Nano-composite cation-exchanger polyvinyl alcohol Sn(IV) tungstate

Preparation, characterization, thermodynamic study and its analytical application for the adsorption of aniline

Ali Mohammad · Inamuddin · Arshi Amin

Abstract The thermodynamics of aniline adsorption from aqueous solution on polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger was studied. The nano composite cation-exchanger was prepared by surfactant assisted sol–gel precipitation method and characterized to elucidate the morphology, particle size, crystallinity and structure using SEM, TEM, X-RAY and FTIR. The nano composite cation-exchanger possessed flakes like morphology with particle size in the nano range. The analytical applicability and thermodynamic parameters like ΔH, ΔG and ΔS of this nano composite were also calculated. The thermodynamic parameters showed that the adsorption of aniline onto nano composite cation-exchanger is feasible, spontaneous and exothermic.

Keywords Nano-composite · Cation exchanger · Polyvinyl alcohol · Sn(IV) tungstate · Thermodynamics · Aniline

Introduction

Nitrogen containing organic compounds, specially aniline and its derivatives are the most widely used raw materials and intermediate chemicals in manufacturing of pesticides, herbicides, rubber, dyestuff, varnishes, organic paints and pigments, azo dyes, pharmaceuticals, petrochemicals and other industries [1, 2]. Consequently, they are entering directly as partially or untreated industrial residue or indirectly as breakdown products of various organic compounds into water bodies causing environment pollution. These are considered to be very toxic water pollutants even in very low concentration to aquatic life and human beings [3–6]. They can exist either as non-dissociated or dissociated species in aqueous solutions [4]. Due to their relatively higher solubility, they can seep through soil and contaminate ground water [7]. Aniline has been found in drinking and surface water [8]. Hence, there is a huge probability to join the food chain consequently causing the persistent diseases in human body. A number of environmental protection agencies have included aniline in the list of hazardous pollutants and have taken concern to restrict their untreated discharge into public sewers, rivers, sea and on land. Due to negative impact of aniline on environment and its derivatives in wastewater, various methods such as biological degradation [9–13], catalytic oxidation process [14–17], electrochemical techniques [18], irradiation treatment [19], adsorption [4–6, 11, 20–22] and other methods [16, 23–25] have been proposed for the successful removal of aniline compounds from wastewater. Among these methods, adsorption is one of the most attractive, cost effective, simple and widely used technique for the treatment of wastewater. The adsorption process is primarily focused on the use of activated carbon as adsorbent, due to large surface area and predominant proportion of mesopores [26]. Nowadays, composite materials specially, nanomaterials, are considered as alternatives to activated carbon for efficient removal of specific organics from contaminated wastewater, due to their large surface area and mechanical strength [27–35]. The adsorption properties of nanomaterials depend upon the particle size and surface morphology of composite. Controlling anisotropic behaviour of composite materials at the nanoscopic level is one of the most challenging issues for the material scientists.

In this study, composite cation-exchanger having particle size in the range of 24–47 nm was prepared by sol–gel

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method. The composite cation-exchanger was used as adsorbent to remove aniline from wastewater and aniline adsorption isotherm was studied.

Experimental

Reagents and chemicals

The main chemical reagents such as stannic chloride, $SnCl_4 \cdot 5H_2O$ (95%), polyvinyl alcohol, sodium tungstate, $Na_2WO_4 \cdot 2H_2O$ (98%) and N-Cetyl-N,N,N-trimethyl ammonium bromide, $C_{19}H_{42}BrN$ (CTAB) (99%) used for the synthesis of the nano composite material were obtained from Central Drug House (CDH) Pvt. Ltd., India. Aniline, $C_6H_5NH_2$ (99%) was obtained from E. Merck, India. The other reagents and chemicals used were of analytical reagent grade and were used without any further treatment.

Instruments/apparatus used

A transmission electron microscope (TEM) and scanning electron microscope (SEM) (Leo 435 VP, Australia) were used to examine the surface morphology and the particle size of the composite material.

An X-ray diffractometer (Phillips, Holland) model PW 1148/89 with Cu Kα radiations) was used to characterize the nature of nano composite material. A water bath incubator shaker (Narang Scientific Works Pvt. Ltd., India) having temperature variation of ± 2 °C was used for all equilibrium and temperature controlled studies. A digital pH metre (Elico LI-10, India) was used to adjust the pH of the solutions. A magnetic stirrer (Macro Scientific Works, India) was used for the mixing during the preparation of the nano composite material.

Fourier transform infra red (FTIR) spectroscopic spectra in the range 450–4500 cm^{-1} was recorded on Fourier transform infra red spectrophotometer (Perkin Elmer spectrum-BX, USA). Thermogravimetric analyser (Perkin Elmer TGA) system of type TGA-7 was used to carry out TG analysis of composite material in the temperature range from 60 to 870 °C at heating rate of 20 °C min^{-1}.

Experimental studies

Preparation of polyvinyl alcohol Sn(IV) tungstate nano composite cation exchange material

In this study, nano composite cation exchange material polyvinyl alcohol Sn(IV) tungstate was prepared by using sol–gel precipitation technique. Precipitates of inorganic counter part i.e. Sn(IV) tungstate of composite material was prepared by mixing 0.1 M stannic chloride solutions

($SnCl_4 \cdot 5H_2O$) dissolved in 2 M HCl with aqueous solution of 0.1 M sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) in different mixing volume ratios at room temperature (25 ± 2 °C). The resultant solutions were mixed thoroughly using magnetic stirrer for 5 min. Fine light yellow precipitates of Sn(IV) tungstate were obtained, when pH of the solution was adjusted to 1 by adding aqueous ammonia/hydrochloric acid with constant stirring.

Subsequently, 5 mL of N-cetyl-N,N,N trimethyl ammonium bromide (CTAB) was added in each precipitates of Sn(IV) tungstate and were stirred for 10 min. Finally, 2 g of polyvinyl alcohol dissolved in 20 mL of demineralised water (DMW) was added in each precipitates of Sn(IV) tungstate with constant stirring. The resultant polyvinyl alcohol Sn(IV) tungstate gels were stirred for 2 h and kept for 24 h at room temperature (25 ± 2 °C) for digestion. The supernatant liquid was decanted and washed with DMW to remove excess acid till the pH of washing was ~ 4. The washed gels were dried over P_4O_{10} at 40 °C in an oven. The dried product was washed again with acetone to remove impurities present in the material, and dried at 40 °C in an oven. The nano composite cation exchanger carries fixed tungstate ionic groups which are converted into H^+/counter ion form by treating with 1 M HNO_3 for 24 h with occasional shaking and intermittently replacing the supernatant liquid with fresh acid 2–3 times. The excess acid was removed after several washings with DMW and finally dried at 50 °C in an air oven. The nano composite cation exchanger was cracked and the particle size of approximately 125 μm was obtained by sieving and stored in desiccators. The ion exchange capacity was determined as usual by standard column process. For this purpose, one gram (1 g) of the dry cation-exchanger samples in the H^+-forms were taken into different glass columns having an internal diameter (i.d.) ~ 1 cm and fitted with glass wool support at the bottom. The bed length used was approximately 1.5 cm long. Approximately, 250–300 mL of 1 M $NaNO_3$ as eluent was used to elute the H^+ ions completely from the cation-exchange columns, maintaining a very slow flow rate (~ 0.5 mL min^{-1}). Since the extent of elution was found to depend upon the concentration of the eluent, the optimum concentration of the eluent for a complete elution of H^+ ions using 250 mL $NaNO_3$ solution was found to be 1 M. The effluents, thus obtained by the above process, were titrated against a standard 0.1 M NaOH solution for the total ions liberated in the solutions using phenolphthalein indicator, and the ion-exchange capacities in meq dry g^{-1} are determined. The conditions of the preparation, the ion-exchange capacity, and the physical appearances of the organic, inorganic and composite cation-exchangers are given in Table 1. On the basis of ion-exchange, capacity sample (S-6) was selected for characterization and further studies.

Table 1 Conditions for the preparation of polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger

Samples	Mixing volume ratios (V/V)			Polyvinyl alcohol added/g	Colour of beads obtained after drying	Na^+ ion exchange capacity/meq dry g^{-1}
	0.1 M $SnCl_4 \cdot 5H_2O$ in 2 M HCl	0.1 M $Na_2WO_4 \cdot 2H_2O$	pH			
1	1	0.5	1	2	Dull white	0.65
2	1	1	1	2	Light brown	0.79
3	1	1.5	1	2	Dull green	0.87
4	1	2	1	2	Dull green	0.69
5	1	3	1	2	Dull white	1.19
6	1	4	1	2	Light brown	1.45
7	1	4	1	–	Dull white	0.75

Adsorption equilibrium and thermodynamics study

Batch technique was selected to study the equilibrium and thermodynamics for the adsorption of aniline onto the surface of polyvinyl alcohol Sn(IV) tungstate nano composite cation exchange material (S-6). A stock solution of aniline was prepared by dissolving 0.1 N of aniline in distilled water. The solution was further diluted to get the desired concentrations. A 0.5 g of polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger was added in various stoppered conical flasks, each containing 20 mL of aniline solutions of different concentrations ranging from 10×10^{-3} to 22.5×10^{-3} N at three different temperatures viz. 35, 50 and 65 °C. The equilibrium time was measured at different contact duration ranged between 2 and 24 h and at a fixed temperature 25 °C. Each mixture was shaken for 6 h, to attain equilibrium Fig. 1. The nano-composite cation exchange material was filtered off and the supernatant liquid for the residual concentration of aniline was analysed titrimetrically [36]. Initial concentrations of aniline prior to nano composite cation exchanger mixing were also analysed in the similar manner.
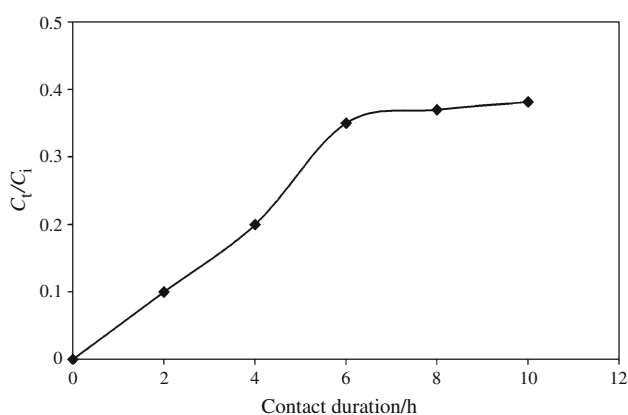

Fig. 1 A plot of time versus the ratio between the aniline concentration at a given moment (C_t) and initial aniline concentration (C_i) for the determination of infinite time of exchange

Results and discussion

A number of samples of polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger were prepared via surfactant assisted sol–gel precipitation method. The required conditions for the preparation of nano composite cation exchanger and the ion exchange capacity are given in Table 1. It was noted that the ion exchange capacity of nano composite cation exchanger was found to be higher as compared to parent counterpart i.e. inorganic ion exchanger Sn(IV) tungstate and organic polymer polyvinyl alcohol. The remarkable increase in the exchange capacity of the synthesized nano composite cation-exchanger may be attributed to the binding of organic polymer with inorganic moiety. The most attractive feature of this cation exchanger is the creation of organic–inorganic nano composite which enhances the ion exchange capacity. Nano composite possesses large surface area and hence it may contribute towards the better adsorption of aniline.

SEM image of polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger (S-6) is shown in Fig. 2. It has flakes like morphology with high surface area suitable for adsorption process. Thus, this nano composite cation-exchanger possessed large surface area for the enhanced adsorption. Transmission electron microscope (TEM) image (Fig. 3) of composite cation-exchanger showed that most of the particles of this composite cation exchanger are spherical in shape with size in the range of 24–47 nm.

The XRD pattern of the nano composite cation exchanger (S-6) is shown in Fig. 4, it showed very small peaks of 2θ values. The XRD pattern reveals that the particles are nano sized and semi-crystalline in nature. In addition, the wide peaks indicate the average crystalline size of the nano composite cation exchanger [37]. The broadening of the peaks in the XRD pattern may be due to the micro straining of the crystal structures arising from the defects like dislocations and twinning [38].

FTIR spectrum of as prepared polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger (S-6) is shown
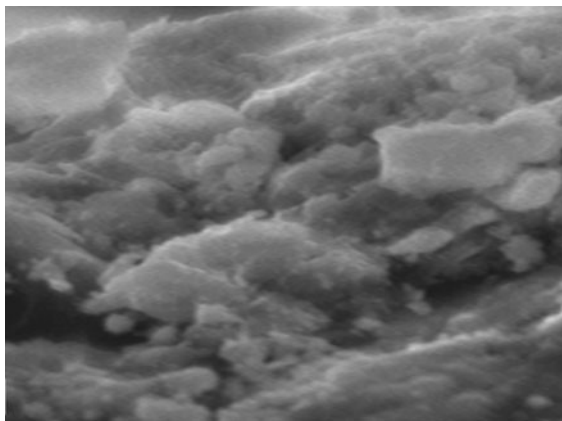
Fig. 2 SEM image of the polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger
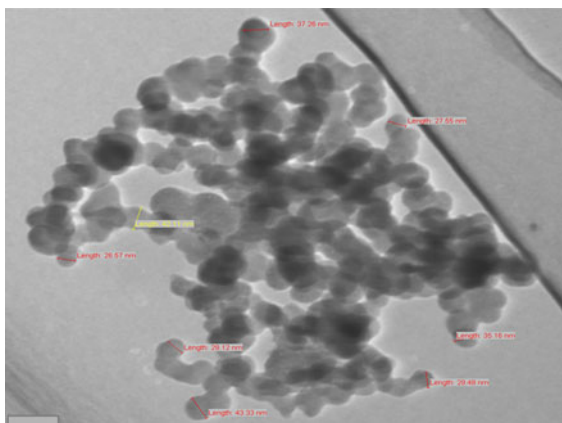

Fig. 3 TEM image of the polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger
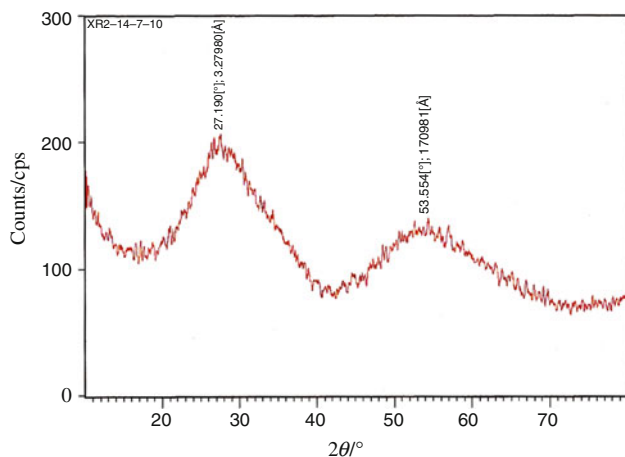

Fig. 4 Powder X-ray diffraction pattern of polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger

in Fig. 5. FTIR spectrum of the nano composite cation exchanger shows the characteristic absorption peaks attributed to the presence of organic polymer polyvinyl alcohol, external water molecule, in addition to –OH groups and metal oxygen bonds.

In the spectrum of composite material, the broad absorption peak at 3419 cm^{-1} indicates to the stretching vibrations of hydroxyl (–OH) groups [39] and peaks at around 2925 cm^{-1} and 2850 may be due to C–H stretching [40, 41]. The broadness of the peaks may be assigned due to the presence of intermolecular and intra-molecular hydrogen bonds [42]. The sharp absorption band around 1620 cm^{-1} confirms the presence of water of crystallization. The band around 1409 cm^{-1} is assigned to –CH$_2$ scissoring, while the broad band around 1093 cm^{-1} is ascribed due to the presence of CHO–CH$_2$ stretching of secondary alcoholic groups, O–H in plane bending vibrations coupled [42]. An assembly of two sharp peaks in the region 791–639 cm^{-1} may be due to the presence of metal oxygen bond [43].

From the thermogravimetric analysis curve of this nano composite (Fig. 6), it is observed that the loss of mass (about 2.77%) up to 126.52 °C may be due to the removal of external water molecule present at the surface of the material [44]. A slow mass loss ($\sim$8.33%) observed in between 126.52 and 200.86 °C may be due to the removal of interstitial water molecules by condensation of –OH groups together with external water molecules from the materials. A loss of mass ($\sim$1.38%) observed in between 200.86 and 302.6 °C may be due to the condensation of phosphate to pyrophosphate groups [44, p. 330]. Further, loss of mass ($\sim$6.94%) between 302.6 and 510 °C may be due to complete decomposition of organic part of the composite material. From 510 °C onwards, a smooth horizontal section represents the complete formation of oxide of the material. The total loss of mass ($\sim$19.650%) is comparatively lower than other composite materials of this class, which indicates towards the better thermal stability of this composite cation-exchanger. The structural transformations observed by TG analysis have also been supported by differential thermal analysis (DTA). The DTA curve showed two endothermic peaks with maxima at 126.52 and 200.86 °C. The first endothermic peak corresponds to the removal of hydrated water and second peak at $\sim$200 °C is due to glass transition temperature, T_g, of polyvinyl alcohol. There is a shift of temperature of polymer composite as compared to the pure polyvinyl alcohol [45].

In the adsorption process of a solute from solution onto a solid surface, the solute adsorbed on the solid surface is in a dynamic equilibrium with the solute remained in solution. Therefore, Freundlich adsorption isotherm for the adsorption of aqueous aniline on the solid surface of synthesized nano composite cation exchanger at three different temperatures viz. 35, 50 and 65 °C was used to understand the mechanism of adsorption and also in analysing the distribution of aniline in aqueous phase and the solid cation exchanger phase at

Fig. 5 FTIR spectrum of polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger
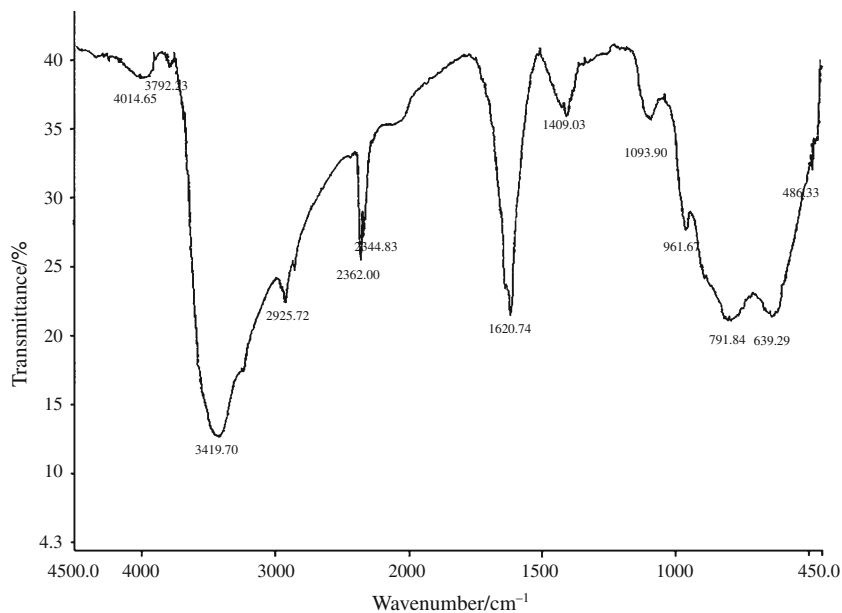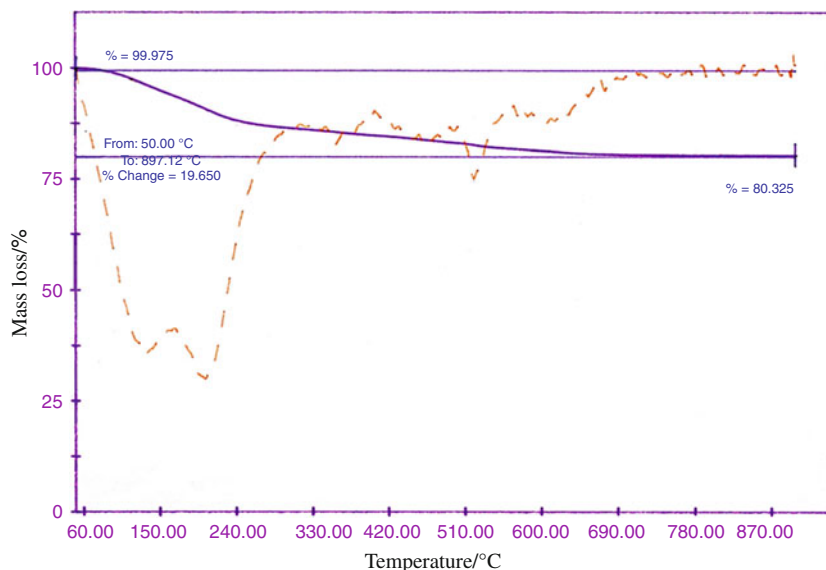

Fig. 6 TG-DTA analysis of polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger

equilibrium. The adsorption isotherms are shown in Fig. 7. All isotherms follow adequately Freundlich adsorption behaviour and can be represented by the equation:

$$x/m = KC^{1/n} \tag{1}$$

where, x/m is the surface concentration of aniline in mmol g^{-1} of the nano composite cation exchanger represented as C_s, C is the equilibrium concentration of aniline (m mol mL^{-1}) in the solution represented as C_e. K and $1/n$ are the constants determined from the intercepts and slopes of the starting lines, respectively, fitted to the points by the least squares method. According to this equation. plots of log C_s versus log C_e are straight lines at all three temperatures Fig. 7, and the values

obtained are listed in Table 2. The values of $1/n$ lying between 0 and 1 confirm the favourable conditions for the adsorption of aniline [46]. Aniline adsorption capacity and adsorption intensity can be measured by the values of K and $1/n$, respectively. The applicability of Freundlich adsorption isotherm for the adsorption of aniline on the solid surface of nano composite cation exchanger is confirmed by the higher value of regression coefficient, R.

Thermodynamic parameters were calculated from the variation of the thermodynamic equilibrium constant K_o (or sorption distribution coefficient) with the change in temperature. The constant, K_o for the adsorption reaction can be defined as follows:
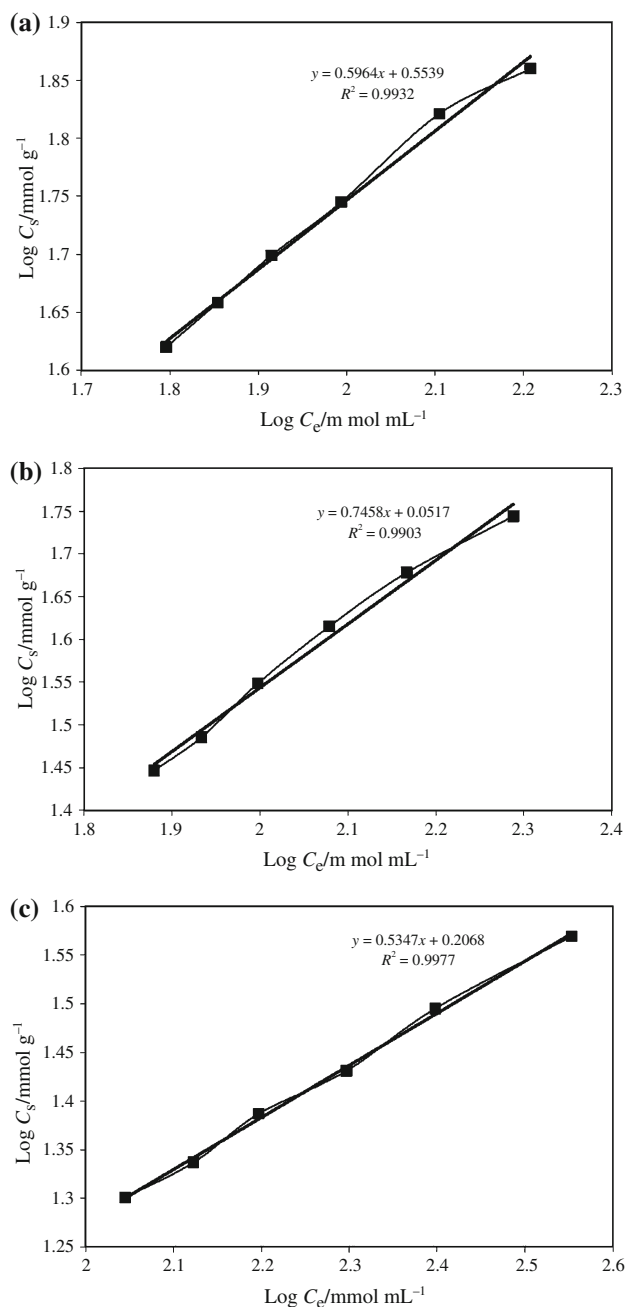
(a)

(b)

(c)

Fig. 7 Freundlich adsorption isotherms of aniline adsorption at temperatures 35 °C (**a**), 50 °C (**b**) and 65 °C (**c**) on polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger

$$K_{\mathrm{o}} = \frac{a_{\mathrm{s}}}{a_{\mathrm{e}}} = \frac{v_{\mathrm{s}} C_{\mathrm{s}}}{v_{\mathrm{s}} C_{\mathrm{e}}} \tag{2}$$

where a_{s} is the activity of aniline adsorbed on the surface of nano composite cation exchanger, a_{e} is the activity of aniline in solution at equilibrium, C_{s} is the surface concentration of aniline in mmol g^{-1} of exchanger, C_{e} is the concentration of aniline at equilibrium (mmol mL^{-1}), v_{s} is the activity coefficient of the aniline adsorbed and v_{e} is the activity coefficient of aniline in solution.

Table 2 Freundlich isotherm constants K and $1/n$ for the adsorption of aniline on polyvinyl alcohol Sn(IV) tungstate composite cation-exchanger

Freundlich constant	Temperature/°C		
	35	50	65
K	0.5539	0.0517	0.2068
$1/n$	0.5964	0.7458	0.5347
R^2	0.9932	0.9903	0.9977

As the concentration of aniline in the solution approaches zero, the activity coefficient approaches unity, reducing Eq. 2 to the following form

$$K_{\mathrm{o}} = \frac{a_{\mathrm{s}}}{a_{\mathrm{e}}} = \frac{C_{\mathrm{s}}}{C_{\mathrm{e}}} \tag{3}$$

The values of sorption distribution coefficient K_{o} are determined by plotting $\ln (C_{\mathrm{s}}/C_{\mathrm{e}})$ versus C_{s} at different temperatures (Fig. 8) and extrapolating C_{s} to zero [47]. The straight line obtained is fitted to the points based on a least squares analysis. Its intercept with the vertical axis gives the values of K_{o}. Standard free energy changes ($\Delta G°$) for interactions using the sorption distribution coefficient (K_{o}) are calculated from the relationship give below [48].

$$\Delta G° = -RT \ln K_{\mathrm{o}} \tag{4}$$

where R is the universal gas constant and T is the temperature in K. The average standard enthalpy change ($\Delta H°$) is then calculated from the well-known Van't Hoff equation:

$$\ln K_{\mathrm{o}}(T_3) \; - \; \ln K_{\mathrm{o}}(T_1) = \frac{-\Delta H°(T_1 \text{ to } T_3)}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right) \tag{5}$$

where T_3 and T_1 are two different temperatures. Standard entropy changes ($\Delta S°$) are calculated using the equation

$$\Delta G° = \Delta H° - T\Delta S° \tag{6}$$

The values of Gibbs free energy, $\Delta G°$ (kcal mol^{-1}), enthalpy, $\Delta H°$ (kcal mol^{-1}) and entropy, $\Delta S°$ (kcal mol^{-1} deg^{-1}) observed for the adsorption process of aniline on the surface of nano composite cation exchanger are given in Table 3.

The Gibbs free energy, $\Delta G°$ followed by positive entropy changes, $\Delta S°$ indicates exothermic and spontaneous nature of the reaction. The negative value of standard enthalpy change ($\Delta H°$) indicates that the aniline-exchanger interaction during adsorption process is favoured by heat given off; as an exothermic reaction and the products are energetically stable with a high binding of aniline to the exchanger sites. Hence, the adsorption of aniline was favoured at lower temperature and molecules of aniline were orderly adsorbed on the surface of nano composite
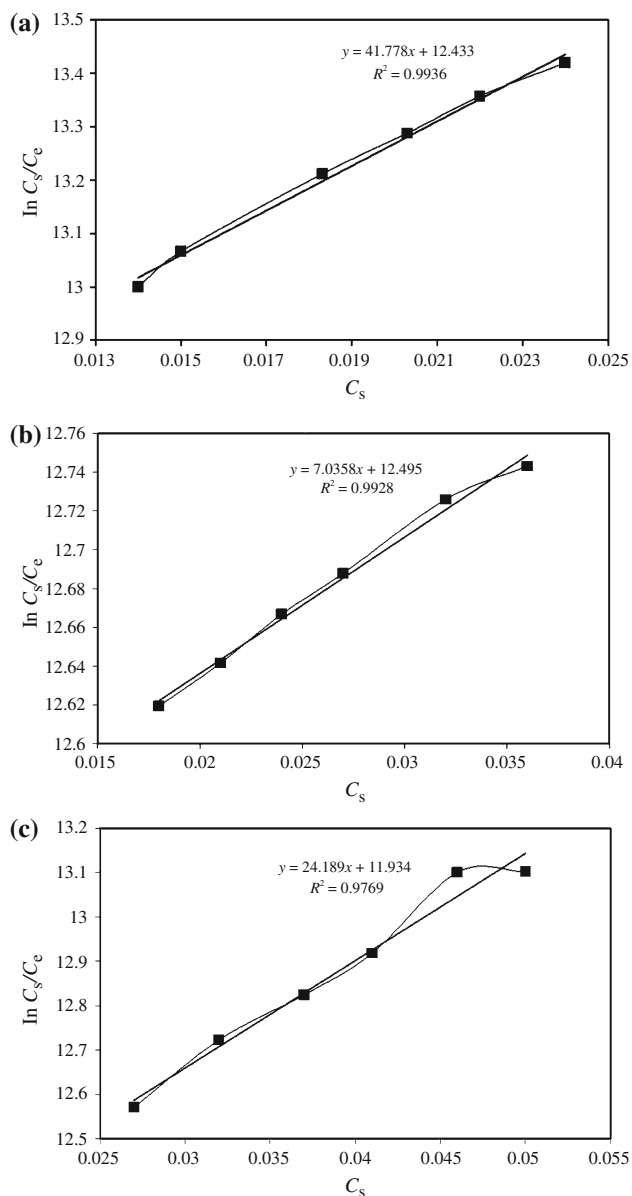
(a)

$y = 41.778x + 12.433$
$R^2 = 0.9936$

(b)

$y = 7.0358x + 12.495$
$R^2 = 0.9928$

(c)

$y = 24.189x + 11.934$
$R^2 = 0.9769$

Fig. 8 Plots of ln C_s/C_e versus C_s at temperatures 35 °C (**a**), 50 °C (**b**) and 65 °C (**c**) on polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger

Table 3 Values of various thermodynamic parameters for the adsorption of aniline on polyvinyl alcohol Sn(IV) tungstate composite cation-exchanger

Thermodynamic constant	Temperature/°C		
	35	50	65
K_o	12.433	12.495	10.984
$\Delta G°$/kcal mol^{-1}	-1.5426	-1.6210	-1.6096
$\Delta H°$/kcal mol^{-1}	-0.85524	-0.85524	-0.85524
$\Delta S°$/kcal mol^{-1} deg^{-1}	7.785×10^{-3}	7.666×10^{-3}	7.457×10^{-3}

cation exchanger. Since the Gibbs free energy, $\Delta G°$, as well as enthalpy changes, $\Delta H°$, are negative and accompanied by increased (positive) entropy changes, $\Delta S°$, the reactions are spontaneous and exothermic with a high affinity for aniline [49].

Conclusions

In this study, polyvinyl alcohol Sn(IV) tungstate nano composite cation-exchanger was prepared by sol–gel process and was characterized to observe the structure, surface morphology and particle size. The adsorption of aniline on the solid surface of nano composite cation exchanger followed Freundlich adsorption isotherm. Adsorption process is driven by decreasing enthalpy i.e. liberation of heat (exothermic process) or negative $\Delta H°$ and negative Gibbs free energy change ($\Delta G°$) i.e. adsorption process is spontaneous while the increase in entropy (positive $\Delta S°$) indicated the increased disorder during the adsorption process. Thus, it may be concluded that this newly synthesized nano composite cation exchanger is a useful ion-exchanger with promising ion-exchange behaviour which may be utilized for the removal of aniline from aqueous solutions due to efficient adsorption process.

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