



# Simple effective new bio-adsorbents for the removal of highly toxic nitrite ions from wastewater

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## Abstract

Bio-adsorbents derived from *Sesbania grandiflora* (SGSP/SGSAC) and *Amorphophallus paeoniifolius* (APSP/APSAC) plants are investigated for their ability to remove nitrite from polluted water. Different extraction conditions have been investigated and optimized for the maximum nitrite removal. Adsorption capacities are found to be 44.5 mg/g for SGSP, 57.5 mg/g for SGSAC, 40.0 mg/g for APSP and 65.5 mg/g for APSAC. Thermodynamic parameters are evaluated. High values of  $\Delta H^\circ$  for SGSAC (50.872 kJ/mole) and APSAC (67.907 kJ/mole) indicate ion exchange mode of sorption. Spontaneous and endothermic nature of sorption is indicated by negative  $\Delta G$  values. Positive values of  $\Delta S$  emphasizes the disorder at solid/liquid interface. The adsorption follows Langmuir isotherm for all the four sorbents, indicating formation of monolayer of nitrite ‘onto’ the surface of sorbents and uniform distribution active sites. Pseudo second-order kinetics explains well the kinetics of adsorption and this reflects that the adsorption is through exchange of electrons or sharing of electrons between nitrite and functional groups sorbents. The developed sorbents are applied effectively for nitrite removal from polluted lake real water samples. The merit of the present investigation is that simple, effective and easily available plant-based bio-materials are identified for the removal of toxic nitrites from water.

**Keyword** Nitrites · Pollution control · Bio-adsorbents

## Highlights

- Bio-adsorbents derived from stems of *Sesbania grandiflora* and *Amorphophallus paeoniifolius* plants are investigated as adsorbents for the removal of toxic nitrite ions.
- Extraction conditions are investigated and optimized for the maximum nitrite removal.
- Adsorption capacities are found to be very high for the stems as well as active carbons.
- Thermodynamic parameters are evaluated.
- The adsorption follows Langmuir isotherm for all the four sorbents
- Pseudo second-order kinetics explains well the kinetics of adsorption.
- The developed sorbents are applied effectively for nitrite removal from polluted lake water samples.

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## 1 Introduction

Nitrite toxicity is well known and its presence in water is attributed to the inadequate oxidation of nitrogen content of organic matter in wastewater [4, 42]. Nitrogen-related compounds are often existing in dangerous proportions in agricultural, public, domestic and industrial wastewater. Of these, nitrite is highly toxic. Some of the potential sources of contamination of nitrate in water are the fermented vegetables, animal/human excretion, decayed fish, cured meat, over utilization of fertilizers and dairy products wastes [19, 20].

Nitrite is widely used since long times as a preservative for curing meat and to impart deep red colour for good look [19]. This practice became an important source for nitrite contamination. Nitrite content in meat is <0.2 to 6.4 mg/kg, dairy products <0.2 to 1.7 mg/kg<sup>3</sup> and in damaged vegetables up to 400 mg/kg—depending upon freshness [42]. The wastewaters from these sources, if not treated, contain dangerous amounts of nitrites and their dumping in water sources causes water pollution [4, 42]).

The consumption of nitrite through drinking water causes dreaded disease like methemoglobinemia especially

in children and may also end up in cancer. Nitrite reacts with blood cells to form various carcinogenic N-nitroso compounds in humans and animals. Many of the death in western countries are directly or indirectly linked to nitrite contamination [62]. Fully oxidized form of nitrite is nitrate and it is inter-convertible depending upon the reduction or oxidation conditions prevailing in the host water: anaerobic conditions reduce nitrate to nitrite and oxidation conditions oxidizes nitrite to nitrate [21]. The conception of nitrates (oxidized form) also results in methemoglobinemia and it is due to the reduction of nitrate to nitrite in stomach of human or animal and thus produced nitrite get reacted with blood cells [19, 28].

Some of Western countries pass stringent legislation for controlling nitrite pollution. The allowed maximum limit in drinking water is 0.5 ppm (European Union), 1 ppm (USA) and 0.002 ppm (China) [4, 62]. So, removal of nitrites from contaminated water is an important aspect of research in pollution control methods [59]. Hence, it is very essential to develop effective materials to adsorb the nitrite ions from infected water samples as high risks are associated with the nitrite ion. The conventional methods investigated for the removal of nitrite are de-nitrification [59], coagulation [36], ozonation and ion exchange [34, 35] and electrocoagulation/flotation processes [18]. Electrochemical treatment of nitrite using stainless steel electrodes [1], iridium-modified carbon fibre electrodes [16] and BDD anode electro-oxidation [17] is investigated. Photochemical oxidation of nitrite using  $\text{TiO}_2/\text{Ti}$  rutile form [48] and anodic oxidation of nitrite ion using 'in situ' electro-generated  $\text{HClO}$  in a  $\text{NaCl}$  aqueous (Chou, 1999) are investigated. A patent with name ALGONE is existing for the extraction of nitrites from marine aquarium.

Besides the techniques listed above, the adsorption methods have been recognized as most efficient technique because of their easy operations, effectiveness, low-costs and low-sludge formation. Various adsorbents are developed for the removal of toxic pollutants from contaminated water and reported in previous papers [5–8, 30]; [44, 45]. Mesoporous silica functionalized with 1-naphthylamine, 4-nitro-1-naphthylamine and BINOL are found to be effective in identifying and removing nitrite from polluted water [14, 30].

The adsorption methods-based ion materials derived from plants are attracting the researchers, as they are simple, effective, eco-friendly and economical. Further, they are based on bio-materials that are abundantly available and are renewable. These materials have high porosity, high surface area, specific functionality, stability and are regenerated without deterioration in their performances up to three/four cycles. The preparation of bio-sorbents does not involve any toxic chemicals/solvents and the materials obtained are eco-friendly and bio-compactable. Therefore, plant-based bio-materials are proving to be effective sorbents for the removal

of pollutants from waters [15, 46, 50]. Adsorbents derived from *Azadirachta indica* plant [57], *Calotropis zygantia*, *Azadirachta indica* and *Eichhornia* [55] and *Phyllanthus neruri* plant [58] and sepiolite and its powdered activated carbon [41] are investigated for the removal of nitrites from wastewater.

While we are investigating various plant materials for their affinity for toxic ions, we noticed that stem powder and  $\text{H}_2\text{SO}_4$ -generated active carbons of *Sesbania grandiflora* and *Amorphophallus paeoniifolius* exhibit strong affinity for nitrite ions. Hence, in this investigation, the stem powders of the said plants and  $\text{H}_2\text{SO}_4$ -generated active carbons are investigated as adsorbents for nitrite removal. Various extraction conditions, namely, pH, time of contact between the sorbent and nitrite solution, sorbent concentration, initial nitrite (adsorbate) concentration, temp., co-ions, etc., are investigated and optimized for the maximum nitrite removal. Thermodynamic parameters are evaluated. Kinetic and adsorption isotherms are analysed. These bio-sorbents possess good adsorptivities for nitrite ions and selectively and effectively remove nitrite from contaminated water.

## 2 Materials and methods

### 2.1 Chemicals and reagents

Pure A.R. chemicals were procured from Merck, India. Simulated nitrite stock solution of concentration 500.0 mg/L was prepared by dissolving requisite amount of A.R.  $\text{NaNO}_3$  in distilled water. It was diluted as per requirement. The reagents sulphanic acid,  $\alpha$ -naphthylamine and sodium acetate (2 M) were prepared as per literature [4, 63].

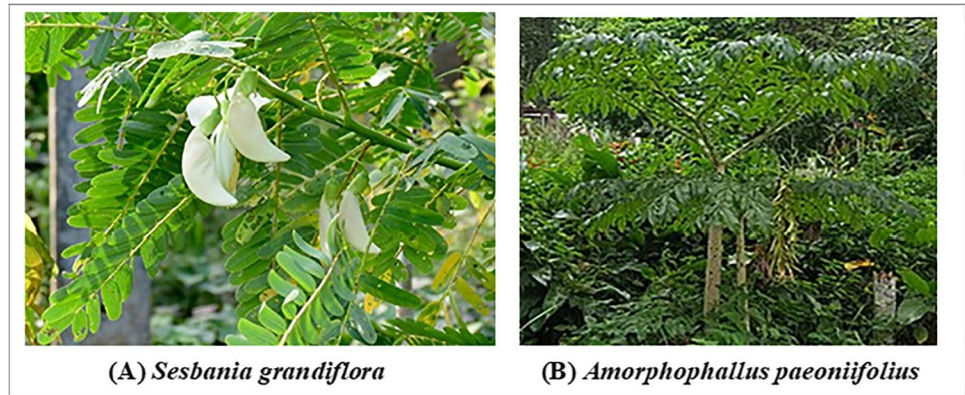
### 2.2 Adsorbents

We carried out preliminary investigations to identify the plant/plant material that had affinity for nitrite ions so that they could possibly be developed as adsorbents for the removal of nitrite from wastewater. Bio-materials of *Sesbania grandiflora* (Fig. 1A) and *Amorphophallus paeoniifolius* (Fig. 1B) were shown strong adsorptivity for nitrite ions.

*Sesbania grandiflora* (trivial name vegetable of hummingbird), Fig. 1A, is a small tree in the genus *Sesbania* and belongs to Fabaceae family of plant kingdom Plantae. It grows well in hot humid atmosphere to a height of 3 to 8 m and it is common plant in South East Asia. Its bio-materials are used in traditional medicines.

*Amorphophallus paeoniifolius*, Fig. 1B (trivial name elephant foot yam), is a tuber vegetable plant and is grown in tropical atmosphere especially in South Asian and African

**Fig. 1** **A** *Sesbania grandiflora*.  
**B** *Amorphophallus paeoniifolius*



countries. It belongs to genus *Amorphophallus*, family Araceae, kingdom Plantae.

### 2.2.1 Preparation of adsorbents

**Raw stem powder.** The stem of *Sesbania grandiflora* and *Amorphophallus paeoniifolius* plants were fragmented, washed with distilled water and dried in hot-air oven at 103 °C for 1 h. Then the bio-materials were powdered to a size of < 75 µm. Then the materials were preserved in air-tight brown bottles. Thus, obtained stem powders of *Sesbania grandiflora* and *Amorphophallus paeoniifolius* plants are named as SGSP and APSP, respectively.

### 2.2.2 Active carbons

Requisite amounts of SGSP and APSP were taken into a suitable size round-bottom flasks and to them, needed quantities of conc. H<sub>2</sub>SO<sub>4</sub> were added until the material was fully immersed. Then reflux condensers were set up to the round-bottom flask. The material in the flasks was refluxed for digestion for 3 h until all the material was completely carbonized. Then materials were taken out from the flasks, diluted with water, filtered and washed the activated carbons for neutrality with water. Then the materials were dried at 105 °C in hot-air oven and preserved in air-tight brown bottles. Thus, active carbons obtained from SGSP and APSP were named as SGSAC and APSAC, respectively.

## 2.3 Adsorption studies

Batch modes of extractions were adopted using simulated nitrite solutions [60]. Extraction conditions were investigated and optimized for the maximum nitrite removal using SGSP, SGSAC, APSP and APSAC [58].

**Procedure** One hundred millilitres of simulated nitrite ion solutions of conc. 50.0 mg/L were taken into 250-mL iodine flasks. To each flask, known quantities of SGSP, SGSAC, APSP or APSAC were added. Initial pHs of solutions were adjusted with dil HCl/dil NaOH. Then solutions were shaken at 350 rpm in orbital shaker for desired time at room temperature. Then the solutions were filtered.

The residual nitrite content was estimated spectrophotometrically adopting ‘sulphanilic acid–α-naphthylamine method’ as described by Vogel [63]. By using the following equations, the adsorbed amounts of adsorptivity of nitrite ( $q_e$ ) and % nitrite removal were calculated:

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

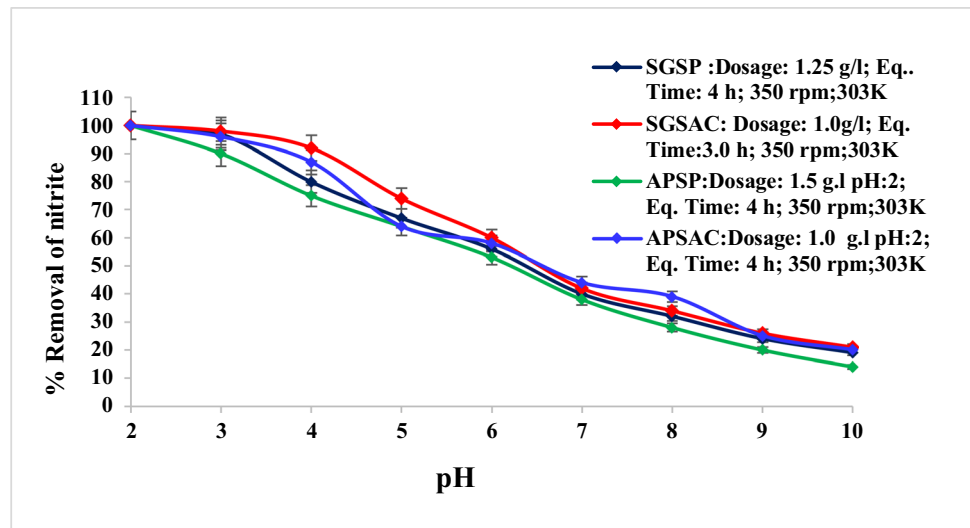
$$\% \text{removal} (\%R) = \frac{(C_i - C_e)}{C_i} \times 100$$

where  $C_i$ =initial nitrite concentration;  $C_e$ =equilibrium nitrite concentration;  $V$ =volume of solution (in litres) and  $m$ =mass of sorbent (g) [58].

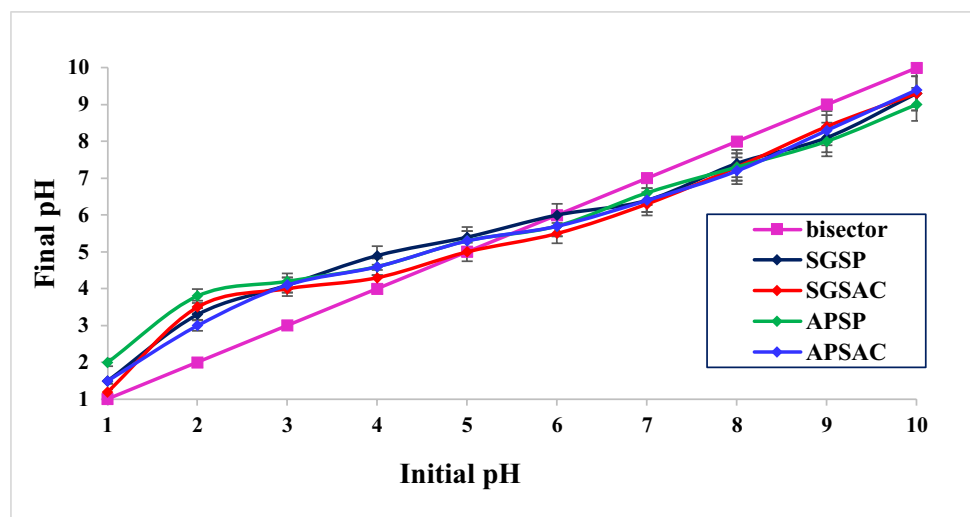
The influences of solution pHs, dosage of adsorbent, time of contact between the sorbent and nitrite solution, initial nitrite concentration, co-ions and temperature on the adsorptivity of SGSP, SGSAC, APSP and APSAC were assessed adopting the above described method. In assessing the nitrite adsorptivity of SGSP, SGSAC, APSP and APSAC, the targeted parameter was progressively changed while all other parameters were kept at optimum and constant levels [52, 57, 58]. The obtained results were presented in Figs. 2, 3, 4, 5, 6, 7, 8 and 9 and Tables 1, 2, 3 and 4.

The inference caused by two-fold excess of co-ions was investigated by using simulated solutions having two-fold excess of concentration of co-ions than nitrite ions concentration. The results were presented in Table 1. SGSP, SGSAC, APSP and APSAC were applied to remove nitrite from polluted lake water samples collected in the Tenali Mandal of Guntur District of A.P. The findings were noted in Table 5.

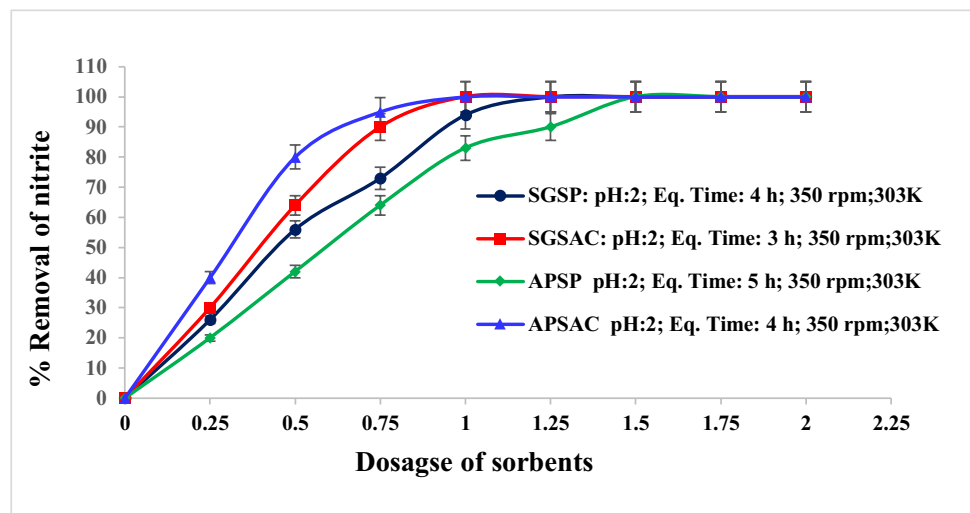
**Fig. 2** pH vs removal of nitrite (conc. of nitrite: 50.0 mg/L)



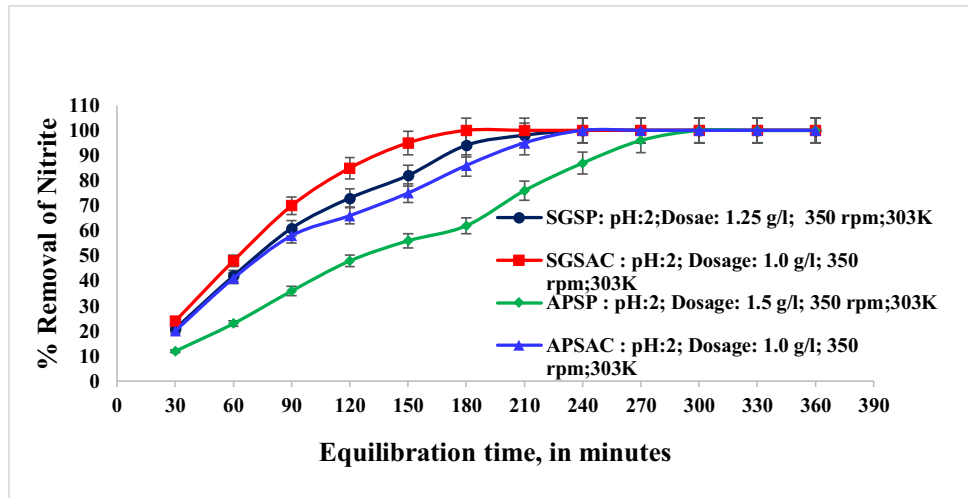
**Fig. 3** pHzpc evaluation for the sorbents



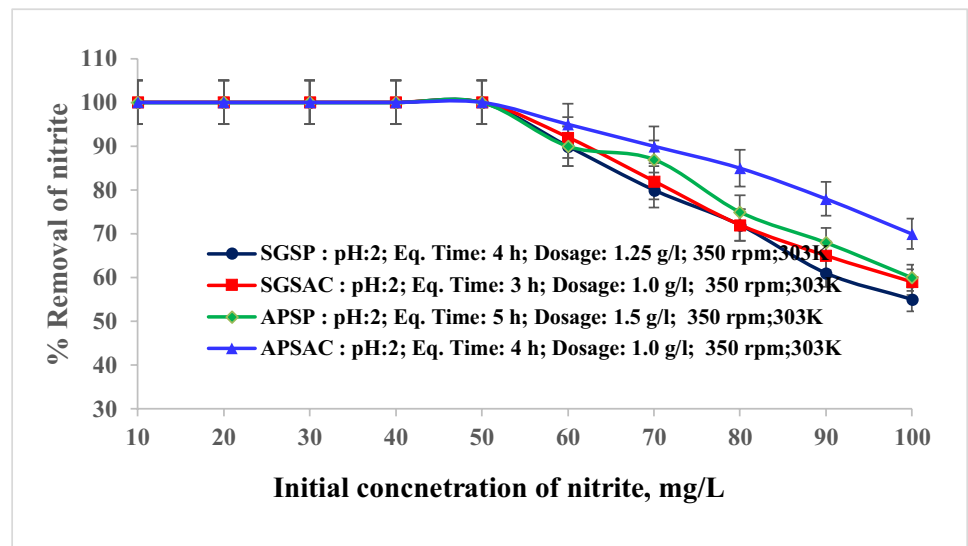
**Fig. 4** Effect of dosage of adsorbents (concentration of nitrite: 50.0 mg/L)



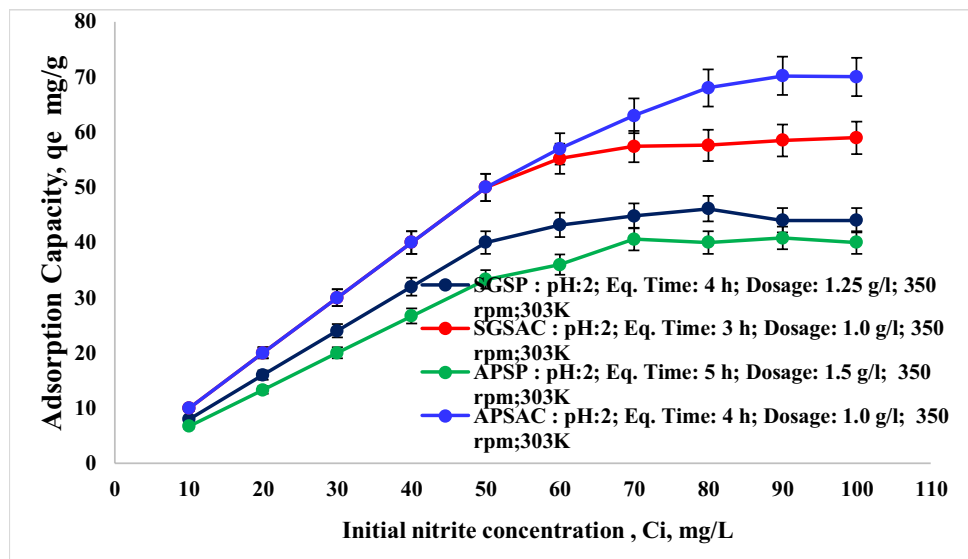
**Fig. 5** Effect of equilibration time on % removal of nitrite



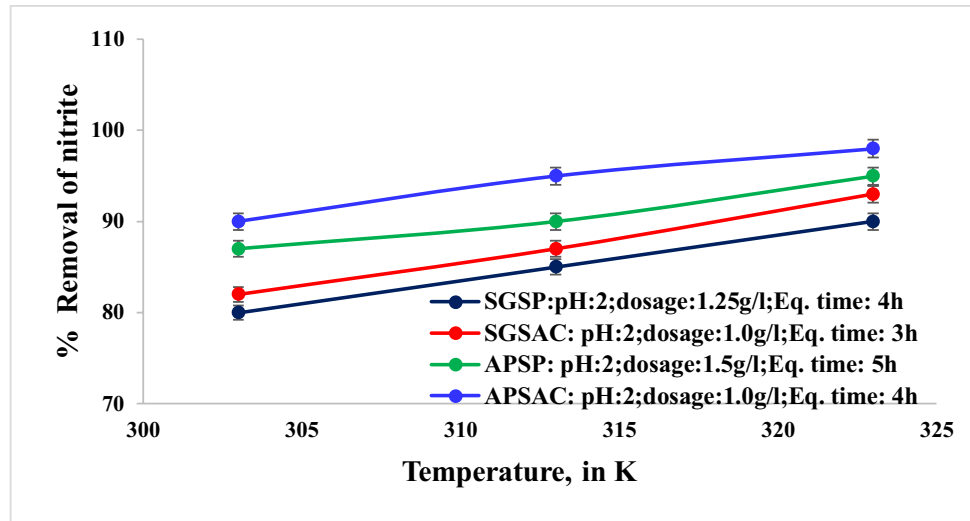
**Fig. 6** Effect of initial concentration of nitrite on % removal of nitrite



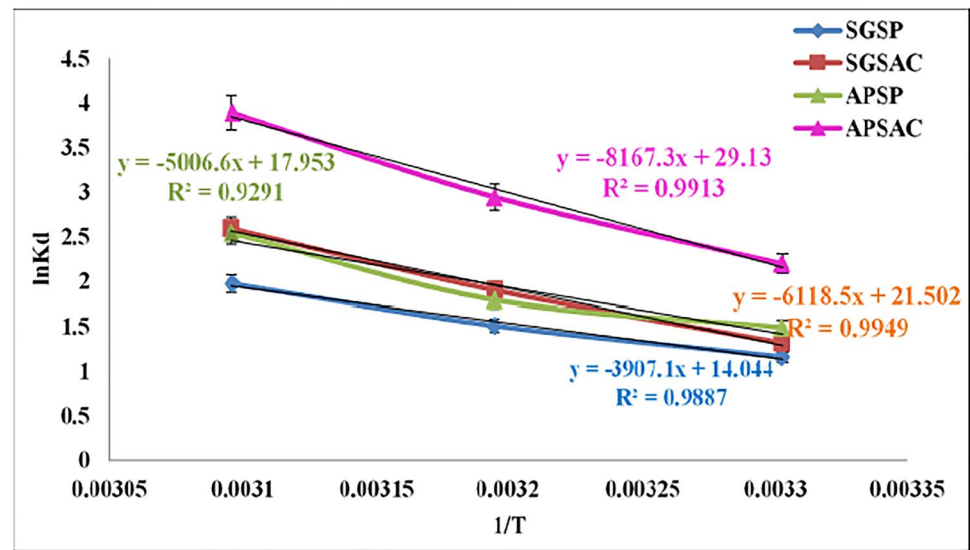
**Fig. 7** Initial concentration vs adsorption capacity,  $q_e$



**Fig. 8** Effect of temperature on % removal of nitrite (initial nitrite conc.: 70 mg/L)



**Fig. 9** 1/T vs lnKd



**Table 1** Effect of two-fold excess of co-ions on % of nitrite removal

S. no	Sorbents	% removal + extraction conditions	Nitrite extraction* (values are average of 5 estimations) (in percentage)									
			SO <sub>4</sub> <sup>2-</sup>	HPO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	F <sup>-</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Fe <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>
1	SGSP	100.0%, pH: 2, 4 h, 1.25 g/L	80.1	97.0	95.0	93.6	96.9	98.5	98.6	98.9	97.9	95.5
2	SGSAC	100.0%, pH:2, 3 h, 1.0 g/L	82.0	95.4	97.6	94.0	97.2	99.0	100	99.5	98.0	98.0
3	APSP	100.0%, pH:2, 5 h, 1.5 g/L	78.0	96.0	94.5	96.2	96.0	98.5	99.0	98.5	97.0	99.0
4	APSAC	100.0%, pH:2, 4 h, 1.0 g/L	76.0	95.0	96.5	95.0	98.0	99.4	100	99.0	96.9	97.5

**Table 2** Thermodynamic parameters: nitrite adsorption onto the surface of sorbents

Sorbent	$\Delta H^\circ$ (kJ/mole)	$\Delta S^\circ$ (J/mole)	$\Delta G^\circ$ (kJ/mole)			R <sup>2</sup>
			303 K	313 K	323 K	
SGSP	32.485	116.769	-2.896	-4.0637	-5.2307	0.9887
SGSAC	50.872	178.78	-3.2983	-5.0861	-6.8739	0.9949
APSP	41.627	149.27	-3.6018	-5.0945	-6.5872	0.9291
APSAC	67.907	242.201	-5.4799	-7.9019	-10.3239	0.9913

**Table 3** Freundlich and Langmuir constants with the correlation coefficients

Adsorbents	Freundlich isotherm			Langmuir isotherm			
	Slope	Intercept	R <sup>2</sup>	Slope	Intercept	R <sup>2</sup>	R <sub>L</sub>
SGSP	0.0084	1.6365	0.7590	0.0226	0.0019	0.9901	0.0016
SGSAC	0.0231	1.7295	0.8843	0.0179	0.0025	0.9982	0.0027
APSP	0.0435	1.5428	0.7432	0.0248	0.0017	0.9990	0.0014
APSAC	0.0950	1.7175	0.9325	0.0143	0.0094	0.9760	0.0129

**Table 4** Kinetics of adsorption: pseudo first and second-order constants and correlation coefficients

Adsorbents	Pseudo first-order			Pseudo second-order		
	Slope	Intercept	R <sup>2</sup>	Slope	Intercept	R <sup>2</sup>
SGSP	−0.0502	1.2002	0.9109	1.2004	1.6232	0.9980
SGSAC	−0.0401	0.9775	0.9201	1.4209	1.5833	0.9912
APSP	−0.0523	1.3014	0.9301	1.3102	0.9784	0.9900
APSAC	−0.0602	1.4201	0.9004	1.0923	1.3452	0.9890

**Table 5** Applications

S. no	Sorbent	Extraction conditions	Simulated water (50 mg/L)	Polluted water samples				
				Sample 1* (20 mg/L)	Sample 2* (30 mg/L)	Sample 3* (35 mg/L)	Sample 4* (40 mg/L)	Sample 5* (45.5 mg/L)
1	SGSP	pH: 2, 4.0 h, 1.25 g/L	100%	96.9%	97.2%	96.0%	97.0%	95.6%
2	SGSAC	pH: 2, 3.0 h, 1.0 g/L	100%	100.0%	99.5%	99.0%	99.2%	100.0%
3	APSP	pH: 2, 5 h, 1.5 g/L	100%	96.0%	96.6%	97.0%	95.9%	98.05%
4	APSAC	pH: 2, 4.0 h, 1.0 g/L	100%	100.0%	99.2%	98.9%	98.0%	99.5%

\*Average value of five determinations; standard deviation: 0.0640%

### 3 Results and discussions

The effect of different extraction conditions was investigated and optimized for the maximum extraction of nitrite from water. Initial pH of extracting solutions, time of contact allowed between the sorbent and nitrite solution, initial conc. of nitrite, dosage of sorbents and temperature were studied. The results were noted in Figs. 2, 3, 4, 5, 6, 7, 8 and 9 and Tables 1, 2, 3 and 4.

Initial pHs of solutions have remarkable effect on adsorptivities of the adsorbents for nitrite. Good adsorption is noted for all the sorbents in the pH range 2 to 4 with the maximum removal at pH 2 (Fig. 2). As the pH is increased, the removal is decreased. pHzpc values for the sorbents are 6.0 for SGSP, 5.0 for SGSAC, 6.5 for APSP and 5.4 for APSAC (Fig. 3).

At these pHzpc values, the negative and positive sites in the adsorbents are equivalent and hence, surface of the sorbents is neutral. Above these pHzpc values, the functional groups of these lingo celluloses' materials, viz., -OH, -COOH, etc., are ionized imparting negative charge to the surface of the said sorbents. Below the pHzpc values, the

dissociation of the functional groups is not favoured and even protonation occurs at low pH values. The protonation endows positive charge to the surface of the sorbents. Thus, at low pHs, the surface of the sorbents is positively charged [11]. Nitrite being an anion is strongly held by the positive charged surface of the adsorbents at low pHs of solutions. The adsorption of nitrite ions onto the surface of sorbent was mainly affected by the surface charge of sorbent that was influenced by solution pH. The similar results were observed in the removal of lead ions (Awual et al. 201d). But as the pH is increased, the positive charge is decreased and hence low adsorption of nitrite. At pHs solution above pHzpc, the surface of the sorbents is negatively charged and hence, nitrite undergoes repulsion and so, the adsorbents show least adsorptivity for nitrite ions.

Another factor that was studied and optimized was sorbent dosage. This is the minimum amount of sorbent required for the maximum possible nitrite removal. This aspect was investigated and results were depicted in Fig. 4. The optimum dosages were found to be 1.25 g/L for SGSP, 1.0 g/L for SGSAC, 1.5 g/L for APSP and 1.0 g/L for APSAC for 100% nitrite removal from 50 mg/L nitrite solution.

The high porosity and surface area of the bio-sorbents permit the strong adsorption of the nitrite ions and the amount of adsorbent has significant effect on percent removal. The similar results were reported in the nickel (II) ions treatment in petroleum samples [45].

It is evident from the nature of the curves that with the increase in dosage, adsorptivities of the sorbents towards nitrite are linearly (nearly) increased initially but slow down with further increase of sorbent dosage and have reached steady states at 1.25, 1.0, 1.5 and 1.0 g/L for SGSP, SGSAC, APSP and APSAC, respectively.

As the amount of adsorbent dosage is increased, proportionally sites for adsorption also are increased. So, initially there exists almost a linear relationship between sorbent dosage and adsorptivity. But at large quantities of dosages, the proportionality is lost and even a steady state is reached after certain dosage. Blocking pathways for nitrite to approach to the active sites and/or overlapping and burying of active sites in the matrix of the sorbents may be the reason for less sorption and subsequent 'steady state' [37].

Contact time is another parameter that was investigated and optimized. Contact time is the duration that a nitrite solution is in contact with the sorbents in constant agitation conditions, i.e. in dynamic equilibrium. The adsorption process taking time to attain the equilibrium by the adsorbent which depends on the nature of the functionality [11]. The results of the present investigation were presented in Fig. 5.

The nature of the curves indicates that with the increase in duration of contact between sorbent and nitrite solution, % removal is also increased. The proportionality is linear initially but lost its linearity at high durations of contact and finally, reached a steady state of equilibration after certain time of contact. At the early stage, the adsorption was rapid due to the availability of more active sites on the sorbent surface and then gradually equilibrated at equilibrium stage [11, 12]. The similar observations were reported in earlier [53, 58]. The optimum time needed is observed to be 240 min for SGSP, 180 min for SGSAC, 300 min for APSP and 240 min for APSAC.

As the time of contact between sorbent and nitrite solution is increased, adsorbate has sufficient time to reach to the active sites of sorbents for getting absorbed and hence, nitrite removal is linearly (nearly) related to contact time initially. But with the lapse of time, active sites are progressively used up and only less sites are available for sorption phenomenon and hence, nitrite removal is mellowed. Steady states are reached after certain time of contact and at which, nitrite sorption and desorption rates are equivalent [43]. Another important factor that was studied and optimized was the effect of initial nitrite concentration on adsorptivity of sorbents for nitrite. The experimental conditions and the variation of adsorptivity with respect to change in initial nitrite concentration were depicted in Fig. 6.

From Fig. 6, it may have inferred that nitrite removal was 100% with all the sorbents as the nitrite concentration is varied from 10 to 50 mg/L. After 50 mg/L, % removal is decreased as the initial concentration of nitrite is varied from 50 to 100.0 mg/L. The decrease is from 100 to 55% for SGSP, 100 to 59% for SGSAC, 100% to 60% for APSP and 100 to 70% for APSAC, at the other optimum extraction conditions noted in Fig. 6. For fixed sorbent concentrations, active sites are limited. At low concentrations of nitrite, sufficient number of active sites is available for the nitrite ions for being adsorbed. With the raise in nitrite ions concentration, proportional amount of sites is not available and hence low % removal at high nitrite concentrations. The similar results were observed in the earlier work reported [54, 58].

It is interesting to note the change in adsorption capacities of the sorbents with the raise in initial nitrite concentration, vide Fig. 7. Up to 50 mg/L of initial concentration of nitrite, the linear raise in adsorption capacities with the raise in initial concentration is observed. But the linearity is lost above 50 mg/L for all the sorbents. Steady states are reached with nitrite concentrations: 70 mg/L for SGSP, SGSAC and APSP and 80 mg/L for APSAC.

If the initial concentration of nitrite is increased more and more, concentration gradient between the nitrite concentrations in the bulk of the solution to the nitrite on the surface layers of sorbent also increases more and more. This will result in drifting the nitrite ions towards sorption sites for being adsorbed. Hence, adsorption capacity of the adsorbent is increased with increase in initial nitrite concentration of adsorbate. The similar results were reported in the removal of lead ions from water [11, 12]. The sorbent dosages used are fixed as follows: 1.25 g/L for SGSP, 1.0 g/L for SGSAC, 1.5 g/L for APSP and 1.0 g/L for APSAC and so, fixed number of sorption sites are only available. When all sorption sites are used up, a saturation-like condition is resulted and only marginal enhancement in  $q_e$  values is observed after certain initial concentrations (Fig. 7) [39].

### 3.1 Effect of temperature

The effect of temperature on the adsorptivity of nitrite was studied. The observed data was presented in Fig. 8.

As is seen from Fig. 8 that as the temperature increases, % removal is also increasing. This indicates the endothermic nature of adsorption.

### 3.2 Effect of interfering ions

The interference caused by two-fold excess of co-ions on the % removal of nitrite was investigated. In Table 1, the results pertaining to it were presented.

From the data in Table 1, it may be inferred that the cations and anions except  $\text{SO}_4^{2-}$  have not interfered (in the



extraction of nitrite) when they are in two-fold excess of nitrite concentration.  $\text{SO}_4^{2-}$  has shown interference to some extent but even then, % removal of nitrite has not come down below 76.0%.

### 3.3 Analysis of thermodynamic parameters

The observed adsorption nature was analysed by finding the thermodynamic parameters, namely, change in free energy  $\Delta G^\circ$  (kJ/mole); change in enthalpy  $\Delta H^\circ$  (kJ/mole) and change in entropy  $\Delta S^\circ$  (J/mole). They were calculated using the following equations [47, 51].

$$\Delta G^\circ = -RT \ln K_d; \ln K_d = \Delta S^\circ/R - \Delta H^\circ/RT \text{ and } K_d = q_e/C_e; \text{ and } \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

where  $K_d$  = distribution coefficient;  $q_e$  = amount of nitrite adsorbed;  $C_e$  = equilibrium nitrite concentration;  $T$  = temperature (K) and  $R$  = gas constant.

The results were presented in Fig. 9 and Table 2.

As is evident from the table that change in enthalpy  $\Delta H^\circ$  (kJ/mole) values are positive for all the four sorbents investigated. This indicates the endothermic nature of adsorption for nitrite ions 'onto' the surface of sorbents. The values for all the sorbents are high and are not less than 32.485 kJ/mole (value for SGSP). From this fact, it may have inferred that the adsorption mechanism may be through a sort complex formation or ion exchange and not by mere coulombic interactions of van der Waals nature or hydrogen bonding. Further,  $\Delta H^\circ$  values for the active carbons SGSAC (50.872 kJ/mole) and APSAC (67.907 kJ/mole) are higher than that of the corresponding raw bio-materials SGSP (32.485 kJ/mole) and APSP (41.627 kJ/mole). These high values, both for raw stem powders and active carbons, indicate that the more probable mechanism of adsorption is 'ion exchange'. The monovalent negatively charged nitrite ions are under ion exchange equilibrium with the surface of the sorbents. With respect to SGSAC and APSAC, this mechanism is more probable in view of very high  $\Delta H^\circ$  values.

Change in entropy  $\Delta S^\circ$  (J/mole) values reflect the disorder at the solid/liquid interface of the sorbents with the solution. More disorder at the interface is a favourable condition for the adsorption of the adsorbate. In the present investigation,  $\Delta S^\circ$  for all the adsorbents are positive and this fact indicates the prevailing of disorder at the boundary [37, 50]. Further, the values fall in the order: APSAC > SGSAC > APSP > SGSP and so, is the order of adsorption.

It is interesting to note the  $\Delta G^\circ$  values for the four sorbents for the nitrite adsorption at different temperatures.  $\Delta G^\circ$  values are negative for all the sorbents at all temperatures. This indicates that the adsorption process is spontaneous and endothermic in nature. Greater is the magnitude of  $\Delta G^\circ$ , more is the spontaneity. With the raise in temperature, the values are also increasing. This indicates that the spontaneity

as well as endothermic nature of adsorption process increase with temperature. The magnitude of negative values shows that forces operating between sorbent surface and nitrite ions are strong enough to cross the solid/liquid potential barrier [38, 43].

### 3.4 Adsorption isotherms

The adsorption phenomenon was analysed using linear forms of Freundlich and Langmuir adsorption isotherm equations. Freundlich isotherm (1906) explains the multilayer adsorption over the heterogeneous surface of the adsorbent [2, 51].

$$\log(q_e) = \log k_F + \frac{1}{n} \log C_e$$

Langmuir isotherm (1918) assumes monolayer, homogeneous adsorption on the surface of the adsorbent. At an equilibrium saturation point, no further adsorption takes place after a molecule occupies an active site of the adsorbent surface [51].

$$\frac{C_e}{q_e} = \frac{a_L}{k_L} C_e + \frac{1}{k_L}$$

The important characteristic of the Langmuir isotherm model is expressed in terms of a separation factor,  $R_L$  [15, 46, 57].

$$R_L = \frac{1}{(1 + a_L C_i)}$$

where  $q_e$  (mg/g),  $C_e$  (mg/lit) and  $C_i$  (mg/lit) are the amount adsorbed, adsorbate concentration in solution at equilibrium and adsorbate initial concentration, respectively.  $k_F$  and  $1/n$  are the Freundlich constants.  $k_L$  and  $a_L$  are the Langmuir constants and  $\frac{k_L}{a_L}$  gives the theoretical monolayer saturation capacity,  $q_m$ .

According to Hall et al. [24], the separation factor,  $R_L$  indicates the adsorption nature to be either unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ).

Freundlich and Langmuir isotherm constants were evaluated. These values and correlation coefficients,  $R^2$ , were presented in Table 3.

From the  $R^2$  values, it may be inferred that Langmuir isotherm is better fit model than the Freundlich model. The straight line of the  $C_e/q_e$  vs  $C_e$  plot of this adsorption plot indicated monolayer adsorption of nitrite ions 'onto' the surface of the adsorbents and also uniform distribution of active sites on the surfaces of sorbents. The separation factor values ( $R_L$ ) were in the range between zero and one. These two facts indicated the favourability of the Langmuir adsorption isotherm than the Freundlich isotherm and confirmed

the monolayer and homogeneous adsorption. The similar results were reported in previous papers [11, 12, 45, 57]. These are some of the features for an ion exchange mode of adsorption process.

### 3.5 Kinetics of sorption

The rate of uptake of nitrite ‘onto’ the adsorbent’s surface was studied by pseudo first-order and pseudo second-order models for the investigating four adsorbents.

Pseudo first-order model is based on the presumption that rate of nitrite sorption is directly related the unoccupied sites on the adsorbent. The linear equation of this model is widely used to describe the adsorption of adsorbate from the liquid phase [32].

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

Pseudo second-order model relates to valence forces between adsorbate and adsorbent through sharing or exchange of electrons [27, 31].

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t)$$

where  $q_e$  and  $q_t$  are respectively the amount adsorbed (mg/g) at equilibrium and at time  $t$ ;  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  (g/mg. min) are the rate constants for pseudo first-order and pseudo second-order rate processes. The evaluated data was presented in Table 4.

From the correlation coefficients, it may be understood that pseudo second-order model is better fit to the experimental data than pseudo first order model for explaining the kinetics of adsorption for all the sorbents in view of the fact that the  $R^2$  values of the former are close to unity than the

$R^2$  values of the latter. The similar results were reported in an earlier work [15, 46, 56, 57].

### 3.6 Regeneration studies

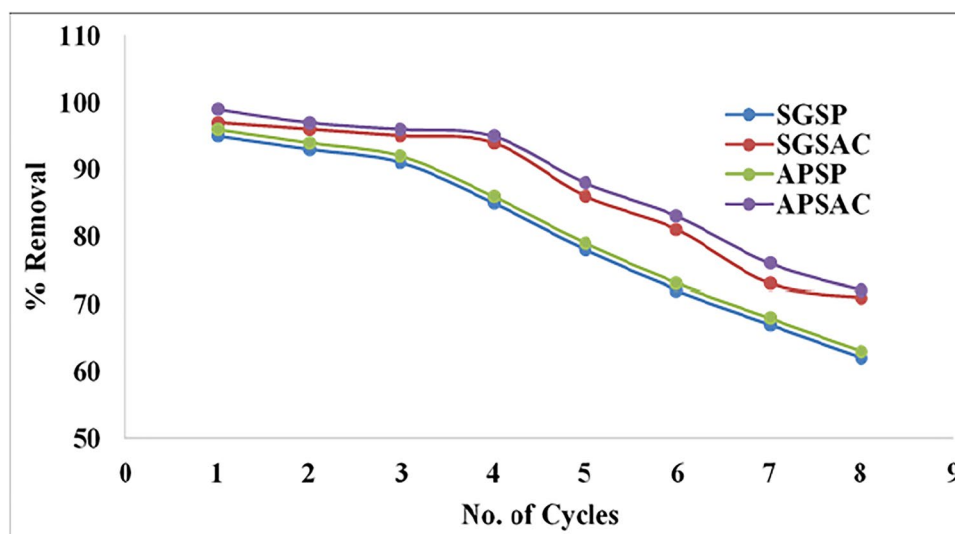
The spent adsorbents were regenerated with various solutions such as acids, bases and salts at different concentrations. An effective regenerating eluent for the used SGSP, SGSAC, APSP and APSAC was 0.1 N HCl. The spent adsorbents were digested overnight in the said solution, filtered, washed with distilled water and dried at 105 °C and re-used as sorbents for the extraction of nitrite ions [15]. Results were presented in Fig. 10.

SGSP and APSP can be used up to 3 cycles while SGSAC and APSAC can be used up to 4 cycles with marginal loss of % of extraction. The decrease in adsorption with the increases in number of cycles of regeneration-cum-reuse may be due to loss and/or non-generation of active sites on the adsorbent’s surface. Some of the active sites may be destroyed during the treatment process.

### 3.7 Applications

The new adsorbents developed in this investigation were applied to purify the nitrite-polluted lake water samples collected from the contaminated lakes in Tenali Mandal of Guntur District, Andhra Pradesh. The samples were treated with the SGSP, SGSAC, APSP and APSAC at the optimum extraction conditions established in this work (vide Table 5 column 2). The results were presented in Table 5. It may be inferred from the table that four sorbents are very effective in removing nitrite from polluted water.

**Fig. 10** Regeneration of spent adsorbents



**Table 6** Comparison of the developed sorbents with the hitherto reported sorbents in the literature

S. no	Sorbent	pH	Adsorbent capacity (mg/g)	Reference
1	Acid treated C-cloth	–	46.7	Afkhami et al. [3]
2	Amine functionalized material	3.5	124.36	Awual et al. [10]
3	Activated carbon derived from rice straw	2–10	8.2	Hanafi and Azeema [25]
4	Organic ligand embedded onto the porous silica	5.5	119.22	Awual et al. [9]
5	Oxidized carbon AG-5	7.0	0.9053	Gierak and Lazarska (2017)
6	Carbon AG-5	7.0	0.3665	
7	Sepiolite	–	0.65	Ozturk and Kose [41]
8	Powder activated carbon	–	1.17	
9	Fe-HT3.0	4–12	30.1	Ogata et al. [40]
10	Fe-HT5.0	4–12	28.0	
11	OSC/ZnCl <sub>2</sub> C/450 (AC no. 7)	4.0	7.0	Hiba Nassar [26]
12	CAC	4.0	2.0	
13	Ligand-based conjugate materials	4.0	135.21	Kamel et al. [30]
14	SGSP	2.0	44.5	Present work
15	SGSAC	2.0	57.5	
16	APSP	2.0	40.0	
17	APSAC	2.0	65.5	

### 3.8 Comparison

The developed adsorbents in this investigation were compared with the different good adsorbents reported in the literature with respect to adsorption capacity values (Table 6). As seen from the table, the present developed sorbents have good sorption capacities than many reported in the literature.

The merit of the present work is that highly toxic nitrite ions can be easily removed by simple bio-materials with low sorbent concentrations at optimum conditions of extraction established in this investigation. Complete nitrite removal from 50 mg/L nitrite simulated solution can be achieved with adsorbent dosages: 1.25 g/L for SGSP, 1.0 g/L for SGSAC, 1.5 g/L for APSP and 1.0 g/L for APSAC. With real nitrite polluted water samples, more than 95.5% extraction of nitrite was observed. All these facts confirm the effective applicability of these sorbents in wider perceptive.

## 4 Conclusions

In the present investigation raw stem powders and active carbon derived from *Sesbania grandiflora* and *Amorphophallus paeoniifolius* plants are investigated for their abilities to remove highly toxic nitrite ions from polluted water. Active carbons are generated by digesting with conc. H<sub>2</sub>SO<sub>4</sub>. Different extraction conditions (pH, contact time, adsorbent concentration, initial nitrite concentration, temperate) have been investigated and optimized for the maximum nitrite removal. Two-fold excess of common cations except sulphate are not

interfering. Even in the presence of two-fold excess of sulphate, the % of removal nitrite has not come down below 75%.

Adsorption capacities are found to be 44.5 mg/g for SGSP, 57.5 mg/g for SGSAC, 40.0 mg/g for APSP and 65.5 mg/g for APSAC. These adsorption capacities are higher than many reported in literature using bio-sorbents.

Thermodynamic parameters are evaluated and observed high values of  $\Delta H^\circ$  especially for SGSAC (50.872 kJ/mole) and APSAC (67.907 kJ/mole). The magnitude of  $\Delta H^\circ$  values indicates ion exchange mode of sorption. Negative values of  $\Delta G$  reflect the spontaneous and endothermic nature of sorption for the said four adsorbents for the adsorbate, nitrite. Positive values of  $\Delta S$  emphasizes some degree of disorder at solid/liquid interface and this is an ideal condition for more adsorption of the adsorbate. The values fall in the order: APSAC > SGSAC > APSP > SGSP and so, is the order of adsorption.

Adsorption phenomenon is evaluated by Langmuir and Freundlich isotherm models. Langmuir isotherm model fits well for all the four sorbents. This indicates monolayer formation of nitrite on the surface of sorbents and further, the homogeneous distribution of active sites. Kinetics of adsorption is also analysed by pseudo first and second-order equations. Pseudo second-order fits well for all the sorbents. This indicates that the adsorption is through exchange of electrons or sharing of electrons between nitrite and sorbents. Spent adsorbents can be reused after treating with 0.1 N HCl. The adsorbents are effectively applied for removing nitrite ions from polluted lake water samples. The merit of

present investigation is that simple and effective sorbents (derived from plant materials) with good sorption capacities are developed for the removal of the toxic nitrite ions from polluted water.

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