7 for phosphates and nitrate and pH: 2 for chromate; adsorbent dosage: 0.25 g/100 mL for removing nitrate + phosphate and 0.10 g/100 mL for chromate; time of equilibration: 50 min – for phosphate and nitrate and 40 min – for chromate); rpm: 300; Temp. 30 ± 1 °C.

FTIR analysis

The FTIR spectra of **ACSCC** – before and after adsorption of chromate, phosphate and nitrate are presented in Figure 2. The following salient features may be inferred. The absorption band observed

Table 3 | Simultaneous removal of phosphate and nitrate ions

Sample number	Concentration, mg/L $PO_4^{3-} + NO_3^-$		After adsorption		%Removal		Adsorbent capacity (mg/g)	
	PO_4^{3-}	NO_3^-	PO_4^{3-}	NO_3^-	PO_4^{3-}	NO_3^-	PO_4^{3-}	NO_3^-
Sample1	5.0	30.0	0	2.94	100	90.2	2.0	10.82
Sample2	10.0	40.0	0.84	5.56	91.6	86.1	3.66	13.78
Sample3	15.0	50.0	1.47	8.30	90.2	83.4	5.41	16.68
Sample4	20.0	60.0	2.04	10.86	89.8	81.9	7.18	19.66
Sample5	25.0	70.0	2.83	13.30	88.7	81.0	8.87	22.68

(Optimum conditions for extraction: pH:7; adsorbent dosage: 0.25 g/100 mL; time of equilibration: 50 min; rpm: 300; Temp. 30 $\pm$ 1 °C.)
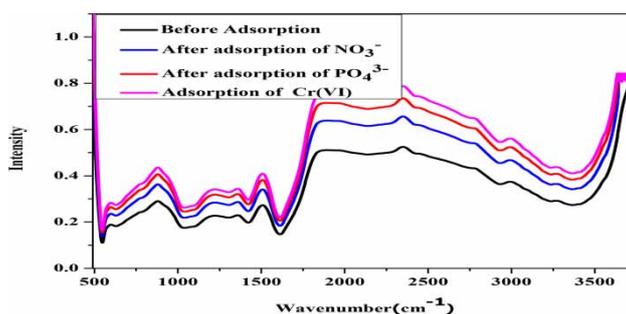
Figure 2 | FTIR spectra of before and after adsorption of chromate, NO_3^- and PO_4^{3-} ions.

at ~3,355 cm^{-1} in the spectrum of **ACSCC** pertains to the stretching vibrations of '–OH' group. This frequency is shifted to 3,358 cm^{-1}, 3,361 cm^{-1} and 3,370 cm^{-1} after adsorption of NO_3^-, PO_4^{3-} and chromate respectively. Further, there is a change in the intensities and broadness of bands between before and after adsorption of the said adsorbates. The frequency at 2,908 cm^{-1} for **ACSCC** is due to stretching of C-H groups. It is shifted to 2,913 cm^{-1}, 2,915.3 cm^{-1} and 2,920.2 cm^{-1} after the adsorption of nitrates, phosphate and chromate respectively. The frequency at 1,615 cm^{-1} for **ACSCC** may be due to C=C or C=O. It is shifted to 1,621 cm^{-1}, 1,625 cm^{-1} and 1,630 cm^{-1}, after adsorption of NO_3^-, PO_4^{3-} and chromate respectively. The weak band at 1,418 cm^{-1} attributes to =C-H- bending vibrations before adsorption, and is shifted to 1,421 cm^{-1}, 1,425 cm^{-1} and 1,430 cm^{-1} after adsorption of nitrate, phosphate and chromate respectively.

The sharp absorption band at 1,035 cm^{-1} (before adsorption) is due to C-O-C stretching vibrations and it is shifted to 1,040 cm^{-1}, 1,042 and 1,045 cm^{-1} after adsorption of NO_3^-, PO_4^{3-} and chromate respectively. The weak absorption band of C-S at 625 cm^{-1} before adsorption is shifting to 628 cm^{-1}, 630 cm^{-1} and 633 cm^{-1} after adsorption for NO_3^-, PO_4^{3-} and chromate respectively. The sulphur-related frequency is expected because the active carbon is generated in this work via Conc. H$_2$SO$_4$ treatment method. The changes in the peak positions and intensities indicate that there are interactions between nitrate, phosphate and chromate with the functional groups of **ACSCC**, namely –CO and –OH.

FESEM spectral analysis

FESEM of **ACSCC** before and after adsorption of chromate, NO_3^- and PO_4^{3-} were noted and presented in Figure 3(a)–3(d). The FESEM images of **ACSCC** show pores, cavities and rough surface. But the images pertaining to after adsorption have shown marked deviations. After adsorption of the adsorbates, the pores, cavities and roughness have disappeared to a major extent. It may be
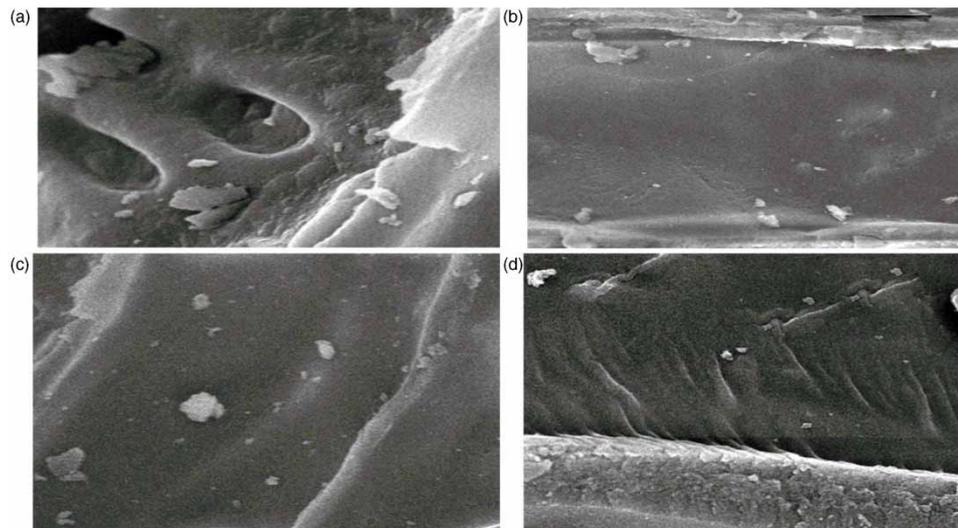
Figure 3 | SEM images: (a) before adsorption-**ACSCC**; (b) after adsorption of chromate ions; (c) after adsorption of PO_4^{3-} ions; and (d) after adsorption of NO_3^- ions.

seen that the SEM images of chromate and phosphate–adsorption have less roughness than the SEM image of nitrate adsorption. Therefore, from FESEM analysis, it can be confirmed the adsorption of nitrate, phosphate and chromate onto the surface of **ACSCC.**

EDX spectral analysis

The EDX spectra of **ACSCC** before and after adsorption of chromate, phosphate and nitrate are presented in Figure 4(a)–4(d). It can be seen that an additional peak pertaining to Cr, P, and N are noticed in the EDX spectra taken after adsorption of chromate, phosphate and nitrate respectively. Figure 4(b)–4(d). These peaks are missing in the EDX spectra taken before adsorption Figure 4(a). This reflects that chromate, phosphate and nitrate are successfully adsorbed onto the surface of **ACSCC**.

Factors influencing the adsorptivity

Effect of pH

The pH of the extracting solution has a marked effect on the adsorptivity of **ACSCC** for chromate, phosphate and nitrate. By varying the pH from 2.0 to 12.0 but keeping all other parameters at constant values, the adsorptivities of **ACSCC** for chromate, phosphate and nitrates were investigated. The results are plotted as 'pH vs. % removal' of chromate, PO_4^{3-} and NO_3^- ions in Figure 5(a).

It may be inferred that as the pH is increased, the % removal is also increased for phosphate and nitrate up to pH: 7, and then onwards the % removal is decreased. The maximum % removal is found to be 91.4% for phosphate and 87.5% for nitrate at the optimum pH:7. In the case of chromate, the maximum % removal noted is: 94.2% at pH: 2, and then onwards the % removal of chromates is decreased with the rise in pH. Thus, at neutral pH, the phosphate and nitrate show maximum removal while, at low pHs, the chromates show good adsorptivity. This is a noteworthy observation because it paves the way for simultaneous and sequential removal of the said ions. At the neutral pH: 7, the simultaneous removal of nitrate and phosphate is possible from water containing the admixtures of said ions. Further, sequential removal of nitrate, phosphate and chromate is possible from the solution containing all three ions by using the said active carbon: first removing the nitrate and phosphate at pH: 7 and then removing chromate at pH: 2.
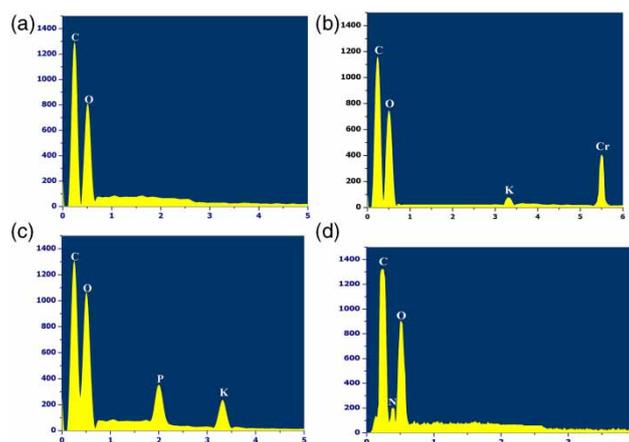
Figure 4 | EDX spectra of **ACSCC**: (a) before adsorption; and (b), (c) and (d) after adsorption of chromate, PO_4^{3-} and NO_3^- respectively.

pHpzc value for **ACSCC** is: 6.7 and so, at this pH value, the surface of the adsorbent is neutral and above this value the surface acquires a negative charge due to dissociation of functional groups and, below this pHpzc, the surface acquires a positive charge due to protonation (Figure 5(b)). Chromate being an anion shows good adsorption at low pHs that it is maximum at pH: 2. This may be attributed to the strong electrostatic interactions between the positively charged surface of the adsorbent and negatively charged chromate ions (Biftu & Ravindhranath 2020). But in the case of phosphate and nitrate, the maximum adsorption is found to be in the neutral pHs. At neutral conditions, the surface of the adsorbent is neutral and hence it cannot exercise electrostatic interactions with the negatively charged phosphate ($H_2PO_4^-$ and HPO_4^{2-}) and nitrate (NO_3^-). Hence, the adsorption of nitrate and phosphate at neutral conditions cannot be due to electrostatic interactions. It may be due to a sort of complex formation between the adsorbates and the functional groups of the adsorbent.

Effect of sorbent concentration

The effect of **ACSCC** dosage on the adsorptivity of chromate, phosphate and nitrate was investigated by changing the dosage from 0.07 to 0.15 g/100 mL while maintaining other extraction conditions at constant levels. The results are plotted as 'Dosage vs.% removal', Figure 5(c). It is seen from the figure that the adsorption of chromate, phosphate and nitrate is progressively increased linearly with the increase in the dosage of the adsorbent initially, but it slows down with further increase in the dosage and reaches a steady state at a certain dosage of the adsorbent. The maximum extraction of chromate, phosphate and nitrate for the minimum dosage of adsorbent is found to be: 94.2% with 0.1 g/100 mL for chromate, 91.4% with 0.11 g/100 mL for phosphate and 87.5% with 0.13 g/ 100 mL for nitrate. With the increase in the dosage of the adsorbent, naturally the number of adsorption sites available increases and hence, more adsorption is observed initially. But when the adsorbent is further increased, a proportional increase in adsorption is not observed to that of the initial stages. This may be due to the blocking of pathways for adsorbates to reach the active sites laid in the matrix of the adsorbent due to aggregation and/or deposition (Biftu & Ravindhranath 2020).

Effect of time

The influence of agitation time on the adsorption of Cr(VI), PO_4^{3-} and NO_3^- was investigated by varying the time from 5 to 60 min while keeping the other extractions conditions at the optimum levels. The plots of % removal of Cr(VI), PO_4^{3-} and NO_3^- vs. contact time are shown in Figure 5(d). The adsorption process is rapid initially and is slow down with the progress of time and attained steady
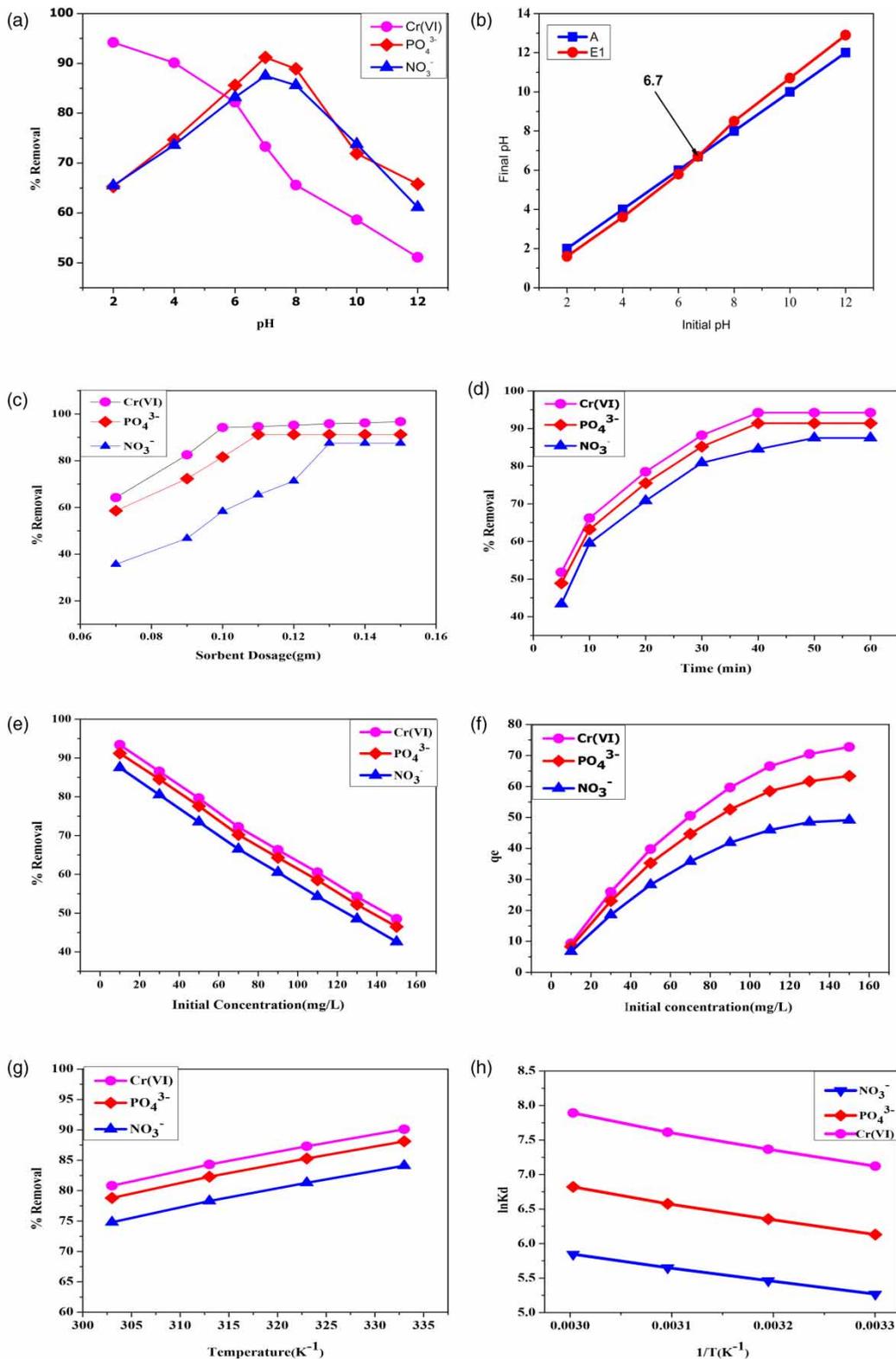
Figure 5 | (a) Effect of pH; (b) evaluation of pHpzc; (c) effect of dosage; (d) effect of contact time; (e) effect of initial concentrations; (f) adsorption capacities, q_e vs. initial concentration and (g, h) effect of temperature.

state after 40 min for chromate and phosphate and 50 min for nitrate. At these steady state times of equilibration, the % removal is: 94.2% for Cr(VI); 91.4% for PO_4^{3-} and 87.5% for NO_3^-. The greater adsorption of Cr(VI), PO_4^{3-} and NO_3^- for a fixed amount of the adsorbent is due to the availability

of more sites initially. But with increase in the time, active sites are progressively used up or blocked by the adsorbed Cr(VI), PO_4^{3-} and NO_3^- and hence the rate of adsorption decreases. When all the sites available are engaged with the adsorption of adsorbates, steady states result.

Effect of initial concentration

Initial concentration of analyte is another parameter that influences the adsorption process. Therefore, the effect of different concentrations of Cr(VI), PO_4^{3-} and NO_3^- on the adsorption performance of **ACSCC** was studied. The results are depicted in Figure 5(e) and 5(f). With the increase of concentrations from 10 to 150 mg/L, % removal decreased from 94.2% to 48.5% for Cr(VI), 91.4% to 46.5% for PO_4^{3-} and 87.5 to 42.6% for NO_3^- (Figure 5(e)). As the sorbent dosage is fixed (0.1 g/100 mL for chromate, 0.11 g/100 mL for phosphate, and 0.13 g/100 mL for nitrate), only a fixed number of active sites are available. So, as the concentration of adsorbate is increased, the number of available active sites per ion is decreased and hence % removal falls. But the adsorption capacity (q_e) is increasing with the increase in concentration of adsorbate (Figure 5(f)). As the concentration is increased from 10 to 150 mg/L, the values of q_e are increased from 9.34 to 72.75 mg/g for Cr(VI), 8.29 to 63.40 for PO_4^{3-} and 6.73 to 49.15 mg/g for NO_3^-. With the rise in concentrations, the concentration gradient between the bulk of the solution and surface of the adsorbent is also increased. This causes the adsorbates to diffuse more towards the adsorbent surface and thereby resulting in greater adsorptivities.

Effect of temperature

The effect of solution temperature on the adsorptivities of **ACSCC** for chromate, phosphate and nitrate was investigated. The findings are noted in Figure 5(g) and 5(h). Adsorptivity is increased with increase in temperature. Increase in solution temperature enhances the vibrational kinetic energy of the functional groups present on the surface of **ACSCC** and thereby decreases the surface-layer thickness. Further, the adsorbate ions acquire more kinetic energy. These two factors help in the penetration of adsorbate deeper into the **ACSCC** and hence more adsorptivity with increase in temperature.

Simultaneous and sequential removal of chromate, phosphate and nitrate

From the Factors influencing the adsorptivity section, it may be inferred that the phosphate and nitrate are extracted to an extent of 91.4% and 87.5% at pH: 7 from the 10 mg/L concentration of the adsorbates at the optimum conditions: equilibration time: 40 min for phosphate and 50 min for nitrate; dosage of **ACSCC**: 0.11 g/100 mL for phosphate and 0.13 g/100 mL for nitrate; rpm: 300; and temperature: 30 ± 1 °C. At pH: 2, 94.2% of chromate can be extracted from chromate solution of concentration: 10 mg/L with 0.1 g/100 mL of **ACSCC** after an equilibration time of 40 min, rpm: 300 and temperature: 30 ± 1 °C. Thus, at pH:7, the simultaneous removal of phosphate and nitrate is possible while at pH: 2, chromate removal is possible. This led to the concept of simultaneously removing the nitrate and phosphate and then sequentially the chromate from the admixtures of said ions. Hence, in this investigation these concepts were investigated.

Different proportions of nitrate and phosphate, as are noted in Tables 2 and 3, were mixed to prepare simulated solutions. These solutions were treated with **ACSCC** at pH: 7. The results were noted in Tables 2 and 3. Similarly, mixed solutions containing different proportions of phosphate, nitrate and chromate were prepared as presented in Tables 2 and 3 and were first subjected to the treatment with **ACSCC** at pH:7 for removing phosphate and nitrate. After removing phosphate and nitrate, the filtrate obtained was treated with **ACSCC** at pH: 2 to remove chromate. The experiments were

repeated five times. The said simultaneous removal of nitrate and phosphate and sequential removal of nitrate, phosphate and chromate from waste water are novel findings of this investigation.

Co- ions interference

The effects of the twofold excess of co-ions naturally found in water on % removal of nitrate, phosphate and chromate were investigated. Results are presented in Figure 6. From the data, it may be inferred that the cations; namely, Mg^{2+}, Ca^{2+}, Fe^{2+}, and Zn^{2+} and anions Cl^-, CO_3^{2-}, and F^- are least interfered. Sulphate has shown some interference. Percentage removals of chromate, phosphate and nitrate in the presence of the said interference anions ions were found to be respectively 81.5, 78.6 and 75.1 for sulphate; 91.0, 88.2 and 84.8 for chloride; 89.1, 86.3 and 82.6 for carbonate; and 92.2, 89.8 and 86.0 for fluoride. Anions being negative in charge will compete with the adsorbate ions (phosphate, nitrate and chromate) for active sites on the active carbon and the extent of interference depends on various factors such as size, charge, polarizability, electro negativity differences of the adsorbates etc. (Onyango et al. 2004). Further, the presence of anions in solution will also enhance columbic repulsion forces between the anions (Onyango et al. 2004). The net result is manifested in the % removal.
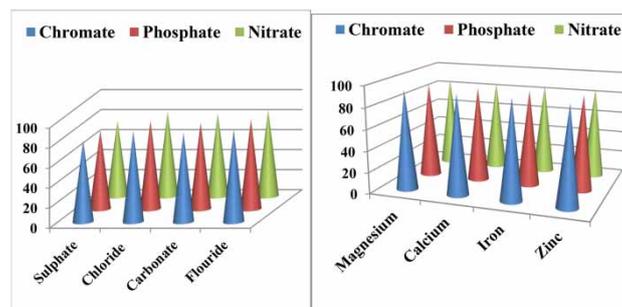

Figure 6 | Effect of Interfering co-anions and co-cations on % removal of chromate, phosphate and nitrate ions.

Thermodynamic studies

The sign and magnitude of thermodynamic properties namely, Gibbs free energy, entropy, and enthalpy provide insight into the strength and type of bonds between adsorbate and adsorbent. These factors are evaluated using the following equations.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -RT \ln Kd$$

$$\ln Kd = \Delta S/R - \Delta H/RT$$

where q_e = adsorbed quantity of adsorbate onto the adsorbent surface, Ce = adsorbate concentration at equilibrium in mg/L, R = gas constant, K_d = distribution coefficient and T = thermodynamic temperature (Alam et al. 2005; Jin et al. 2017). The results are presented in Table 4.

Negative ΔG values reflect the spontaneity and endothermic nature of the adsorption process. The negative values are increasing as the temperature increases. This indicates more favourable conditions of adsorption at elevated temperatures. Change in enthalpy (ΔH) values indicates strong binding between the adsorbate and the functional groups of the sorbent, **ACSCC**. Positive ΔS values and their magnitudes are the testimony of disorder at the 'solid/liquid' interface. As the disorder is

Table 4 | Thermodynamics parameters for the adsorption of chromate, PO_4^{3-} and NO_3^- onto **ACSCC**

Adsorbate	ΔH (kJ/mol)	ΔS (J/mol)	ΔG (kJ/mol)				R²
			303° K	313° K	323° K	333° K	
Cr(VI)	21.45	129.86	−17.89	−19.29	−20.49	−21.79	0.99
PO_4^{3-}	19.18	114.15	−15.41	−16.55	−17.69	−18.83	0.99
NO_3^-	16.1	97.27	−13.37	−14.35	−15.32	−16.29	0.99

more, the chances of adsorbate ions to cross-over the boundary between the solution and solid-adsorbent, is more and hence, has greater adsorptivity.

Adsorption nature

Adsorption mechanism was analysed using various isotherm models, namely Freundlich 1906; Langmuir 1918; Temkin & Pyzhev 1940; Dubinin & Radushkevich 1947. In Figure 7(a)–7(d) and Table 5, the pertaining results are presented. The Langmuir model with $R^2 = 0.99$ for chromate, 0.99 for nitrate and 0.99 for phosphate, describes well the nature of the adsorption. This reflects the homogeneous surface of **ACSCC** and monolayer adsorption of adsorbate viz., nitrate, phosphate and chromates.
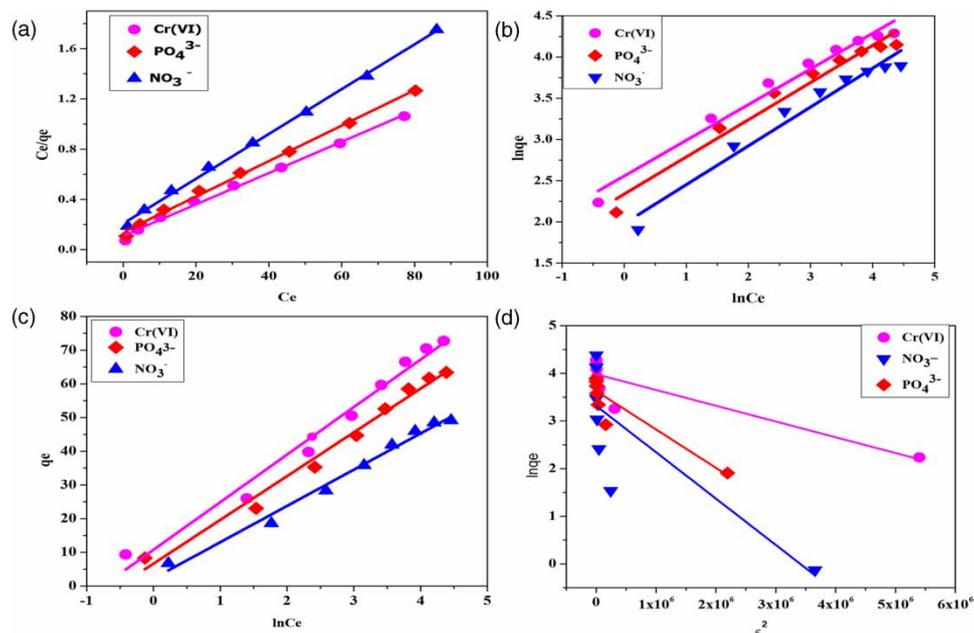
Figure 7 | Adsorption Isotherm models: (a) Freundlich; (b) Langmuir; (c) Temkin; and (d) Dubinin–Radushkevich.

Further, the R_L values are found to be 0.538 for nitrate, 0.467 for phosphate and 0.470 for chromate. As per Hal (Hall *et al.* 1966), these values imply the favourability of adsorption process. Temkin and Dubinin–Radushkevich equations are evaluated for 'E and B' values and are presented in the Table 5.

To assess the nature of adsorption, the magnitude of D-R mean free energy (E) and Temkin heat of sorption (B) values are used. Physisorption dominates if the D-R mean free energy, E, and Temkin heat of sorption (B) are less than 20 kJ/mol (Atkins 1999). As the evaluated values for the adsorption of phosphate, nitrate and chromate are less than 20 kJ/mol, it may be inferred that the adsorption is physisorption in nature, involving electrostatic interactions.

Table 5 | Various assessed parameters of adsorption isotherms

Adsorbate		Freundlich isotherm	Langmuir isotherm	Temkin isotherm	Dubinin-Radushkevich isotherm
Chromate	Slope	0.43	0.0125	14.1	−3.3E-07
	Intercept	2.56	0.11	10.75	4.0
	R^2	0.96	0.99	0.96	0.65
		$1/n = 2.3$	$R_L = 0.470$	$B = 14.1$	$E = 1.23$ kJ/mol
Phosphate	Slope	0.45	0.014	12.98	9.7E-07
	Intercept	2.33	0.13	6.69	3.3
	R^2	0.95	0.99	0.97	0.64
		$1/n = 2.22$	$R_L = 0.467$	$B = 12.98$	$E = 0.72$ KJ/mol
Nitrate	Slope	0.47	0.018	10.76	− 8.1E-07
	Intercept	1.98	0.21	2.23	3.6
	R^2	0.95	0.99	0.97	0.66
		$1/n = 2.12$	$R_L = 0.538$	$B = 10.76$	$E = 0.79$ KJ/mol

Table 6 | Evaluated parameters for kinetics of adsorption

Models		NO_3^-	PO_4^{3-}	Cr(VI)
Pseudo-first order model	R^2	0.98	0.97	0.97
	Intercept	0.7	0.75	0.8
	Slope	−0.033	−0.032	−0.033
Pseudo-second-order	R^2	0.997	0.995	0.994
	Intercept	0.63	0.52	1.07
	Slope	0.11	0.10	0.13
Elovich model	R^2	0.98	0.96	0.96
	Intercept	0.63	0.52	1.07
	Slope	0.11	0.10	0.13
Bangham's pore diffusion	R^2	0.95	0.95	0.95
	Intercept	−1.80	−1.83	−1.97
	Slope	0.26	0.27	0.34

Kinetics of adsorption

Pseudo-first order (Corbett 1972), pseudo- second-order (Ho & McKay 1999), Bangham's pore diffusion model (Mohan *et al.* 2019) and Elovich model (Wu *et al.* 2009), were employed in analysing the kinetics of adsorption. The pertaining evaluated factors are depicted in Table 6. From the Table, it may be inferred that the R^2 values fall in the order: pseudo-second-order > Bangham's pore diffusion > Elovich > pseudo-first-order.

The data of Cr(VI), NO_3^- and PO_4^{3-} are better modelled by pseudo-second-order rate kinetics (as in Figure 8) as their correlation coefficients (R^2) are 0.997, 0.995 and 0.994 for Cr(VI), NO_3^- and PO_4^{3-} respectively as compared to the other rate models. So, pseudo second-order model describes well the adsorption process.

Regeneration and reuse

Regeneration of spent adsorbents by treating with suitable eluents and their subsequent use as adsorbent is one of the important features of this aspect of research. This recycling helps to decrease the cost of the treatment process. Number of cycles allowed for treatment determines the merit of the process. Hence, in this work many eluents comprising acids, bases and salts were investigated for the regeneration of the spent **ACSCC**. It was observed that 0.1 N NaOH was effective in restoring the adsorption capacity of the spent **ACSCC**. The findings are presented in Figure 9.
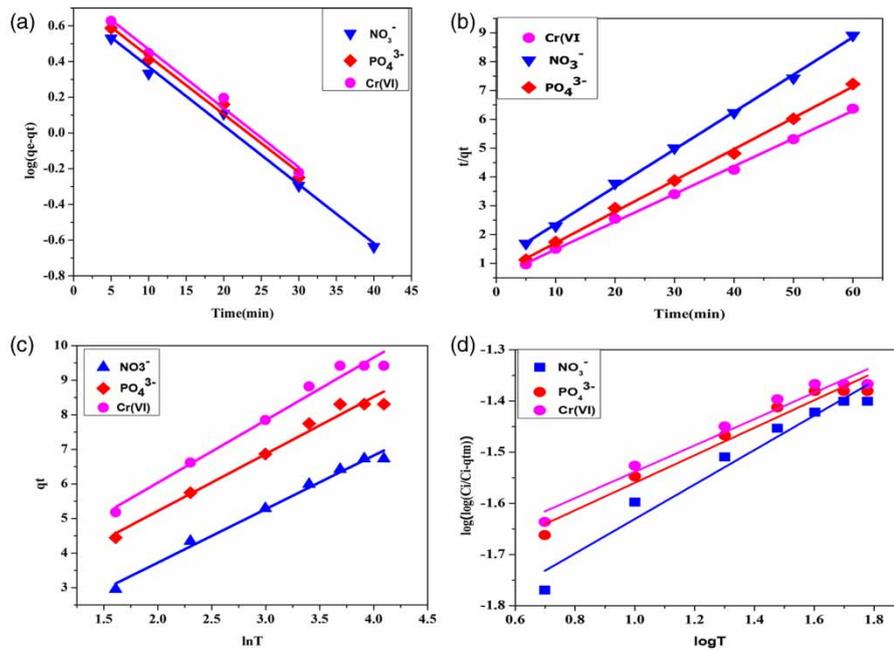
Figure 8 | Adsorption kinetics: (a) pseudo-first order kinetics; (b) pseudo-second order kinetics; (c) Elovich model; (d) Bangham's pore diffusion model.
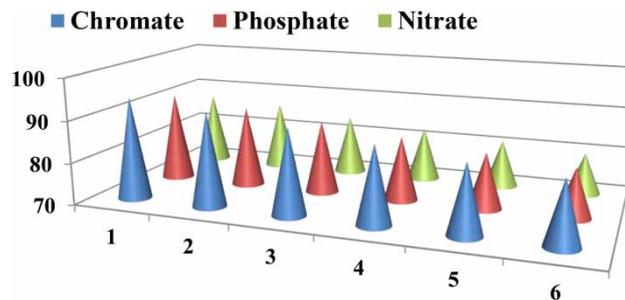

Figure 9 | Number of regenerations versus % removal.

It may be inferred that until six cycles of regeneration and reuse, there is only marginal loss of adsorption capacity. **ACSCC** structure did not deteriorate and was robust enough as an adsorbent. % remove of Cr(VI), PO_4^{3-} and NO_3^- even with six times regenerated **ACSCC** are: 85.2%, 81.8% and 80.4% respectively. This is a good finding. Further, the repeated use of the regenerated **ACSCC** can completely remove Cr(VI), PO_4^{3-} and NO_3^- ions from polluted water.

After six cycles of regeneration and reuse, there is a noticeable change and decrease in adsorption capacities of the adsorbent. This may be attributed to the deterioration and/or destruction of the some of active sites of **ACSCC**.

Applications

The active carbon, **ACSCC**, developed in this investigation was applied to treat polluted lake waters samples collected from Tenali Mandal of Guntur District of Andhra Pradesh, India. Due to intensive agricultural activities and over use of fertilizers, the water bodies of this area were reportedly polluted with respect to nitrate and phosphate. Further, the samples from the effluents of Ethiopia tannery

companies at Kombolcha City, located in the north part of Ethiopia were collected because they were causing chromate and nitrate pollution to the Leyole and Worka rivers.

The collected samples were analysed for the existing concentrations of nitrate, phosphate and chromate. The samples from Guntur District Lakes had nitrate and phosphate while the samples from effluents of Tannery industries in Ethiopia contained nitrate and chromate as cited in Table 7. The samples from the lake water were subjected to treatment with **ACSCC** for the simultaneous removal of nitrate and phosphate at pH:7 with the sorbent dosage 0.25 g/100 mL; time of equilibration 50 min; rpm 300; Temperature 30 ± 1 °C. The samples from the leather industry effluents were treated for the sequential removal of nitrate and chromate. In the sequential method, the water was treated for removing nitrate in the first instance using 0.13 g/100 mL of **ACSCC**; time of equilibration 50 min; rpm 300; Temperature 30 ± 1 °C. After completing the time of equilibration; that is, 50 min, the solution was filtered and the filtrate containing chromate was subjected to treatment with 0.1 g/100 mL of **ACSCC** for a duration of 40 min at rpm: 300 and temp. 30 ± 1 °C as described in the Materials and methods section. The results are presented in Table 7.

Table 7 | Applications: adoptability of **ACSCC** as adsorbents for real polluted water samples

A) Lake water samples
(collected in Tenali Mandal, Guntur District, Andhra Pradesh, India)

	Initial concentration of ions, C_i^a (mg/L)		Concentration of ions after treatment, C_e^a (mg/L)		% Removal[a]	
Samples	NO_3^-	PO_4^{3-}	NO_3^-	PO_4^{3-}	NO_3^-	PO_4^{3-}
1	7.4	1.8	0.444	0	94.0	100
2	17.1	2.5	2.27	0.08	86.7	96.8
3	21.4	2.9	2.274	0.119	85.2	95.9
4	24.6	3.1	3.813	0.177	84.5	94.3
5	33.3	3.6	5.90	0.306	82.2	91.5

B) Effluents from leather industry
(Collected from Ethiopia tannery companies at Kombolcha City, located in the north part of Ethiopia)

	Initial concentration of ions, C_i^a (mg/L)		Concentration of ions after treatment, C_e^a (mg/L)		% Removal[a]	
Sample number	NO_3^-	CrO_4^{2-}	NO_3^-	CrO_4^{2-}	NO_3^-	CrO_4^{2-}
1	8.2	1.6	0	0	100	100
2	14.3	2.2	0.715	0	85.1	100
3	18.2	4.4	1.73	0	83.2	100
4	22.5	4.1	3.51	0	82.4	100
5	24.3	3.2	3.90	0	83.2	100

[a]Average of five determinations; S.D. $\pm$ 0.15.

It is revealed from the table that the **ACSCC** is very effective in the treatment of water for the removal of nitrate, phosphate and chromate. A simple bio-char derived from the stems of *Carissa carandas* plant provides a solution for the purification of the said toxic ions.

Comparison with previous works

The present developed adsorbent, **ACSCC,** is compared with different good adsorbents based on bio-materials that are so far reported for the removal of Cr(VI), PO_4^{3-} and NO_3^-. They are compared with respect to pH and adsorbent capacities. The data are presented in Table 8. It can

Table 8 | Comparison of Cr(V), NO_3^- and PO_4^{3-} uptake capacities of **ACSCC** with other reported good adsorbents in literature

S. no.	Adsorbent	pH	Names of ions	Adsorbent capacity (mg/g)	Reference
1	*Chenopodium album* plant materials	2	Cr(VI)	17.8	Babu *et al.* (2016)
2	ACSLC	2	Cr(VI)	26.5	Ravulapalli & Kunta (2018)
3	Spent coffee ground (SCG)	2	Cr(VI)	22.75	Krishna *et al.* (2017)
4	Biochar supported ZnO nanoparticles	5.5	Cr(VI)	43.48	Yu *et al.* (2018)
5	Activated carbon residue (ACR)	4	NO_3^-	3.8	Kilpimaa *et al.* (2015)
		6	PO_4^{3-}	0.8	
6	Biochar from wheat straw (*Triticumaestivum* L.)	3	NO_3^-	2.47	Li *et al.* (2016)
		6	PO_4^{3-}	16.58	
7	CNT	5.6	PO_4^{3-}	15.4	Mahdavi & Akhzari (2016))
8	Granular activated carbon	7	NO_3^-	21.51	Mazarji *et al.* (2017)
9	Activated coir-pith carbon	7	PO_4^{3-}	7.3	Kumar *et al.* (2010)
10	Modified sugarcane bagasse biochar	6	NO_3^-	28.21	Hafshejani *et al.* (2016)
11	**ACSCC**	2	Cr(VI)	72.75	Present work
12	**ACSCC**	7	PO_4^{3-}	63.4	
13	**ACSCC**	7	NO_3^-	49.15	

be observed that **ACSCC** is more effective than many of the adsorbents reported. Further, the present investigation permits the simultaneous removal of nitrate + phosphate and sequential removal of nitrate + phosphate + chromate.

CONCLUSIONS

A simple active carbon synthesized from the stems of *Carissa carandas* plant has been found to be effective for the sequential removal of toxic nitrate, phosphate and chromate ions from water. Simultaneous removal of nitrate and phosphates was also possible at pH:7. Various factors affecting adsorption were optimized for the maximum removal of the said anions. The active carbon was characterized for physicochemical parameters and also with FTIR, FESEM and EDX. The nature of sorption was investigated adopting various adsorption isotherms and kinetic models. Thermodynamics parameters were also evaluated. The data revealed the Langmuir isotherm model of adsorption, pseudo-second-order kinetics and spontaneity of the sorption process. Langmuir maximum adsorption capacity (individual) is: 72.75 mg/g for chromate, 63.40 mg/g for phosphate and 49.15 mg/g for nitrate. **ACSCC** can be regenerated and reused for six cycles. The adsorbent was robust enough until the sixth cycle of regeneration with marginal loss of adsorption capacity. The adsorbent developed, **ACSCC**, was successfully used to treat the polluted lake water samples and effluent samples from leather industries. Thus we claim a simple adsorbent for the sequential removal of nitrate, phosphate and chromate and simultaneous removal of nitrate and phosphate from polluted water.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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