Korean J. Chem. Eng., **29**(10), 1459-1465 (2012)
DOI: 10.1007/s11814-012-0022-3

Preparation of poly(vinyl alcohol)/tetraethyl orthosilicate hybrid membranes modified with TMPTMS by sol-gel method for removal of lead from aqueous solutions

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(*Received 13 November 2011 • accepted 29 February 2012*)

Abstract−Poly(vinyl alcohol)/tetraethyl orthosilicate (PVA/TEOS) ion exchange hybrid membranes modified with 3-mercaptopropyltrimethoxysilane (TMPTMS) were prepared by the sol-gel method, and their applications for the removal of lead ions from aqueous solutions in a batch sorption process were studied. The functional groups of the hybrid membranes were characterized by FTIR. Batch adsorption studies such as TMPTMS content, pH, adsorbent dose, contact time, initial concentration and temperature were evaluated. The maximum adsorption capacity of lead ions was found to be 61.62 mg g^{-1}, respectively. The kinetic data were analyzed by pseudo-first-order and pseudo-second-order kinetic models. The Freundlich and Langmuir isotherm models were applied to describe the equilibrium data. Thermodynamic parameters indicated that the lead adsorption onto the membrane is an endothermic and spontaneous process. The PVA/TEOS/TMPTMS hybrid membrane is regenerated by 0.5 M HNO_3/0.1 M HCl in equal ratio solution and the adsorption capacity did not change remarkably after five sorption-desorption cycles.

Key words: PVA, TEOS, TMPTMS, Hybrid Membrane, Sol-gel, Sorption

INTRODUCTION

The removal of heavy metal ions from wastewater is important to protect human health and the environment [1]. Lead is one of the major environmental pollutants, and lead poisoning in human beings is harmful to the nervous system, the reproductive system, the liver and the brain [2]. Lead is observed in a variety of industrial wastes, for instance, those of battery manufacturing, printing and pigment, ceramic and glass industries, ammunition and mine tailing. So the removal of lead ions from waste water is very important with respect to the environmental issue and public health.

Several methods have been used for the treatment of heavy metal ions from wastewater; these methods include chemical precipitation, ultrafiltration, reverse osmosis, electrodialysis, ion-exchange, flotation and adsorption. Among all, the adsorption and ion-exchange mechanisms have been used widely for the removal of heavy metal ions from aqueous solutions [3,4].

In most recent researches, the heavy metal ions were removed from water and wastewater by using an ion exchange hybrid membrane. The sol-gel technique is a suitable method for the preparation of organic-inorganic hybrids from the precursors containing alkoxysilyl groups by hydrolysis and condensation [5]. By using sol-gel method, it is possible to hybridize the organic-inorganic membranes. Traditionally, the hybrid membranes of poly (vinyl alcohol)/tetraethyl orthosilicate (PVA/TEOS) [6], chitosan/γ-glycidoxypropyltrimethoxysilane [7], glass fiber membrane/N-[3-(trimethoxysilyl)propyl] ethylene diamine [8] were prepared by the sol-gel technique and were applied to various cases.

Silica-based adsorbents due to their large specific surface areas and well modified surface properties were used widely in the removal of heavy metal ions. Moreover, they could be reused several times without any significant loss in the adsorption performance [9,10]. Furthermore, the removal efficiency of metal ions increases remarkably in the wake of the adsorbent surface modification by the functional groups such as $-NH_2$, -SH and -S- groups [10,11].

In this study TEOS was used as a silica precursor, and PVA/TEOS ion-exchange hybrid membrane was prepared by the sol-gel method for the adsorption of lead ions from the aqueous solutions. Furthermore, 3-mercaptopropyltrimethoxysilane (TMPTMS) as -SH functional groups was added to the PVA/TEOS hybrid membrane for the modification of the adsorbent surface. Also, the effect of pH, contact time, initial lead concentration, adsorbent dosage and temperature on the adsorption process was investigated. The equilibrium data were fitted to Freundlich and Langmuir isotherm models. To investigate the sorption behavior, pseudo-first-order and pseudo-second-order kinetic models were studied. The thermodynamic parameters were evaluated for lead sorption onto the PVA/TEOS/TMPTMS hybrid membranes. The hybrid membranes were also regenerated with 0.5 M HNO_3/0.1 M HCl in the equal ratio solution.

EXPERIMENTAL

1. Materials

PVA polymer (99% hydrolyzed, average MW=72000), TEOS (density=940 kg m^{-3}), (TMPTMS, 99%), cetyltrimethylammonium bromide (CTAB), ethanol and HCl were provided by Sigma-Aldrich. Deionized water was used throughout this work.

The solutions of lead ions were prepared by dissolving weighed amounts of lead nitrates (Aldrich) in deionized water.

2. Preparation of Membranes

In this work the PVA membrane, PVA/TEOS and PVA/TEOS/

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TMPTMS hybrid membranes were prepared. For the preparation of PVA membrane, first, aqueous 10 wt% PVA solutions were provided by dissolving 10 grams of PVA in 100 ml deionized water and then refluxing at 80 °C for 4 hrs. Then, the homogeneous solution was poured onto the glass plate and was allowed to be dried for 4 days. The dry membranes were peeled from the plate and were subjected to thermal treatment for 1 hr at 80 °C.

The PVA/TEOS hybrid membrane, using the PVA and sol-gel derived silica, was prepared by dissolving PVA in water, and was followed by the addition of the TEOS mixture to the solution. The TEOS mixture was prepared by mixing CTAB : TEOS : HCl : H_2O : ethanol in the molar ratio of 1 : 4 : 0.1 : 200 : 50. First, CTAB was mixed with water and ethanol for 10 min at 30 °C. Second, 20 weight percentage of TEOS with respect to the weight of the polymer was added to the solution and stirred continuously for 1 hr at 30 °C. Third, HCl was dropped slowly into the solution and was stirred for 2 hrs at 30 °C to prepare the TEOS mixture. Then TEOS mixture was added to the PVA solution and the PVA/TEOS mixture was stirred at 60 °C for another 4 hrs. Finally, the solution was cast with a knife on the glass plate, and was allowed to be dried for 4 days and then was heated in a vacuum oven at 120 °C for 1 hr to evaporate the solvent completely.

For preparation of PVA/TEOS/TMPTMS hybrid membrane, TMPTMS was added to the TEOS stirred mixture and the stirring was continued at 30 °C for 1 hr via the sol-gel method. Then the prepared solution was dropped slowly into the PVA solution and was mixed together at 60 °C for another 4 hrs. Finally, the homogeneous solution was cast with a knife on the glass plate (average thickness of 250 μm) and was introduced at room temperature for 4 days and then heated in a vacuum oven at 120 °C for 1 hr to evaporate the solvent completely. For comparative sulfur contents, four PVA/TEOS/TMPTMS hybrid membranes with different TMPTMS contents were prepared in the same way.

3. Measurements and Methods

FTIR spectroscopy was used in the range of 400-4,000 cm^{-1} to determine the type of functional groups on the PVA, PVA/TEOS and PVA/TEOS/TMPTMS membranes (Vector22-Bruker Company, Germany). The potentiometric method was used to determine the pH of the zero-point charge, pH_{pzc} [12] and a pH meter (827-pH lab, Switzerland) was used for the measurement of pH solutions. The concentration of lead ions in the adsorption medium was determined by using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Thermo Jarrel Ash, Model Trace Scan). Analytical wavelength was set at 220.553 nm for lead ions.

4. Batch Adsorption Experiments

The adsorption of lead ions was studied as a function of pH, contact time, dosage of adsorbent, initial concentration of lead and temperature. Adsorption processes were carried out by a batch method. The effect of pH of the solution on the lead sorption was studied in the range of 2-7. The initial pH of the solution was adjusted with 0.1 M HCl and/or 0.1 M NaOH. The experiments were performed in 250 ml Erlenmeyer flasks containing 0.1 g of the adsorbent in 100 ml of lead solutions at 25 °C on a rotary shaker at 150 rpm for 6 hrs at the different pH levels. The effect of adsorbent dosage on lead sorption was studied by varying the dosage in the range of 1-20 gL^{-1} at 25 °C, and the optimum pH and the lead solutions were agitated magnetically at a speed of 150 rpm for 6 hrs. For determining the effect of contact time on lead sorption, experiments were done by placing 0.1 g of adsorbent in 100 ml of lead solutions (100 mg L^{-1}) at 25 °C and the optimum pH on a rotary shaker at 150 rpm at definite time intervals. For examining the effect of initial lead concentration and temperature, 0.1 g of the membrane samples was rinsed in 100 ml of lead solutions with concentrations varying in the range of 10-500 mgL^{-1} at three different temperatures (25 °C, 35 °C and 45 °C) for 4 hrs. Each experiment was repeated three times and the results were given as averages which the error ranges for all data were less than ±5%.

C_0 and C_e are the initial and equilibrium lead concentrations (mg L^{-1}), respectively. The amount of lead adsorbed per unit mass of adsorbent at equilibrium, q_e (mg g^{-1}) was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{1000M} \tag{1}$$

where V is the volume of the solution (ml) and M is the weight of the dry membrane (g).

RESULTS

1. Characterization of the Prepared Membranes

The functional groups of samples are characterized by Fourier transform infrared (FTIR) and the results are shown in Fig. 1. The samples contain pure PVA membrane, PVA/TEOS20% hybrid membrane and PVA/TEOS20%/TMPTMS10% hybrid membrane. In all the samples, there is a broad bond at around 3,100-3,600 cm^{-1}, which is assigned to O-H stretching for the hydrogen bonded hydroxyl groups present in the samples. The peak at around 2,850-2,950 cm^{-1} is due to the alkyl stretching groups. The C-O ester group peak was observed at around 920-950 cm^{-1}, this peak because of the etherification reactions in some vicinal OH groups during the dissolution of PVA in boiling water [13]. For silica material spectra, the broad bonds appeared at around 1,080-1,200 cm^{-1} due to the siloxane bonds (Si-O-Si) which was observed in the spectra of the PVA/TEOS and PVA/TEOS/TMPTS hybrid membranes; moreover, the vibrations of Si-OH were observed at 1,653 and 3,400 cm^{-1} indicating uncondensed silanols in the structure of PVA/TEOS 20%

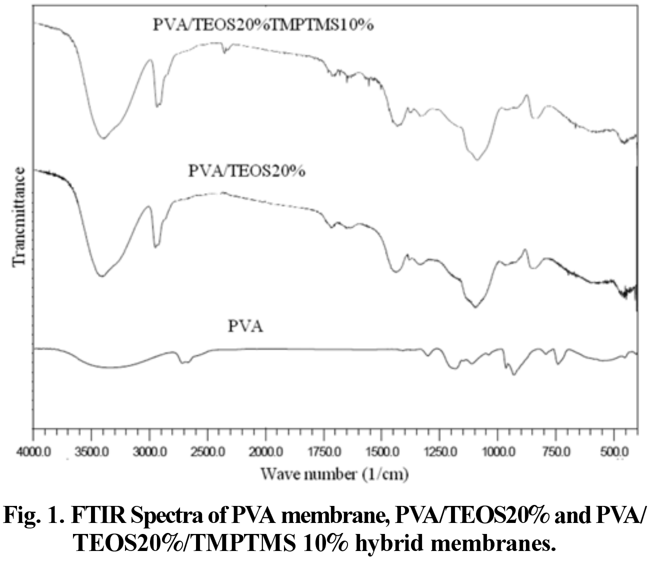

Fig. 1. FTIR Spectra of PVA membrane, PVA/TEOS20% and PVA/TEOS20%/TMPTMS 10% hybrid membranes.

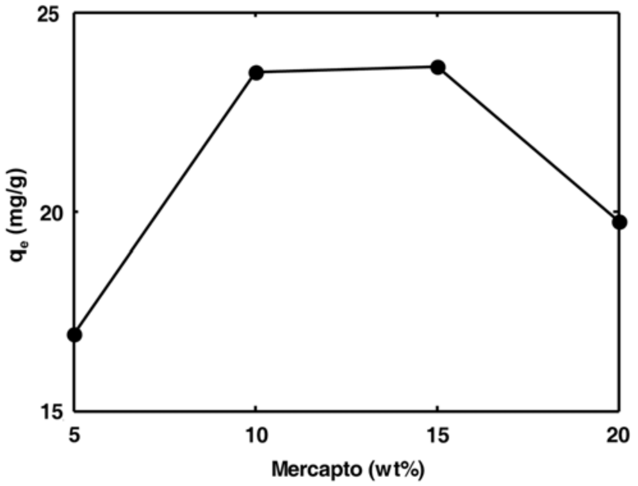

Fig. 2. Effect of the TMPTMS weight percentage in PVA/TEOS 20%/TMPTMS membrane.

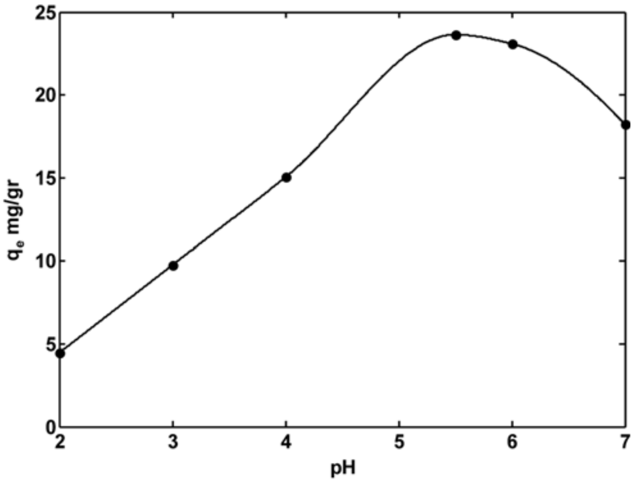

Fig. 3. Effect of pH on the lead sorption onto PVA/TEOS20%/ TMPTMS 10% membrane.

and PVA/TEOS 20%/TMPTMS 10% hybrid membranes. A weak S-H stretching peak was seen at 2,550-2,580 cm^{-1} which indicates that mercapto groups have been successfully added to the mesoporous silica skeleton of PVA/TEOS/TMPTMS hybrid membrane.

2. Effect of TMPTMS Weight Percentage in PVA/TEOS20% TMPTMS Hybrid Membrane

In this section, PVA/TEOS20% membrane is functionalized with mercapto functional group. The mercapto functional group is able to chelate with lead ions; the sulfur atom of the S-H group has great ability to interact with lead metal ions and to cause an increase in adsorption capacity of lead ions by the prepared membrane.

For optimization amount of TMPTMS into the PVA/TEOS/ TMPTMS hybrid membranes, 5, 10, 15 and 20 weight percentages of TMPTMS with respect to the polymer weight are added into the fabricated hybrid membranes and the adsorption capacity of lead is studied with a pH of 5.5, initial concentration 100 mgL^{-1}, adsorbent concentration 1 g L^{-1}, and 25 °C. The results are shown in Fig. 2. It can be seen that the adsorption capacity of lead ions increases with increasing TMPTMS amount up to 15%; further increase in TMPTMS amount leads to the decrease of adsorption capacity of the hybrid membranes. Increasing adsorption capacity with the increase of TMPTMS is due to the unique large surface, regular pore structure and well modified surface properties. Reduction in adsorption capacity of lead ions in mercapto higher than 15% can be attributed to the agglomeration of particles which decreases the available surface of adsorption. Another reason can be due to the decrease in diffusivity of lead ions into the membrane; that causes interaction between -SH groups of membrane and the lead ions are decreased [14, 15]. Since values of the adsorption capacity between PVA/TEOS20%/ TMPTMS10% and PVA/TEOS20%/TMPTMS15%, are low, it is economical to use PVA/TEOS20%/TMPTMS10% hybrid membrane for the adsorption process; consequently, the optimum weight percentage of TMPTMS in the PVA/TEOS 20% is selected as 10% for the further experiments.

3. Effect of pH

In the metal ion adsorption process, the pH is one of the most important variables which affects the surface change of the adsorbent. The effect of the initial solution pH is studied by interacting 1 g L^{-1} of the hybrid membrane in the pH range of 2-7 at 25 °C for the initial metal concentration of 100 mg L^{-1} lead solution. The results are presented in Fig. 3.

Lead ion precipitation in solution depends on the lead concentration in the medium. With an over pH 7, precipitation occurs in the solution [16,17]. As can be seen from Fig. 3, experiments are not conducted beyond a pH of 7. It is observed that the capacity of the adsorption increases with increasing pH for lead ions; moreover, with a pH of 5.5, the adsorption capacity reaches the maximum value, and then declines with the increase of pH values. With a lower pH, the low adsorption of lead ions is due to the increase of H$^+$ concentration, and it reduces the ability of anion functional groups on the adsorbent surface. By raising the pH, the protonation degree decreases, which leads to the increased the capacity of lead adsorption. The effect of pH on lead adsorption could be also explained on the base of the pH$_{pzc}$ value of the membrane, which is 3.1. At pH<pH$_{pzc}$ the membrane surface is positively charged due to the protonation. There is an electrostatic repulsion between both positively charged membrane surface and lead ions, which leads to the low sorption. With a pH$_{pzc}$, the membrane surface is neutral. With a pH>pH$_{pzc}$, the membrane surface becomes more and more negatively charged and that causes more attraction of the lead ions into the surface membrane and increases the adsorption capacity. With the optimum pH, the adsorbent surface has a net negative charge leading to the maximum sorption [18]. The decrease in the adsorption lead ions with an over pH 5.5 is due to the formation of hydroxylated complexes of the lead ions (in the form of $Pb(OH)_2$) that ruins the surface of the membrane [19]. Consequently, the optimum pH for further adsorption studies is selected as 5.5.

4. Effect of Adsorbent Dosage

The adsorbent dosage indicates the potential of the adsorbent through a number of binding sites available to the adsorption of metal ions in a specified initial concentration in which the number of active sites increases with the elevating adsorbent dosage. The adsorption capacity of lead ions as a function of adsorbent dosage for initial lead concentration of 100 mg L^{-1} and 25 °C is presented in Fig. 4. As can be seen from Fig. 4, adsorption capacity decreases with the increase in the dose of adsorbent; it can be because of the remain-

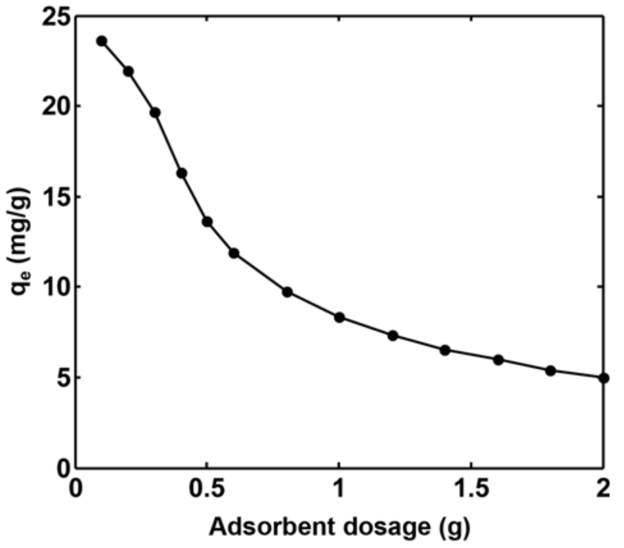

Fig. 4. Effect of adsorbent dosage on the lead sorption onto PVA/ TEOS20% TMPTMS 10% membrane.

ing unsaturated sites during the adsorption process. Also, by increasing the adsorbent concentration, the availability of lead ions to the remaining sites decreases, so the adsorbent dosage and adsorbent concentration for further adsorption studies are selected as 1 g and 1 g L^{-1}.

5. Effect of Contact Time

The contact time plays an important role in modeling and designing a adsorption process in industry. Therefore, the effect of contact time on lead sorption onto the hybrid membrane in the initial concentration 100 mg L^{-1} and 25 °C is shown in Fig. 5. The adsorption capacity increases with time. When the adsorption sites saturate during the adsorption process, the adsorption capacity does not change any more with time, which is known as equilibrium time. This time is very important for process optimization in industry.

It can be seen from Fig. 5 that the adsorption of lead ions into the membrane reaches the equilibrium time after 4 hours. More than 90% of total adsorption of lead occurs within the first 2 hours. The fast sorption at the first 2 hours is due to the large number of vacant surface sites of membrane which are available for adsorption of lead. After 2 hours the active external sites are almost saturated, and the adsorption process needs more time to be performed by active intraparticular sites. After 4 hours, almost all of the internal and external active sites are saturated and the system reaches the sorption equilibrium.

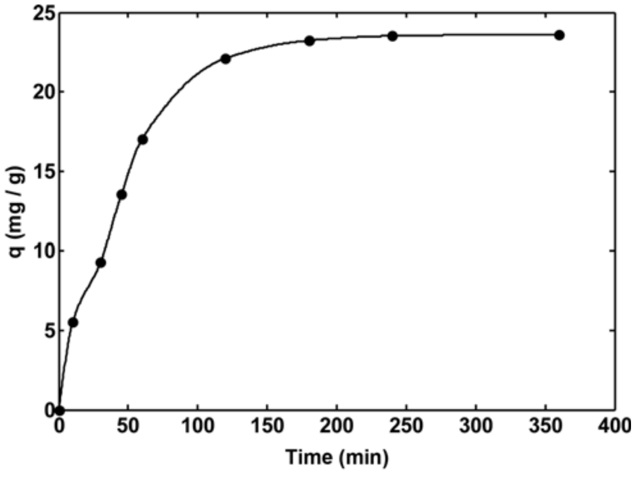

Fig. 5. Effect of contact time on the lead sorption onto PVA/TEOS 20% TMPTMS 10% membrane.

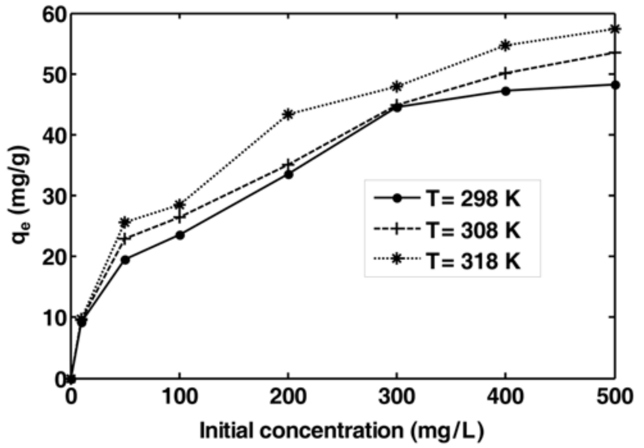

Fig. 6. The effect of initial concentration of lead ions on the adsorption capacity of PVA/TEOS20%/TMPTMS 10% membrane at 298, 308 and 318 K.

6. Effect of Initial Concentration and Temperature

The initial concentration of metal ions is a critical parameter which indicates the driving force gradient of mass transfer between the solid phase and liquid phase in the adsorption process; therefore, the effect of the initial concentration of lead ions (10-500 mg L^{-1}) on the adsorption capacity of membrane at three different temperatures (298, 308, 318 K) is shown in Fig. 6. It can be seen that the adsorption capacity of lead ions onto the hybrid membrane is slowly increased with increasing lead concentration and then approaches a fixed value. The increasing adsorption capacity is due to the increase of the driving force gradient for mass transfer created by the increase of initial concentration. The fixed value of the adsorption capacity is due to the saturation of the active adsorption sites of the membrane. Furthermore, the adsorption capacity of lead increases with raising the temperature, which indicates that the process is endothermic as regards the adsorption.

7. Kinetic Models

The study of kinetic data in the adsorption process, which is based on the diffusion mass transfer or chemical reaction, is useful for sorption modeling. Kinetic models, namely pseudo-first-order and pseudo-second-order models are used to describe the adsorption kinetics of lead ions onto the PVA/TEOS 20%/TMPTMS 10% hybrid membrane.

The pseudo-first-order kinetic model by Lagergren [20] is given as:

$$q_t=q_e\,(1-\exp(-k_1t)) \tag{2}$$

where q_t and are q_e (mg g^{-1}) the amounts of lead adsorbed at time t and equilibrium time, respectively. k_1 (min^{-1}) is the pseudo-first-order model rate constant. Parameters of the pseudo-first order kinetic model were calculated by plotting the experimental data of q_t versus

Table 1. Kinetic parameters of lead sorption onto PVA/TEOS20% TMPTMS 10% hybrid membrane

Pseudo-first-oder model			Pseudo-second-oder model		
q_{eq} (mg g^{-1})	k_1 (min^{-1})	R^2	q_{eq} (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
23.91	0.0194	0.986	26.96	0.00137	0.993

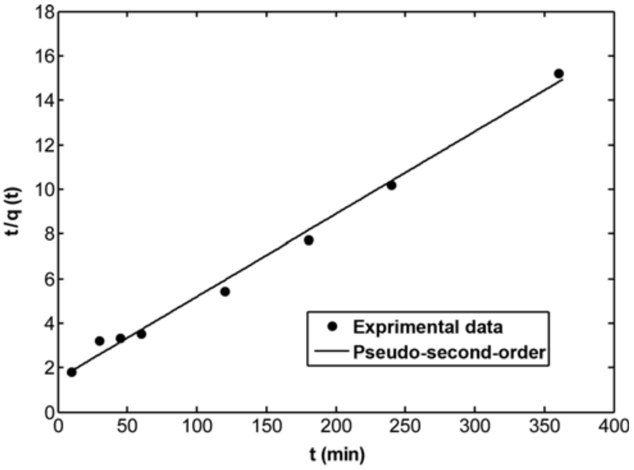

Fig. 7. Pseudo-second-order kinetic plot for lead sorption onto PVA/TEOS20%/TMPTMS 10% membrane.

t and the results are presented in Table 1, (figure is not presented).

The pseudo-second-order kinetic model by Ho and Mc Kay [21] is given as:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{3}$$

The linear form of pseudo-second-order kinetic model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_e} \tag{4}$$

where k_2 is the adsorption rate constant (g mg^{-1} min^{-1}). Kinetic parameters of the pseudo-second-order model were obtained from the linear plot of t/q_t versus t (Fig. 7), and the results are presented in Table 1.

By contrasting the correlation coefficient for pseudo-first-order (R^2=0.986) and pseudo-second-order (R^2=0.993), it was found that the pseudo-second-order model fitted better than the pseudo-first-order model with kinetic data.

8. Adsorption Isotherms

Equilibrium data of lead sorption onto PVA/TEOS20%/TMPTMS 10% hybrid membrane have been described by isotherm models, namely Freundlich and Langmuir.

8-1. Freundlich Isotherm

The Freundlich isotherm is an equation which indicates heterogeneous surface adsorption with nonuniform energies of active sites. This model can be expressed as follows [22]:

$$q_e = k_F C_e^{1/n} \tag{5}$$

where k_F (mg g^{-1}) and n are Freundlich parameters related to sorption capacity and sorption intensity. Parameters of the Freundlich model were calculated by plotting out q_e versus C_e at different temperatures (25, 35 and 45 °C) (Fig. 8). The results of which are presented in Table 2. It can be seen from Table 2 that the values of k_F increase with rising temperature, indicating that the adsorption process is endothermic; moreover, values of 1/n less than one at all three temperatures indicate the favorability of lead sorption onto the membrane. A correlation coefficient greater than 0.967 shows that the Freundlich isotherm fitted well with equilibrium data of lead ions at different studied temperatures.

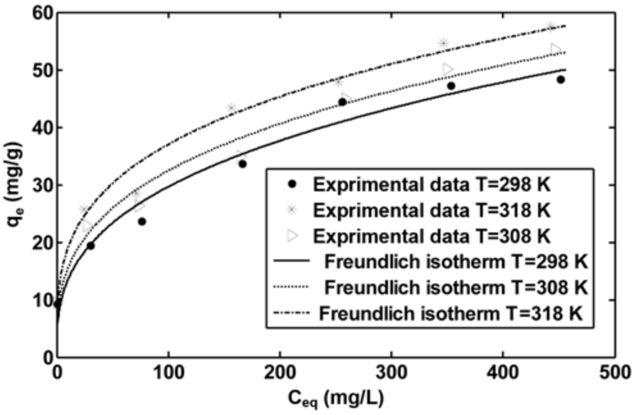

Fig. 8. Freundlich isotherm plots for lead sorption onto PVA/TEOS20%/TMPTMS 10% membrane.

Table 2. Isotherm parameters for lead adsorption onto PVA/TEOS20% TMPTMS 10% hybrid membrane at different temperatures

Temperature (K)	Freundlich isotherm			Langmuir isotherm		
	k_F (mg/g)	n	R^2	q_{max} (mg/g)	K_L (L/mg)	R^2
298	6.08	2.896	0.967	57.85	0.0110	0.908
308	7.28	3.085	0.976	58.74	0.0145	0.880
318	9.63	3.421	0.977	61.62	0.0174	0.893

8-2. Langmuir Isotherm

The Langmuir isotherm model is an equation which indicates homogeneous surface adsorption with uniform energies of active sites. This model can be expressed as follows [23]:

$$q_e = q_m \frac{bC_e}{1 + bC_e} \tag{6}$$

where q_m (mg g^{-1}) and b (mg^{-1}) are the Langmuir model constants. q_m is the maximum value of metal ion adsorption per unit weight of membrane that is related to the monolayer adsorption capacity, and b represents the enthalpy of adsorption. The parameters of the Langmuir model were calculated by plotting q_e versus C_e at different temperatures (25, 35 and 45 °C). The results of which are presented in Table 2, (figure is not presented). It can be seen that the adsorption capacity of lead ions by the membrane increases from 57.85 to 61.62 mg g^{-1} with the increase of the temperature from 25 to 45 °C.

The maximum adsorption capacity of lead ions onto the hybrid membrane is compared with other adsorbents reported in the literature [16,24-33] and is listed in Table 3. It can be seen that the ad-

Table 3. Comparison of adsorption capacity (mg g^{-1}) of PVA// TEOS20% TMPTMS 10% hybrid membrane for lead sorption in the literature

Adsorbent	Lead adsorption capacity (mg g^{-1})	Ref.
Poly(VP-PEGMA-EGDMA)	18.23	16
Amberlite XAD-2 functionalized with Tiron	12.60	24
Turkish kaolinite clay	31.75	25
Poly (EGDMA-VIM)	114.80	26
PEI-Silica	82.64	27
PEI-Silica-$GA_{0.5}$	50.76	27
MnO_2-loaded D301 resin	80.64	28
γ-MPTMS-SCMNPs	70.40	29
HS-SBA 15	64.79	30
MP-PCH	22.77	31
PHMS/TEOS/MPTMS/APTES	144.0	32
SBA-15/SH-30	39.33	33
PVA/TEOS20%TMPTMS10%	61.62	In this study

sorption capacity of PVA/TEOS20%/TMPTMS10% hybrid membrane for lead ions was found to be comparable and moderately higher than those of many corresponding sorbents in the literature.

By comparing the correlation coefficients it was found that the Freundlich isotherm (R^2>0.967) fitted better than Langmuir isotherm model (R^2>0.880).

9. Thermodynamics of Adsorption

Thermodynamic parameters play an important role in the adsorption process, which determines the degree of the spontaneous process by the calculation values of Gibbs free energy and entropy change.

The Gibbs free energy change (ΔG^o), the enthalpy change (ΔH^o) and the entropy change (ΔS^o) were calculated using the method applied by Ahmaruzzaman and Gayatri [34].

The calculated values of thermodynamic parameters are presented in Table 4. As can be seen, ΔG^o was found to be −6.361, −8.176 and −9.864 kJ mol^{-1} for the adsorption of lead at 25, 35 and 45 °C, respectively. The negative values of the Gibbs free energy changes indicate the feasibility and spontaneous nature of lead sorption onto the hybrid membrane. Also, the more negative value of ΔG^o by raising temperature indicates that the higher temperature proceeds earlier than the adsorption of lead ions by the membrane.

ΔH^o for the adsorption of lead by the membrane had a value of 46.420 kJ mol^{-1}. The positive value of enthalpy change implies that the adsorption process by the PVA/TEOS20%/TMPTMS10% hybrid membrane is endothermic. Furthermore, the value of enthalpy change determines the nature of physical or chemical adsorption process [35,36]. In this study, the enthalpy change was found to be 46.42 kJ mol^{-1} that indicates that the adsorption process is endothermic and the chelating adsorption is a chemisorption process. The entropy change of the process was found to be 0.175 kJ mol^{-1} K^{-1}, which indicates the increased disorder and randomness at the solid-solution interface of lead ions with the membrane.

Table 4. Thermodynamic parameters for lead adsorption onto PVA/ TEOS20% TMPTMS 10% hybrid membrane

Temperature (K)	K_C	ΔH^o (kJ/mol)	ΔS^o (kJ/mol·K)	ΔG^o (kJ/mol)
298	13.017	46.420	0.175	−6.361
308	24.395	46.420	0.175	−8.176
318	41.643	46.420	0.175	−9.864

10. Regeneration of Membrane

Regeneration of adsorbent is very important in the adsorption process, because the reuse of the adsorbent is a key factor in improving process economics. Therefore, five cycles of adsorption-desorption of lead ions onto PVA/TEOS20%/TMPTMS10% hybrid membrane were performed at initial lead concentration of 100 mgL^{-1} and 25 °C. The desorption step of lead ions from the membrane was treated with 0.5 M HNO_3/0.1 M HCl in equal ratio solution. The desorption time was fixed as 4 hrs throughout the adsorption period. The adsorption capacity of lead ions onto the membrane from 23.64 mg g^{-1} in the first step decreased to 21.85, 20.37, 19.12 and 18.51 mg g^{-1} in the second step to fifth step, respectively. This shows that the hybrid membrane can be reused for many times without almost any significant loss in adsorption performance and can be utilized extensively in industrial activities. Of course, the reduction of the adsorption capacity of the membrane is because of physically losing some -SH groups by the acid cleavage [9].

CONCLUSIONS

PVA/TEOS/TMPTMS hybrid membranes were prepared by sol-gel method as an adsorbent to examine the removal of lead from aqueous solutions. The kinetic data were best described by pseudo-second-order model (R^2=0.993). The equilibrium data followed well the Freundlich isotherm model (R^2>0.967). ΔG^o, ΔH^o and ΔS^o of the adsorption process were calculated as −9.864 kJ mol^{-1}, 46.42 kJ mol^{-1} and 0.175 kJ mol^{-1} K^{-1}. These values indicate the spontaneous and endothermic nature of lead sorption onto the membranes. PVA/TEOS20%/TMPTMS10% hybrid membrane was regenerated with 0.5 M HNO_3/0.1 M HCl in equal ratio solution and was not observed to be significantly lost in adsorption performance after five adsorption-desorption cycles.

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