Efficient removal of Cr (VI) using raw and phosphoric acid modified *Sterculia Alata* nutshell

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The adsorption behaviour of Cr (VI) onto raw *Sterculia Alata* nutshell (RSN) and phosphoric acid modified *Sterculia Alata* nutshell (PSN) from aqueous solution has been studied. Specific constraints such as initial pH (2-12), adsorbent dose (0.4-3.2 g/L) and temperature (24-32°C) have been investigated to examine the optimum process parameter for adsorption. Both the biosorbents are characterized based on their physicochemical characterization such as FTIR, SEM-EDS and XRD. The adsorption characteristics were assessed using the isotherms (Langmuir and Freundlich) to match the adsorption details. The maximum chromium adsorption capacity is obtained to be 39.89mg/g and 88.30mg/g for RSN and PSN at 28°C respectively. Both the biosorbents confirmed the aptness of pseudo second order kinetics throughout the chromium (VI) abstraction phase with R^2 value greater than 0.99.

Keywords: Biosorption, Cr (VI), Isotherm, Kinetics, *Sterculia Alata* nutshell

Water pollution as a result of technological development appears to be of great concern. With the increasing production of heavy metals from technological activities, most aquatic ecosyst-ems face concentrations of metals that surpass water quality standards. Massive industrial urbanisation emanates various toxicants which pollutes water, soil and air; although it elevated the life style of human beings. Among these, removal and disposal of noxious elements form untreated wastewater is necessary due to increasing paucity of potable water worldwide. Among organic and inorganic pollutants, heavy metals such as lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe) removal draw more attention to the environmentalists due to its chemical properties. Chromium is one of the toxic metals which found in aqueous solutions is used by various industries (Electroplating, pigment manufacturing, leather industry, glass making, pigment additive, stainless steel plant) due to its versatile nature. Cr (VI) is more malignant, carcinogenic and teratogenic in the form of chromate and dichromate as it is more soluble and mobile in liquid effluent rather than Cr (III). Cr (VI) is acknowledged to be a very lethal contamination to people and animals as well as plants[3]. Indeed, the release of Cr (VI) furthest range was confined by the U.S.EPA to be only 0.05 mg L^{-1}. While the release furthest limit of the total Cr [Cr (VI), Cr (III) what's more, different types of them] is managed to be 2 mg/L^4.Due to their high water solubility, heavy metals such as chromium can easily come into the food chain causing several diseases causing harm to the human renal and liver[5]. There are basically two different methods (chemical and physical) for removing chromium containing discharges[6,7]. Currently lot of research has been done on adsorption of Cr (VI) using different types of low cost adsorbent.Several techniques have been tested for the expulsion of dissolved heavy metal ions, including solvent extraction, ion exchange, membrane process, electro-dialysis, precipitation, phyto-extraction, ultrafiltration, reverse osmosis and adsorption.These methods required huge operational and capital costs[8]. However, adsorption is more approved method for heavy metal removal due to its low and negligible cost[9].

In this investigation, a comparative study was done in order to eradicate hexavalent chromium from aqueous solution using raw and phosphoric acid modified *Sterculia Alata* nutshell. *Sterculia Alata* (Pterygota Alata) trees are abundant in East Asian countries like southern China, India, Bhutan, Bangladesh, Malaysia, Philippines. A very few studies have been reported regarding preparation of adsorbent from *Sterculia Alata* nutshells. In the previous work Mohanty et al., has proposed

preparation and characterization technique to prepare activated carbon using $ZnCl_2$ as precursor from Sterculia Alata nutshells for phenol removal from wastewater[18]. However, it is not advisable to use $ZnCl_2$ for activated carbon preparation due to its harmful effect on aquatic animals and may cause severe unfavourable condition for the environment[19]. The nutshell is a type of agricultural waste and it can be used as biosorbents to expel Cr (VI). Adsorption study was done by using the adsorbent (raw and phosphoric acid modified nutshell) and the influence of various chemical properties such as *p*H, biosorbent amount, temperature was investigated. The biosorbents were characterized by TGA, SEM-EDS, FTIR and XRD. Thermodynamic and dynamic study was also performed using Langmuir, Freundlich isotherm models and pseudo first, second kinetic models respectively with intra particle diffusion models.

Experimental Section

Materials and instrument

The *Sterculia Alata* nutshells were cut into small pieces after procured from the campus of IIT (BHU) Varanasi (25.2623 N 82.9893 E) Uttar Pradesh, India. Phosphoric acid, potassium hydroxide, potassium dichromate, acetone, 1,5-diphenylcarbazide, hydrochloric acid and other chemicals which are required for the adsorption studies were all analytical grade type. The instruments employed for this study were disintegrator, electric oven (NSW-143), double beam UV visible spectrophotometer (LMSP-UV1900), orbital shaking incubator (ASCO-34B), and *p*H meter (CL 54+).

Raw and acid modified adsorbent preparation

The procured nutshell was dehydrated under sunlight for 2 days. The dried nut shell was cleaned with double distilled water to eradicate dirt and impurities followed by drying at 105 °C for 18 h. The dehydrated raw materials were powdered and sieved to obtain the desired average particle size (Mesh: 45-50) and kept in desiccator for further use and named as raw *Sterculia Alata* nutshell (RSN).

The ortho-phosphoric acid (88% w/w) has been used for the acid treatment of the biosorbent. The nut shell is impregnated in the ratio of 2:1(weight of phosphoric acid to weight of biosorbent) for whole day and after that it was rinsed many times in double distilled water until the *p*H of the wash water become greater than 6. The material obtained after washing

has been put in the laboratory drying oven at 105°C for 18 h. Finally the acid modified nut shell was put in the desiccator and named as phosphoric acid modified *Sterculia Alata* nutshell (PSN).

Characterization of the biosorbent

Proximate analysis such as moisture, ash, volatile matter content is estimated using the standards of ASTM (E-871, D-102 and E-872), however fixed carbon content was calculated on the difference basis. Elemental analyser (Euro EA) was used for elemental analysis, whereas oxygen was calculated from the difference. BET surface was calculated employing Micromeritics ASAP 2020 surface area analyzer. Thermal stability analysis of the raw biomass was performed using a thermogravimetric analyser (TGA-50, Shimadzu Asia) in the temperature range of ambient to 800°C at 10°C/min heating rate. The topography and surface composition of the sample was obtained by using scanning electron microscopy (SEM-EDS) (EVO- SEM-MA15/18). FTIR analysis (NICOLET 5700 spectrophotometer) was used to recognize the presence of specific bonds in the form of functional groups in the sample. The X-ray diffractometer (Rigaku SmartLab) was used to determine the phases of the biomass.

Chromium adsorption studies

The experiments related to adsorption on both the biosorbent ware carried out by preparing a stock solution of 1000 mg/L. A desired amount of 2.828g of $K_2Cr_2O_7$ was dissolved in 1 litre of double distilled water which was to be used as test samples by diluting the above stock solution.Batch reactors were prepared by adding biosorbents (RSN and PSN) into Cr (VI) test samples in erlenmeyer flasks. The flasks were covered with a sealing film and put into the orbital shaking incubator (160 rpm) at specific temperature for certain duration of time. The sample has been obtained through the micro pipette, filtered with whatman filter paper (No 1) and concentration of Cr (VI) was measured with 1, 5-diphenylcarbazide method. The adsorption percentage (%R) and adsorption capacity q_t of Cr (VI) on biosorbents were determined by the following formula represented by Eqn. (1) and (2) respectively:

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \qquad \dots (1)$$

$$q_t = \frac{C_o - C_t}{W} \times V \qquad \dots (2)$$

where, C_o(mg/L)and C_e (mg/L) are the initial and final concentrations of Cr (VI), respectively, q_t (mg/g) corresponds to the ratio of mass of adsorbate to the mass of biosorbent, C_t is the equilibrium concentration of Cr (VI) at time t (min), W (g) is the mass of adsorbent used, V (L) is the volume of Cr (VI) solution.

Results and Discussion

Physicochemical characterization

Physicochemical characterization of the RSN and PSN biomass is presented in Table 1. It can be seen from the table that moisture content of the RSN biomass was found to be 7.13%, whereas for PSN it is 5.25%. Ash content was found to be 15.36% and 14.15% for RSN and PSN biomass respectively. Ash content gets reduced after acid treatment due to removal of inorganic salts. Biomass having lower moisture and ash content and higher volatile and fixed carbon content is suitable candidate for adsorbent. Further, ultimate analysis revealed high amount of carbon followed by hydrogen and nitrogen with no sulphur. The point of zero charge for the RSN was 5.07 and 4.89 for PSN which shows that biosorbents have positive surface charge below their $pH_{pzc.}$

SEM-EDS

SEM analysis of biosorbent (RSN and PSN), prior and laterto Cr (VI) expulsion are displayed in Fig. 1. (a), (c), (e) and (g) respectively. As seen from the Fig. 1 (c) the porosity of the sample has been increased after chemical treatment as compared to raw biomass. Before Cr (VI) treatment the surface of the biosorbent has rough, bumpy, pores and uneven layer as shown from the Fig. 1. (a) and (c) which was not present after Cr (VI) removal and the surface become smooth as shown in Fig. 1. (e) and (g). EDS analysis was performed to check chromium spectra before and after adsorption that was displayed in Fig. 1. (b), (d), (f) and (h). There was no Cr (VI) characteristic signal prior to biosorption on to RSN and PSN but after Cr (VI) adsorption on to RSN and PSN, the signals was clearly seen from the Fig. 1. (f) and (h).

FTIR and XRD

The XRD analysis for RSN and PSN biomass was executed to understand whether the biosorbent has amorphous or crystalline nature as shown in Fig. 2.(a). The peak confirms the presence of substantial amount of crystalline material due to CH_5N_3 (guanidine) and $Si_{64}O_{128}$ (β-zeolite). After chemical treatment no appreciable peak change was noticed, but increase in peak intensity. No considerable change in peak position denotes chemical composition of the biosorbent has not changed after chemical treatment.

FTIR analysis for RSN and RSN-Cr was carried in between the spectra range of 400-4000 cm^{-1} as shown in Fig. 2. (b). Peak at 3058.2 cm^{-1} present in RSN confirms the presence of CH stretching vibration after adsorption onto RSN it shifts to 3183.3 cm^{-1}. Peak at 2344.1 cm^{-1} indicates the presence of C≡C and C≡N functional group. Peak at 1723.6 cm^{-1} confirms the presence of C=O stretching vibrations of aldehyde, ketone and carboxylic acid. Peak at 1521.6 cm^{-1} indicates the existence of secondary amine. Peak at 1329.1 cm^{-1} shows the presence of aromatic amine. Peak shifted to upward after adsorption confirms the biosorption of Cr (VI) on RSN. The FTIR analysis for PSN was shown in Fig. 2. (c). Peak at 3749.9 cm^{-1} was due to presence of C≡H stretching of alkynes. Peak at 3486.4, 3386.8, 3292.4 and 3166.8 cm^{-1} was due to presence of N-H amine or amide group. Peak at 2902.3 cm^{-1} was due to presence of C-H stretching vibration of alkyl group. Peak at 2349.8 cm^{-1} was due to existence of aldehyde group. Peak at 1683.2 cm^{-1} was due to C=C stretching vibration of amide group. The shifts in peaks from mentioned spectra band was the clear indication of Cr (VI) adsorption onto PSN.

Thermal stability of the RSN biomass

Thermal stability behaviour of RSN biomass was carried out in a thermogravimetric analyzer (TGA-50, Shimadzu) in the temperature range of 20 to 800°C at heating rate of 10°C /min under inert condition of N_2 (100 mL/min). It can be seen from the Fig. 3 that thermogravimetric profile of the RSN biomass can be divided into three degradation stage. The first stage

Table 1 — Physicochemical characterization of raw and chemically treated biomass

Analysis	RSN	PSN
Proximate analysis (wt %)		
Moisture content	7.13	5.25
Ash content	15.36	14.15
Volatile matter	71.03	75.56
Fixed carbon	6.48	5.04
Ultimate analysis (wt %)		
Carbon	37.32	42.75
Oxygen	56.7	50.31
Nitrogen	0.71	0.98
Hydrogen	5.27	5.96
Sulphur	ND	ND
Specific surface area (m^2/g)	0.2933	0.4131
pH_{pzc}	5.07	4.89
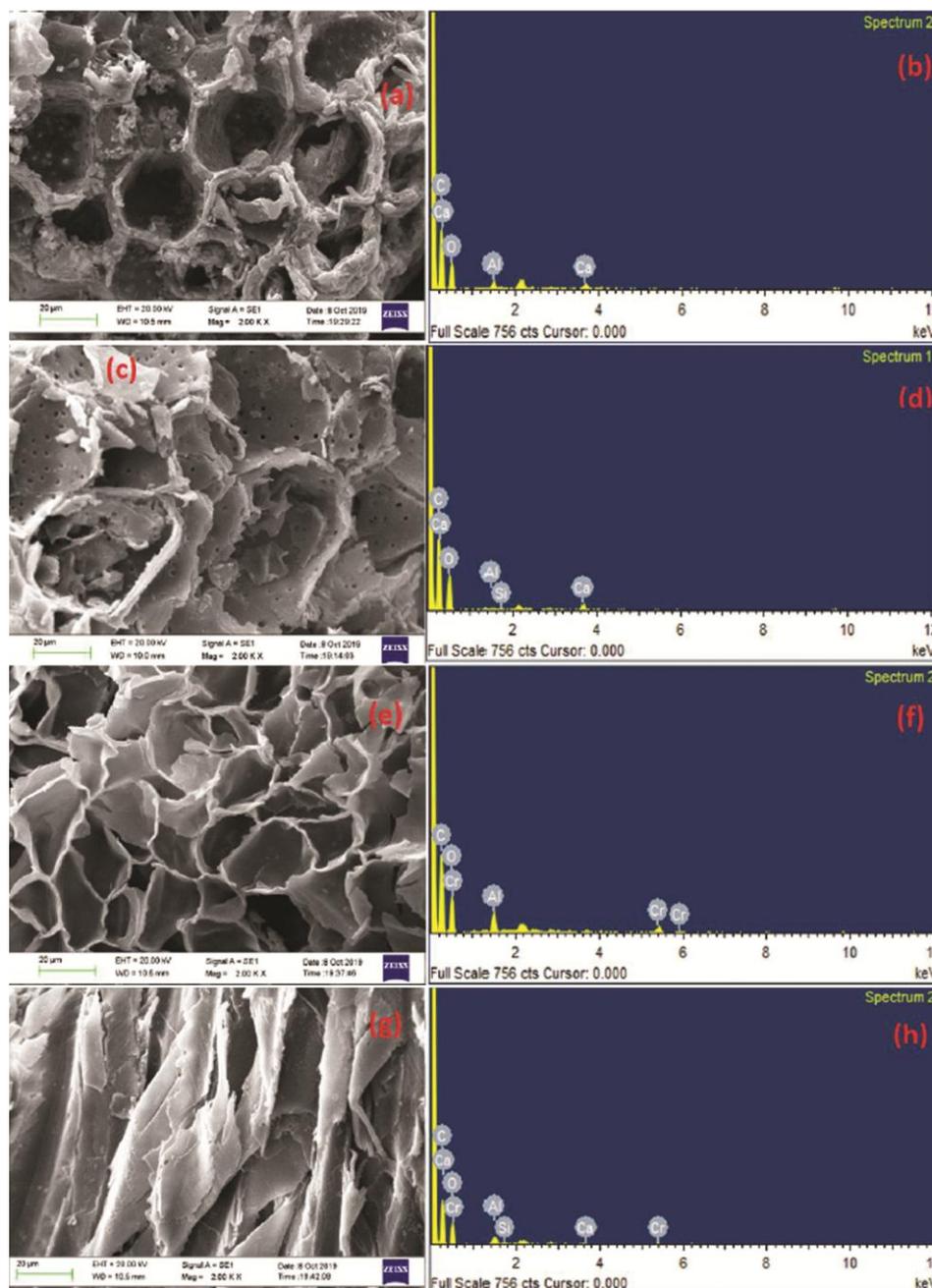
Fig. 1 — SEM coupled with EDS spectra of (a, b) RSN, (c, d) PSN, (e, f) Cr-RSN and (g, h) Cr-PSN

ranges from ambient to 130°C attributes to the moisture removal stage. In this stage weight loss was found to be 6.5% due to inherent moisture retained in the biomass. The second stage also called as active pyrolysis stage ranges from 130 to 418°C where weight loss was observed to be 50.28% due to deterioration of cellulose and hemicellulose content of the biomass[20,21]. The third stage ranges from 418 to 800°C, where slow degradation of mass loss to be occurred due to degradation of lignin and complex organic constituents. From the DTG thermograph Fig. 3, the maximum peak temperature was observed at 301°C, however the amount of residue left was 27%.

Influence of different parameters in hexavalent chromium removal

Influence of pH

In this experiment, the *p*H of the solution was varied in between 2 to 12 with initial Cr (VI)
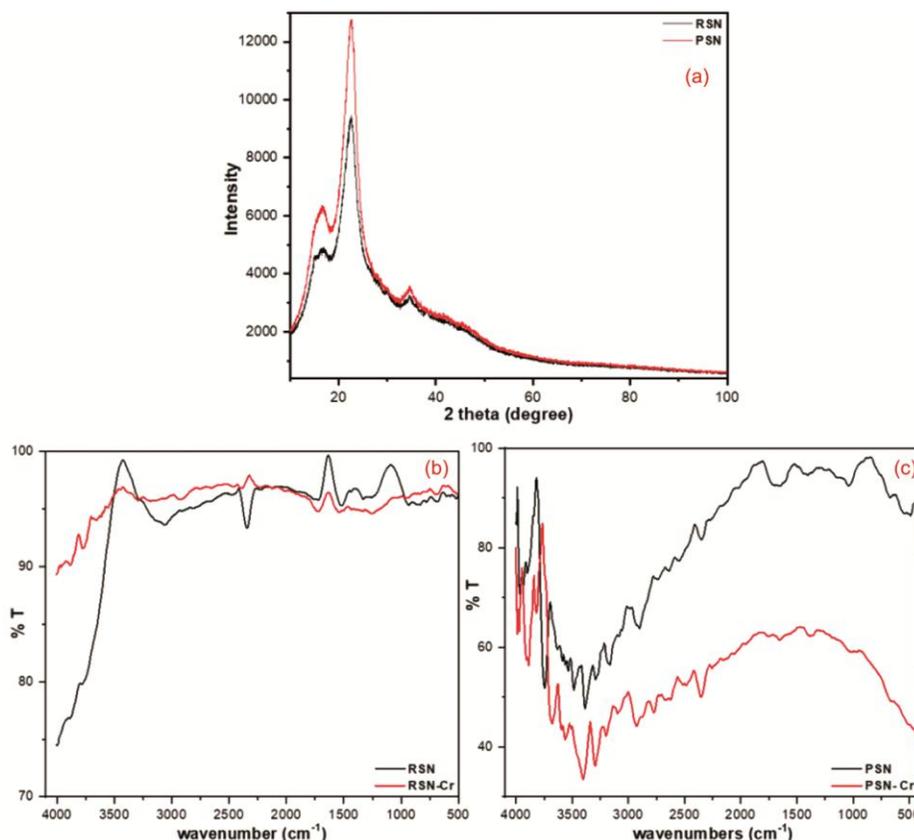
Fig. 2 — (a) XRD spectra of RSN and PSN, (b) FTIR spectra of RSN and Cr-RSN, and (c) FTIR spectra of PSN and Cr-PSN
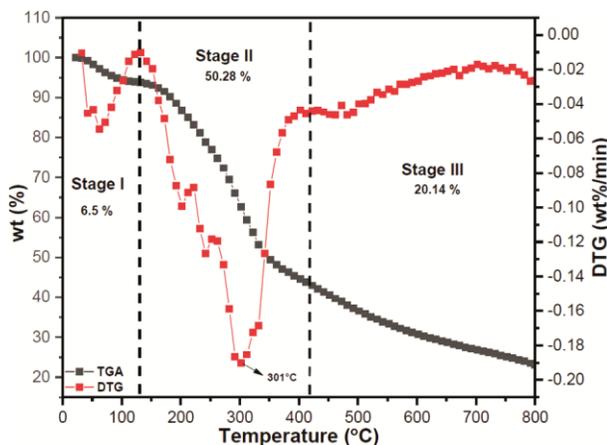
Fig. 3 — Thermal stability analysis of RSN biomass

concentration of 25 mg/L, biosorbents dosage 0.8 g/L, temperature 28°C, shaking speed 160 rpm and adsorption capacity was measured which can be seen from the Fig. 4 (a) and(b). The adsorption capacity decreased from 31.2 to 13.23 mg/g with equilibrium pH changes from 2.03 to 8.91 and 28.36 to 12.13 mg/g with equilibrium pH changes from 2.02 to 8.98 for PSN and RSN respectively by increasing pH from 2 to 12. This happens because at

low pH values, Cr (VI) ions exist in the most predominant form such as $HCrO4^-$, which attracted the negatively charge Cr (VI) ions because the surface of the PSN and RSN is charged positively but as the acidic character was decreased, the biosorbents nature changes to be negative hence OH^- concentration was increased by predominating the CrO_4^{2-}, $Cr_2O_7^{2-}$ and $Cr_3O_{10}^{2-}$ which causes hindrances in the adsorption process by decreasing the adsorption capacity[10,11]. The equilibrium pH also increased with increasing initial pH because concentration of OH^- ions also get increased.

Influence of adsorbent dosage

In this experiment, RSN and PSN dose was varied in between 0.4 to 3.2 g/L at temperature 28°C, shaking speed 160 rpm, initial Cr (VI) concentration 50 mg/L, contact time 120 minutes and pH 2. By increasing the adsorption dose adsorption capacity decreased from 83.03 to 15.6 mg/g for PSN and 46.52 to 15.6 mg/g for RSN as shown in Fig. 4 (c). This was because large number of active sites of the biosorbents has been left over with increasing dose, as the Cr (VI) concentration remains the same

which has been adsorbed already and also due to accumulation of adsorption particle at higher adsorption dose[12].

Influence of temperature

In this experiment three temperatures (24, 28 and 32 °C) were selected to understand the influence of temperature on Cr (VI) adsorption onto RSN and PSN in which the initial Cr (VI) concentration was 50 mg/L, *p*H 2, biosorbents dose 0.8g/L, contact time 120 min and shaking speed 160 rpm which was depicted in Fig. 4 (d). The adsorption capacity was increased from 29.7 to 54.45 mg/g and 51.71 to 62.1 mg/g for RSN and PSN respectively when temperature was raised from 24 to 32 °C showing that the biosorption process are endothermic.

Thermodynamic study

The thermodynamic parameters ΔG_o (KJ/mol, Gibbs free energy), ΔS_o, (KJ/mol K, entropy) and ΔH_o (KJ/mol, enthalpy) were calculated by the following formulae:

$$\Delta G_o = -RT \ln k_c \qquad \ldots(3)$$

$$\ln k_c = \frac{S_o}{R} - \frac{H_o}{RT} \qquad \ldots(4)$$

where, T is temperature in kelvin, k_c is Langmuir constant and R is the gas constant (8.314 J/mol K). The values of ΔG_o, ΔS_o and ΔH_o are given in Table 2. The value of ΔS_o for PSN is more positive than RSN which shows that Cr (VI) adsorption using PSN has more randomness than RSN[13]. ΔH_o value was positive which showed that the adsorption process was endothermic. The values for ΔG_o are decreasing which implies that the biosorption process was spontaneous.

Adsorption Isotherm

Langmuir and Freundlich

In Langmuir isotherm, it is expected that at extreme exposure, there is only a monomolecular layer on the surface while Freundlich isotherm is
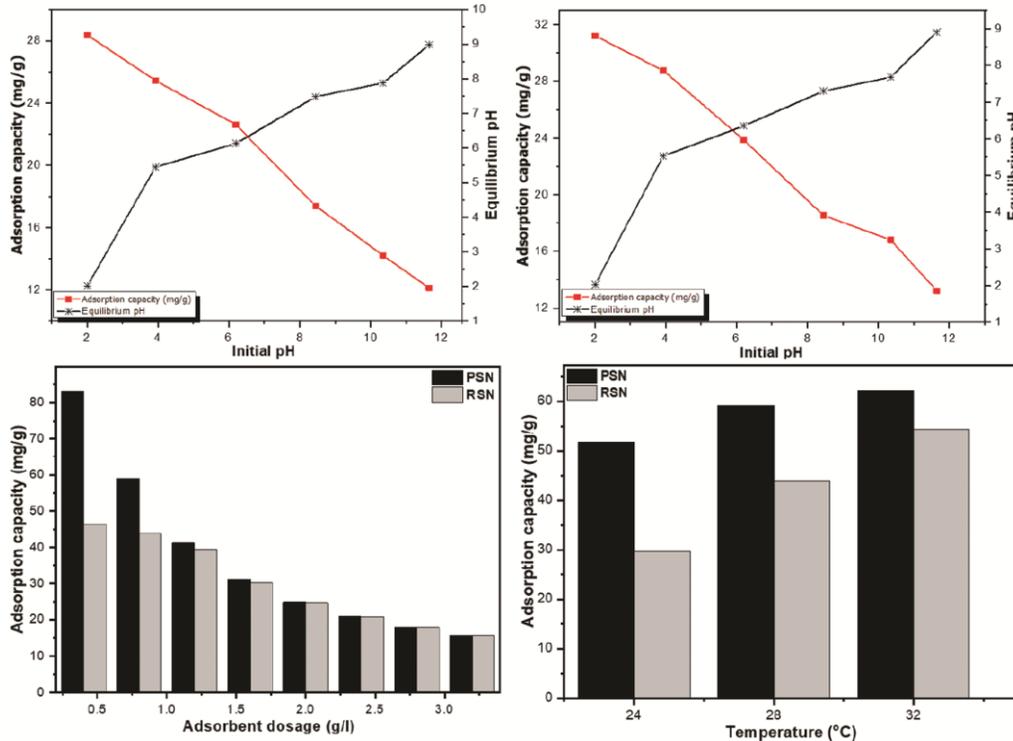
Fig. 4 — Influence of various factors, (a) initial and equilibrium *p*H of RSN; (b) initial and equilibrium *p*H of PSN; (c) adsorbent dose and (d) temperature

Table 2 — Thermodynamic study of Cr (VI) removal onto PSN and RSN

Experimental circumstances	ΔS_o	ΔH_o	ΔG_o		
			297 K	301 K	305 K
PSN	1.177	346.203	4.419	7.677	14.04
RSN	0.636	189.75	0.3017	1.143	5.413

Table 3 — Isotherm parameters for biosorption of Cr (VI) onto RSN and PSN			
Langmuir constant	q_m	k_1	R^2
RSN	39.89	9.36	0.79
PSN	88.30	0.933	0.99
Freundlich constant	n	k_2	R^2
RSN	0.151	27.36	0.99
PSN	0.227	44.70	0.94

built on the empirical relationship between solution concentration on the layer of an adsorbent and solute content in the liquid to which it is in touch. The equation describing Langmuir and Freundlich isotherm are presented by the equation (5) and (6) respectively[14,15].

$$q_e = \frac{q_m k_1 C_e}{1 + k_1 C_e} \quad \dots(5)$$

$$q_e = k_2 C_e^n \quad \dots(6)$$

where, C_e (mg/L, equilibrium concentration), q_e (mg/g, equilibrium adsorption capacity), q_m (mg/g, maximum adsorption capacity), k_1 and k_2 Langmuir and Freundlich constant and n is Freundlich coefficient.

In this experiment, the temperature was set to be 28°C, biosorbents dosage range from 0.4 to 3.2 g/L, initial Cr (VI) concentration was 50 mg/L, pH 2, contact time 120 minutes and shaking speed 160 rpm. The values of the above mentioned factors are given in Table 3 and also shown in Fig 5. As seen from the Table 3 the adsorption of Cr (VI) onto PSN follows Langmuir isotherm (R^2=0.99) while Cr (VI) adsorption onto RSN follows Freundlich isotherm (R^2=0.99).

Adsorption kinetic studies

Kinetic parameters give useful information regarding modeling and designing of the process. The two kinetic models pseudo first and second order was selected to know the phenomenon of kinetics for the Cr (VI) adsorption onto RSN and PSN which is presented by the equation (7) and (8) respectively[16].

$$\log(q_e - q_t) = \log \, q_e - \frac{k_3 \, t}{2.303} \quad \dots(7)$$

$$\frac{t}{q_t} = \frac{1}{k_4 \, q_e^2} + \frac{t}{q_e} \quad \dots(8)$$

where, k_3 (min^{-1}) and k_4 (g/mg.min) are the rate constant for pseudo first and second order respectively. q_t and q_e are adsorption capacity (mg/g) at any time '*t*' and at equilibrium respectively.
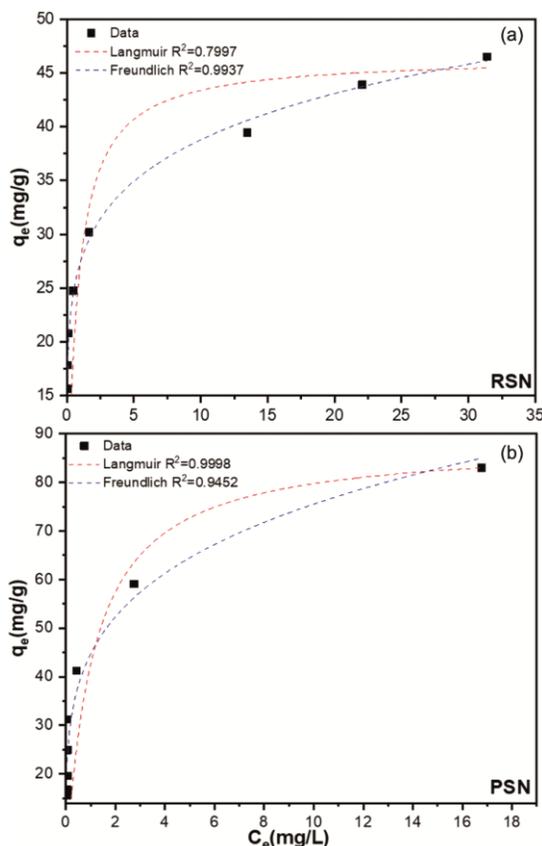
Fig. 5 — Langmuir and Freundlich isotherm, (a) RSN, and (b) PSN

In this study pH was set to be 2.01, biosorbents dose 1g/L, initial Cr (VI) concentration 50 mg/L and temperature 24 and 32°C with shaking speed 160 rpm. The data of the kinetic parameters are given in Table 4. On comparing the regression coefficients (R^2) value with both the models, the pseudo second order models was applicable for both the biosorbents because R^2 values at both temperature (24°C and 32°C) was high for pseudo second order as shown from Fig.4. (a, b).

Further, during adsorption mass can also transferred due to intra particle diffusion (IPD) that was given by Weber and Morris and was given below:

$$q_t = k_d \, t^{0.5} + C \quad \dots(9)$$

where, k_d (mg g^{-1} min$^{-1/2}$) denotes the IPD constant and C (mg g^{-1}) is that constant which give details

Table 4 — Pseudo first and second order kinetic models for RSN and PSN						
Experimental	Pseudo first order			Pseudo second order		
	q_e	k_3	R^2	q_e	k_4	R^2
24 °C RSN	81.90	0.02632	0.51	53.59	0.000385	0.91
24 °C PSN	34.12	0.01856	0.79	56.08	0.000701	0.98
32 °C RSN	121.60	0.03618	0.51	55.24	0.000586	0.94
32 °C PSN	180.56	0.05506	0.60	52.82	0.001492	0.99
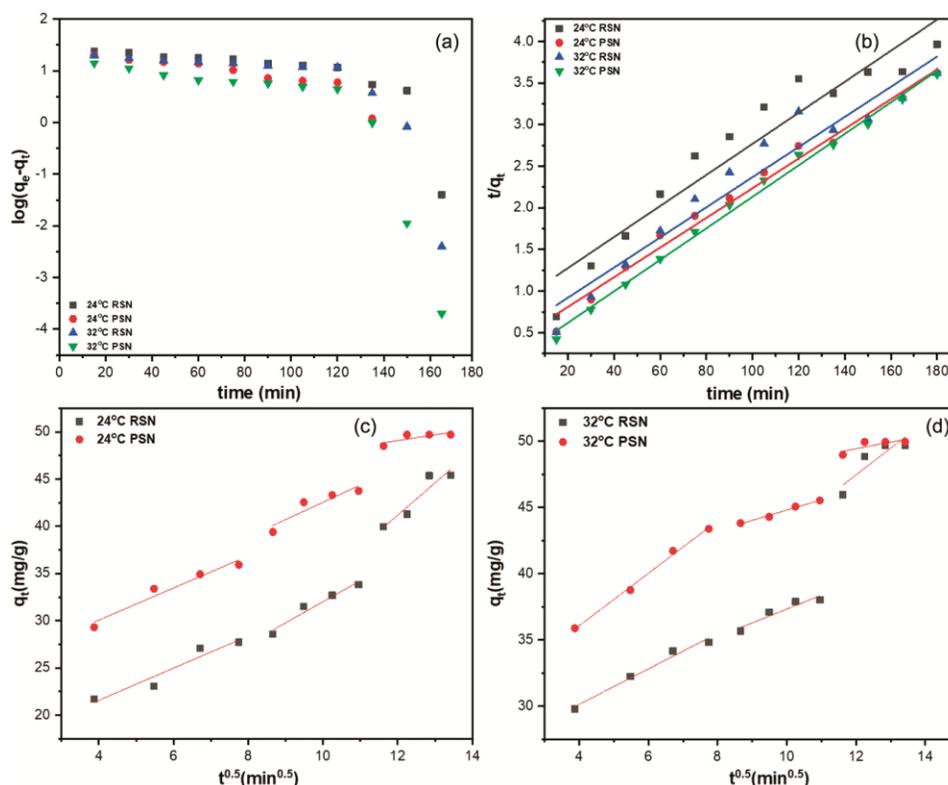
Fig. 6 — Adsorption kinetics model of Cr (VI) onto RSN and PSN (a) pseudo first order; (b) pseudo second order; (c) IPD plot at 24 °C and (d) IPD plot at 32 °C

about boundary layer. According to this model, if q_t verses $t^{0.5}$ results in a straight line passing through the origin, then intra-particle diffusion controls the adsorption process. However, if the figure does not show a straight line through the origin, it means that adsorption is influenced not just by intra-particle diffusion but also, to some extent, by film diffusion. From Fig. (6), it is seen that the plot has several linear section during the time interval and it does not pass through the origin. As a result, Cr (VI) adsorption onto RSN and PSN was a multi-stage process that includes exterior surface adsorption as well as interior diffusion.

Conclusion

The present work gives the idea of using the agricultural waste RSN and PSN as an effective biosorbents to remove Cr (VI) from aqueous solution. The SEM-EDS analysis revealed the change in morphological structure and surface irregularities with presence of Cr (VI) signals after adsorption of Cr (VI). FTIR analysis after biosorption has shifts in peak and change in intensity which confirms the biosorption of Cr (VI) onto RSN and PSN. The adsorption of Cr (VI) onto PSN follows Langmuir isotherm (R^2=0.99) while Cr (VI) adsorption onto RSN follows Freundlich isotherm (R^2=0.99). The maximum chromium adsorption capacity obtained was 39.89 and 88.30 mg/g for RSN and PSN respectively. Both the biosorbents (RSN and PSN) followed pseudo second order kinetics and was a multi stage process. The thermodynamic study suggested the spontaneous and endothermic nature of the biosorption process.

Acknowledgements

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