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Preparation of organic-inorganic polyurethane-Al_2O_3 anion exchange fibrous composite and its application in development of membrane electrode for determination of chromium(VI) in water

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Abstract: Polyurethane-Al_2O_3 organic-inorganic anion-exchange fibrous composites were prepared by simple stirring with magnetic bar in different stoichiometric ratios of polyurethane and Al_2O_3. The structure and morphology of the prepared fibrous composite were ascertained by fourier transform spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), thermal analysis (TGA and DTG) and X-ray diffraction analysis (XRD). The material was found to be highly desirable for electroanalytical application as ionic sensor, its membrane electrode have been developed for the detection of Cr(VI) in aqueous solutions. The membrane electrode shows the best result with linear potential response in the concentration range of 1×10^{-1} mol L^{-1} to 1×10^{-8} mol L^{-1} of Cr(VI) ion with a slope of 30.36 mV/decade. The selectivity coefficients values for interfering ions indicate good selectivity for Cr(VI) over interfering anions. The accuracy of the procedure has been tested on chromium-free drinking water samples spiked with known amount of Cr(VI) and results were comparable to these generated by AAS (Atomic absorption spectroscopy).

Keywords: polymer, fibrous composite, anion exchanger, Cr(VI) selective electrode.

1. Introduction

Chromium and its compounds have been widely used in different commercial ventures, such as mining, tanning, concrete, generation of steel or other metal compounds, electroplating operations, photographic materials, destructive painting, metal businesses etc. [1-2]. Epidemiological studies conveyed in the UK, Europe, Japan and the US have reliably indicated that specialists in the chromate generation industry have high risk of respiratory illness, fibrosis, puncturing of the nasal septum, advancement of nasal polyps and lung disease [3]. In the watery environment chromium can exist in either as Cr(VI) or Cr(III) of which, the Cr(VI) is known to be profoundly lethal, mutagenic and cancer-causing [4-6]. Its vicinity in nature also poses huge risk to oceanic life and also to open wellbeing [5, 7]. As per the standards, the maximum permissible limit of Cr(VI) for discharge to inland surface water and portable water is 0.1 mg L^{-1} and 0.05 mg L^{-1} respectively [7-8]. In perspective of such poisonous impacts of Cr(VI), its checking and regulation in ecological specimens is of utmost importance.

A lot many sophisticated techniques such as spectrophotometry [9], spectrofluorimetry [10], ion chromatography coupled with atomic absorption spectroscopy [11], differential pulse polarography [12] and differential pulse voltammetry [13] have generally been utilized for the determination of trace amount of Cr(VI) in waste water and other water bodies. However, most of these techniques suffer from many disadvantages such as high cost, unsuitability for routine analyses of large number of analysis and non-applicability in field work. Recently, ion-selective electrode have provided a solution to many of these problems due to its portability, high sensitivity and low cost which gives a convenient, quick and online strategy for the determination of Cr(VI). A number of works have described the fabrication of ion-selective membrane electrode using organic-inorganic composite ion-exchange materials [14-15]. Among organic polymers, polyurethane has received significant interest of researchers as it is widely used in fabricating fibrous precursors and also shows high environmental stability in comparison to other polymers [16-21]. It finds wide variety of applications such as metal ion adsorption [22], separation of organic liquids, organic vapors and water [23]. A few reports on polymeric organic-inorganic cation exchange fibrous composite materials with their electroanalytical applications have already been published [24-25]. However, organic-inorganic anion exchange fibrous composite materials have been poorly reported in literatures and thus more research work needs to be focused in this area. Literature survey reveals that the alumina (Al_2O_3) is amphoteric in nature and thus can be used as cation and anion exchanger [26]. Al_2O_3 modified with polymers was proposed to be used in chromatographic ion exchange separations and can be exploited for the preparation of anion exchange materials. Owing to the advantageous properties of both polyurethane and Al_2O_3 it is of much interest to prepare the organic-inorganic anion exchange fibrous composite based on polyurethane and Al_2O_3 by an ecofriendly route for making ion-selective membrane electrode. However determination of anions above the permissible limit is also important from ecological point of perspective. Potentiometric method employing an ion sensor or ion-selective membrane electrode is an alternative, simple and low cost method for determination of Cr(VI). Thus, in this work, a new Cr(VI) selective electrode based on polyurethane-Al_2O_3 anion exchange fibrous composite is prepared and characterized for the potentiometric determination of Cr(VI).

2. Experimental

2.1 Reagents and chemicals

For the preparation of anion exchange fibrous composite the main chemical were used: Al_2O_3 (E-Merck, India), polyurethane from Research, design and standard organization, India, tetrahydrofuran (Qualigens, India) and potassium dichromate ($K_2Cr_2O_7$) from Qualigens (India Ltd.). All other reagents and chemicals were of analytical grade (AR).

2.2 Preparation of polyurethane-Al_2O_3 anion exchange fibrous composites

Fibrous polyurethane-Al_2O_3 anion exchange composites were synthesized in different weight ratio of Al_2O_3 with polyurethane by putting in on vigorous stirring conditions [27-28]. In a typical process, 500 mg polyurethane was dissolved in tetrahydrofuran (THF) at room temperature to which different amounts of Al_2O_3 (100, 200, 300, 400 and 500 mg) were dispersed. The dispersion was put under mechanical stirring for 24h at room temperature which gave homogeneous Al_2O_3 dispersed in polyurethane solution. The above Al_2O_3 dispersed polyurethane solution was dropped in water (DMW) with the help of needle syringe under vigorously stirring resulting in fibrous composite which accumulated on the surface of the water. Thus prepared fibrous polyurethane-Al_2O_3 composite were filtered, washed with doubly distilled water and later dried at room temperature. The dried fibrous composite was converted into Cl^- form by treating with 1 mol L^{-1} NaCl for two days with occasional shaking and intermittently replacing the supernatant liquid with fresh 1 mol L^{-1} NaCl two to three times. The excess was removed after several washings with DMW (demineralized water) and finally dried at room temperature. The condition of preparation and the ion-exchange capacity (IEC), of the anion exchange fibrous composite are given in Table 1. A schematic representation of the formation of polyurethane-Al_2O_3 fibrous composite is shown in Scheme 1.

2.3 Ion-exchange capacity (IEC) measurements

IEC of the anion exchange fibrous composite samples in the Cl^- form were determined using the Mohr method [29]. Accurately weighed dry exchanger was converted in to Cl^- ionic form through immersion in 1 mol L^{-1} NaCl for two days. Excess NaCl was washed off and then the AEFC were immersed in 200 mL 0.5 mol L^{-1} Na_2SO_4. The amount of Cl^- was determined using titration with $AgNO_3$; anion exchange values were obtained and expressed as meq g^{-1} of dry exchanger (In Cl^- form).

2.4. Characterizations

2.4.1. Fourier transform infra red (FTIR) studies

The FTIR spectrum of polyurethane, Al_2O_3 and polyurethane-Al_2O_3 fibrous composite were obtained by FTIR spectrophotometer (Perkin-Elmer, USA, model Spectrum-BX) by KBr disc method at room temperature.

2.4.2. X-Ray diffraction analysis

X-Ray diffraction patterns (XRD) of polyurethane, Al_2O_3 and polyurethane-Al_2O_3 fibrous composite were obtained by PHILIPS PW1710 instrument equipped with a Cu anode, automatic divergence slit and a graphite monochromator, under the following experimental conditions: CuKα radiation, 1.54 Å; generator tension, 45 kV; generator current, 40 mA; intensity ratio (α_2/α_1), 0.500.

2.4.3. Field emission Scanning electron microscopy (SEM) studies

The surface morphology of polyurethane, Al_2O_3 and polyurethane-Al_2O_3 fibrous composite were studied by field emission scanning electron microscopy (FE-SEM) using a LEO microscope (435–VF) at various magnifications.

2.4.4. Thermal studies

The thermal stability of polyurethane, Al_2O_3 and polyurethane-Al_2O_3 fibrous composite were studied by TGA and DTG techniques using thermal analyzer-EXSTAR TG/DTA 6300. The samples (10.00 mg of each) were heated in alumina crucible from 30 to 1000 °C at the rate of 10 °C min^{-1} in the nitrogen atmosphere at the flow rate of 200 mL min^{-1}.

2.5 Preparation of polyurethane-Al_2O_3 fibrous composite membranes

Polyurethane-Al_2O_3 anion exchange fibrous composite membranes were prepared in various weight ratios of constituting components by simple solution casting method. Different weight ratios of polyurethane-Al_2O_3 (100, 150 and 200 mg) were dispersed in THF at room temperature. Mechanical stirring was applied for 6h at room temperature in order to obtain well dispersed composite solution. Thus obtained polyurethane-Al_2O_3 dispersed solution was casted onto clean glass plates and kept for 48 h at room temperature for complete evaporation of THF. The resultant composite membranes were cautiously peeled out of the glass plate, rinsed with doubly distilled water on both sides, dried at room temperature and later stored in desiccator to further experiments.

2.6 Physicochemical characterization of polyurethane-Al_2O_3 fibrous composite membranes

The Water content (% total wet weight), porosity, thickness and swelling etc. were determined by the same method as discussed in our previous studies [14]. Those membrane which exhibited good surface qualities like porosity, thickness and swelling etc. were selected for further investigation.

3. Fabrication and conditioning of ion-selective membrane electrode

The ion-selective membrane electrode was fabricated by the same method as we have described previously [14]. The membrane sheet of 0.145 mm thickness as obtained by the above procedure was cut in the shape of disc and mounted at the lower end of a Pyrex glass tube (outer diameter 0.8 cm, internal diameter 0.6 cm) with araldite. Finally, the assembly was allowed to dry in air for 24 h. The glass tube was filled with 0.1 mol L^{-1} potassium dichromate solution. Electrode was then equilibrated with Cr(VI) solution (0.1 mol L^{-1}) for 5-7 days. The tube was filled 3/4th with potassium dichromate solution (0.1 mol L^{-1}) and then immersed in a beaker containing the test solution of varying concentration of Cr(VI) ion, keeping the level of inner filling solution higher than the level of the test solution to avoid any reverse diffusion of the electrolyte.

3.1. Potential measurements

All the potential measurements were carried out using the following cell assembly:

SCE | 0.1 mol L^{-1} Cr(VI) **|| Membrane || test solution| SCE**

A saturated calomel electrode (SCE) was inserted in the tube for electrical contact and other saturated calomel electrode (SCE) was employed as an external reference electrode. Potentiometric measurements were observed for a series of standard solutions of potassium dichromate (10^{-12}–10^{-1} mol L^{-1}), set up by gradual dilution of the stock solution, as defined by

IUPAC Commission for Analytical Nomenclature [30]. The calibration graphs of potential versus logarithm of dichromate ion concentration were plotted.

3.2. Characteristics of the electrode

The characteristics of the fabricated membrane electrode such as the effect of pH, response time, potentiometric selectivity coefficient and storage of electrodes were measured by the methods as described earlier [14].

3.2.1. Effect of pH

Solutions with pH ranging from 1-6 were prepared at 1×10^{-5} mol L^{-1} constant ion concentration. The value of electrode potential at each pH was recorded and plot of electrode potential versus pH was plotted.

3.2.2. The response time

The method of determining response time in the present work is being outlined as follows. The electrode is first dipped in a 1×10^{-5} mol L^{-1} solution of potassium dichromate and then 10 fold higher concentrations. The potential of the solution was read at zero second; just after dipping of the electrode in the second solution and subsequently recorded at the intervals of 10 s. The potentials were then plotted vs. the time.

3.2.3. Potentiometric selectivity coefficient

In the present work the potentiometric selectivity coefficient (K_{AB}^{pot}) of interfering anions was determined by using the mixed solution method [31]. The selectivity coefficient was calculated using the equation given below:

$$K_{AB}^{\mathrm{pot}} = a_A/(a_B)^{zA/zB} \qquad \text{……..(2)}$$

where a_A and a_B activities of primary and interfering ion and zA and zB are charges on the ions.

3.2.4. Storage of electrodes

The membrane electrode was stored in distilled water when not in use for more than one day. It was activated with (0.1 mol L^{-1}) Cr(VI) solution by keeping immersed in it for 2 h, before use, to compensate for any loss of metal ions in the membrane phase that might have taken place due to a long storage in distilled water. Electrode was then washed thoroughly with DMW before use.

4. Results and discussion

Various samples of organic-inorganic polyurethane-Al_2O_3 anion exchange fibrous composites were prepared by stirring with magnetic bar [27-28] under different stoichiometric ratios. Although we have prepared a variety of anion exchange fibrous composites by varying the stoichiometry between polyurethane and Al_2O_3 but highest anion exchange capacity was observed in 1:1 stoichiometry (Table 1). Due to higher ion-exchange capacity and thermal stabilities, sample AEFC-5 (Table 1) was selected for further studies. All polyurethane-Al_2O_3 anion exchange fibrous composites samples were in white color, light weight and suitable for use in the ion-exchange process. The proposed mechanistic representation of formation of polyurethane-Al_2O_3 fibrous composite showing interaction of Al_2O_3 with polyurethane is shown in Scheme 2.

4.1. FT-IR spectroscopic analysis

The FTIR spectra of polyurethane, Al_2O_3, and polyurethane-Al_2O_3 anion exchange fibrous composite are shown in Fig. 1. In the polyurethane spectrum, the absorption band at 3333

cm^{-1} corresponds to NH stretching. The sharp peaks at 2874 cm^{-1} and 2959 cm^{-1} are associated with $-CH_2$ stretching, while other modes of $-CH_2$ vibrations are identified by the bands at 1457, 1415, 1311, and 1228 cm^{-1}. In addition, the absorption band at 1735 cm^{-1} is associated with a C=O group in polyurethane. The group of NH vibrations is identified by the bands at 1532 cm^{-1}. The band at 1703 cm^{-1} is assigned to hydrogen bonding between N-H and C=O groups in the hard segment and the ester or ester-oxygen groups of the soft segments of urethane linkage. The presence of Al_2O_3 in the polyurethane-Al_2O_3 fibrous composite is further strengthening from the presence of broad band at 3400 cm^{-1} which may be due to the vibration of hydroxyl groups. The bands at 757 and 588 cm^{-1} due to the stretching vibration of Al−O bond in polyurethane- Al_2O_3 fibrous composite. Compared with Fig. 2(a), some peaks are shifted in the polyurethane-Al_2O_3 fibrous composite from 1248, 1595, 2010, 2250 cm^{-1}, to 1100, 1250, 1600, 1785 cm^{-1} respectively, indicating the formation of polyurethane-Al_2O_3 fibrous composite.

4.2. Field emission scanning electron microscopy (FE-SEM) studies

Fig. 2 shows the FE-SEM image of polyurethane and polyurethane-Al_2O_3 anion exchange fibrous composite at different magnifications, indicating the binding of inorganic material i.e. Al_2O_3 with organic polymer i.e. polyurethane. The images showed the difference in surface morphology of organic polymer, inorganic material and composite fibers. It has been revealed that after binding of polyurethane with Al_2O_3, the morphology has been changed. Fig. 2(b-d) shows the fibrous composite were randomly distributed to form the fibrous web. The polyurethane-Al_2O_3 anion exchange fibrous composites were observed soft and flexible.

4.3. X-ray diffraction (XRD) analysis

Fig. 3 illustrates the XRD pattern of pure polyurethane and polyurethane-Al_2O_3 anion exchange fibrous composite in the 2θ range between 5 and 70 degree. In the XRD pattern of pure polyurethane there is no sharp diffraction peaks, confirming their non-crystalline nature. The polyurethane is known to be an amorphous polymer and shows a broad peak at 2θ value 17°. However, in the case Al_2O_3 of some peaks can be observed at 15°, 35.5°, 45.1°, 60° and 68°. On the addition of Al_2O_3 in the polyurethane matrix, the XRD spectra of polyurethane-Al_2O_3 anion exchange fibrous composite clearly exhibit the major peaks of polyurethane and Al_2O_3 indicating the successful incorporation of Al_2O_3 in polyurethane-Al_2O_3 anion exchange fibrous composite.

4.4. TGA and DTG analysis

Fig. 4a shows a comparison of mass losses of pure polyurethane, Al_2O_3 and polyurethane-Al_2O_3 fibrous composite upon heating in nitrogen atmosphere. Pure polyurethane was initially stable up to 150 °C (0.91% mass loss, probably due to physisorbed water evaporated at this temperature); thereafter gradual weight loss with the same rate up to about 500 °C (88.11% mass loss), takes place by heat adsorption, is ascribed to the degradation of the polymers unsaturated groups. In the case of Al_2O_3, the first weight loss was observed at 100 °C (2.41%) due to removal of external water molecules and next on 300 °C (2.98%) and after 400 °C the Al_2O_3 was found stable up to 1000 °C with 2.84% further mass loss. However in case of polyurethane-Al_2O_3 fibrous composite the first weight loss at 200 °C (1.22% weight loss) due to removal of external water molecules and second weight loss up to 500 °C (54.09 % weight loss) because of degradation of polyurethane and after 500 °C the polyurethane-Al_2O_3 fibrous composite remain stable up to 1000 °C with 3.88% further mass loss. It can be concluded from Fig. 4a that the thermal stability of the polyurethane-Al_2O_3 fibrous composite is better than that of pure polyurethane. The total mass loss up to 1000 °C has been estimated to be about 92.87%, 8.23% and 59.19% for polyurethane, Al_2O_3 and polyurethane-Al_2O_3 fibrous composite respectively. These results confirm that the presence of Al_2O_3 in polyurethane-Al_2O_3 fibrous composite is responsible for the higher thermal stability of the composite material in comparison to pristine polyurethane.

DTG analysis of pure polyurethane, Al_2O_3 and polyurethane-Al_2O_3 fibrous composite was studied as a function of rate of weight loss (µg min^{-1}) versus temperature (Fig. 4b). In case of pure polyurethane decomposition at 287 °C and 356 °C was found with 260 µg min^{-1} and 910 µg min^{-1} weight loss, respectively and in case of Al_2O_3 decomposition at 53 °C and 258 °C was found with 35 µg min^{-1} and 34 µg min^{-1} weight loss, respectively. However, in the case of polyurethane-Al_2O_3 fibrous composite, the decomposition was observed at 306 °C and 368 °C with 360 and 540 µg min^{-1} weight loss, respectively. Thus, it could be concluded from the DTG studies that the rate of thermal decomposition was higher in the case of pristine polyurethane, where as in the case of polyurethane-Al_2O_3 composite, the rate of thermal decomposition is lower. The better thermal resistance of polyurethane-Al_2O_3 fibrous composite was due to incorporation of Al_2O_3 composite in the polyurethane matrix.

4.5. Physicochemical properties of polyurethane-Al_2O_3 fibrous composite membrane

The thickness, swelling, porosity, water content capacity etc. of the polyurethane-Al_2O_3 anion exchange fibrous composite membrane was investigated and the results are summarized in Table 2. It was noted that as the amount of illustrative components of the membrane, i.e. polyurethane-Al_2O_3 increased, the thickness, swelling, water content, porosity increased. Therefore, the lower orders of water content, swelling and porosity with less thickness of this membrane suggest that the interstices are negligible and diffusion across the membrane would occur primarily through the exchange sites. Hence, membrane sample AEFCM-1 (thickness 0.145 mm) was selected for the preparation of an ion-selective electrode for further studies. Nevertheless, further various characteristics are necessary for a membrane ion-selective electrode to be regarded as a suitable sensor for the quantitative measurement of ions. The most important features are the slope, working concentration range, response time, pH, selectivity and life span of the membrane electrode.

Membrane of polyurethane-Al_2O_3 anion exchange fibrous composite carry positive charges due to the interaction between the nitrogen on the polymer backbone and Al of Al_2O_3 as given in Scheme 2, therefore they show strong affinity for the anions instead of cations and hence are permeable to anions. Thus the selectivity of polyurethane-Al_2O_3 anion exchange fibrous composite membrane results from the exclusion of cations (co-ions) from membrane phase and permits transfer of anions (counter ions). As the concentration of versatile anion is higher in the solution than membrane, the concentration gradients are created between the membrane and the solution. This gradient difference allows the versatile anions to move into the film. Due to electro neutrality conditions, the permeation of cations into the solution and anions into the membrane prompts a counter-acting charge because of uncompensated ions and equilibrium is created between the attempts of diffusion on one side and the establishment of an electrical potential difference on the other. Thus electrical potential difference between polyurethane-Al_2O_3 anion exchange fibrous composite membrane and adjacent salt solution can be measured.

In the preliminary tests, polyurethane-Al_2O_3 membrane electrode indicated stable potential responses in solutions containing dichromate ion while all other anions show negligible potential responses in the concentration ranging from 1×10^{-1} mol L^{-1} and 1×10^{-8} mol L^{-1}. In this manner, the detailed performance of the membrane electrode, in aqueous solutions containing dichromate ion was studied.

4.6. Potentiometric Selectivity

The selectivity is one of the important characters of the ion-selective electrodes, determining whether reliable measurement in the target sample is possible or not. The selectivity was determined by the mixed solution method (MSM) and is evident from Table 3. Most of the interfering ions showed low values of selectivity coefficient, indicating no interference in the performance of the membrane electrode assembly. Such high selectivity of the proposed ion-selective electrode over other ions reflects high affinity of the membrane towards the Cr(VI) ions.

4.7. Performance of Cr(VI) selective electrode

4.7.1. Working concentration range and slope

Polyurethane-Al_2O_3 anion exchange fibrous composite membrane based Cr(VI) ion-selective electrode gave a linear relationship between electrode potential and the negative logarithm of Cr(VI) concentration ranging from 1×10^{-1} to 1×10^{-8} mol L^{-1}. Suitable concentrations were chosen for sloping portion of the linear curve. The limit of detection (LOD) was determined from the intersection of the two extrapolated segments of the calibration graph [32] was found to be 1 × 10^{-9} mol L^{-1}, thus it can be concluded that the working concentration range is 1 × 10^{-1} to 1 × 10^{-8} mol L^{-1} (Fig. 5) for Cr(VI) ions with a slope of 30.36 mV/decade for the calibration curve.

4.7.2. Effect of pH on electrode potential and response time

The pH effect on the potential response of the electrode was measured for 1 × 10^{-5} mol L^{-1} of Cr(VI) ion concentration at different pH values. The pH of the solution was adjusted with HCl and NaOH. From Fig.6 it can be seen that the pH dependence on the potential is insignificant in the pH range of 2.0-4.0 which can be taken as working pH range for the electrode. Another important factor is the promptness of the response of the ion-selective electrode and the average response time is defined as the time required for the electrode to reach a stable potential. The response time of the membrane in contact with 1 × 10^{-5} mol L^{-1} Cr(VI) was found to be ~20 s which is evident from the Fig.7. The shelf life was also measured and it was found that the membrane could be successfully used up to 12 months without any notable drift in potential during which the potential slope is reproducible within ±1 mV per concentration decade. Whenever a drift in the potential was observed, the membrane was re-equilibrated with 0.1 mol L^{-1} potassium dichromate solutions for 3-4 days.

4.7.3. Accuracy

The ion selective membrane electrode was found to work well under laboratory conditions. In order to evaluate the accuracy, an Cr(VI) selective electrode was applied for the determination of arsenate in various samples of drinking water containing different amount of Cr(VI), ranging from 5 to 20 mg L^{-1}. Each sample was analyzed in triplicate by membrane electrode and results were tested by standard addition method. The results given in Table 4 show that the amount of Cr(VI) recovered with the help of the membrane electrode is in good agreement with that determined by AAS, thereby reflecting the high accuracy as well as utility of the proposed method.

Table 5 shows the comparative working concentration range, response time, life time, pH range and detection limit of the proposed electrode in comparison to other reported Cr(VI) ion-selective electrode [33-35]. The results clearly indicated the superiority of the proposed electrode in terms of linear range, pH, response behavior and detection limit.

The traditional plasticized PVC membrane with no carrier showed inconsequential selectivity towards dichromate ion and its response was not reliable as shown by Benvidi et al. [36], while, polyurethane-Al_2O_3 membrane exhibited Nernstian response and had discernible selectivity for dichromate ion compared with the other anions.

5. Conclusion

In the present paper, new and novel polyurethane-Al_2O_3 anion exchange fibrous composite containing different amount of Al_2O_3 were prepared by using a simple chemical route. The obtained results show that the composite fibers have good ion-exchange capacity, thermal stability and its Cr(VI) selective membrane electrode has good operating characteristics, including Nernstian response, reasonable detection limit, relatively high selectivity, wide dynamic range and fast response. These characteristics and the typical applications presented in this work make the sensor a suitable one for measuring Cr(VI) content in real samples without a significant interaction from anionic species. It may be suggested that polyurethane-Al_2O_3 fibrous composite can be used as a new sensing material for detection of Cr(VI) from water and wastewater. Beside these polyurethane-Al_2O_3 fibrous composite may find practical applications as potential adsorbent for removal of Cr(VI) from water and wastewater.

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Figure Captions

Fig. 1. FTIR spectra of polyurethane (a), Al_2O_3 (b) and polyurethane-Al_2O_3 anion-exchange fibrous composite (c).

Fig. 2. FE-SEM image of pure polyurethane (a) and polyurethane-Al_2O_3 anion-exchange fibrous composite at different magnifications (b-d).

Fig. 3. XRD patterns of polyurethane (a), Al_2O_3 (b) and polyurethane-Al_2O_3 anion-exchange fibrous composite (c).

Fig. 4. TGA and DTG of polyurethane (a), Al_2O_3 (b) and polyurethane-Al_2O_3 anion-exchange fibrous composite (c).

Fig. 5. (a) Calibration curve for polyurethane-Al_2O_3 anion-exchange fibrous composite membrane (AEFCM-1) electrode in aqueous solution of $K_2Cr_2O_7$ and (b) Nerstian value of linear working range of calibration plot.

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Scheme 1. Schematic diagram of the formation of polyurethane-Al_2O_3 anion-exchange fibrous composite.

Scheme 2. The proposed mechanistic representation of formation of polyurethane-Al_2O_3 fibrous composite showing interaction of Al_2O_3 with polyurethane.

Table 1. Conditions of preparation and ion-exchange capacity of various polyurethane-Al_2O_3 anion exchange fibrous composite.

Sample ID.	Amount of Polyurethane in mg	Amount of Al_2O_3 (mg)	Amount of Tetrahydrofuran (T.H.F) in mL	Stirring time (h)	Appearance of the sample	Ion-exchange capacity (meq g^{-1})
AEFC-1	500	100	50	24	white	0.40
AEFC-2	500	200	75	24	white	0.55
AEFC-3	500	300	75	24	white	0.90
AEFC-4	500	400	75	24	white	1.30
AEFC-5	**500**	**500**	**75**	**24**	**white**	**1.95**

Table 2. Characterization of polyurethane-Al_2O_3 fibrous composite membranes.

Membrane No.	Amount of Polyurethane-Al_2O_3 composite (mg)	Amount of T.H.F (mL)	Thickness (mm)	Total wet weight (%)	Porosity (-)	Swelling (%)
AEFCM-1	**100**	**50**	**0.145**	**1.950**	**0.0020**	**0.009**
AEFCM-2	150	50	0.155	2.450	0.0040	0.017
AEFCM-3	200	50	0.185	3.650	0.0060	0.030

Table 3. Potentiometric selectivity coefficient values of interfering ions.

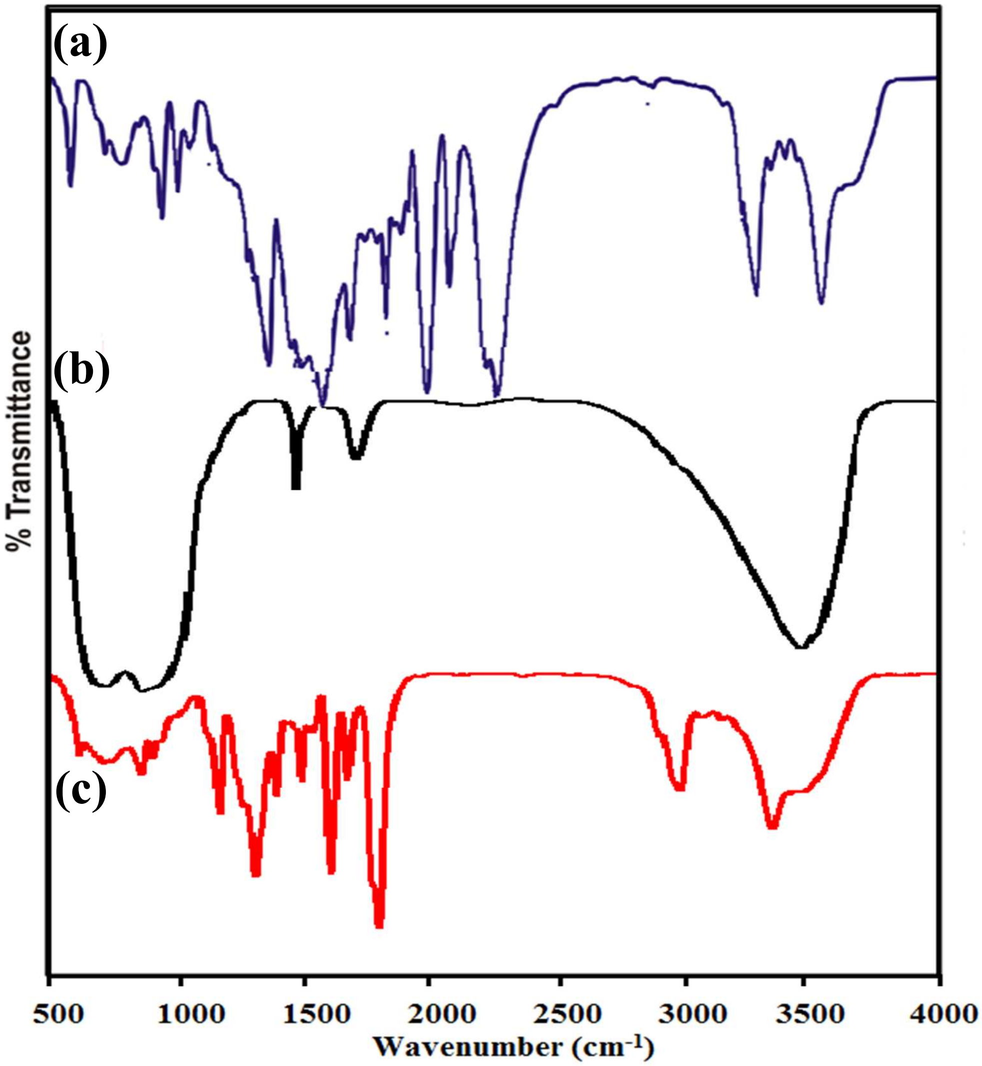
Interfering ions	**Selectivity coefficient (K_{MSM})**
SO_4^{2-}	5.66×10^{-3}
SCN^-	2.88×10^{-3}
NO_3^-	6.15×10^{-3}
Cl^-	3.90×10^{-3}
AsO_3^{3-}	5.80×10^{-3}
$H_2PO_4^{3-}$	4.55×10^{-2}
$Cr_2O_7^{2-}$	1

Table 4. Determination of Cr(VI) added to a drinking water sample containing different concentrations of Cr.

Cr(VI) added (mg L^{-1})	**Cr(VI) found by ISE (mg L^{-1})**	**Recovery by ISE (%)**	**Cr(VI) found by AAS (mg L^{-1})**	**Recovery by AAS (%)**
5.0	4.55	91.00	4.89	**97.80**
7.5	7.23	96.40	7.40	**98.66**
10.0	9.60	96.00	9.89	**98.90**
12.5	12.34	98.72	12.45	**99.60**
15.0	14.60	97.33	14.90	**99.33**
20.0	19.65	98.25	19.95	**99.75**

Table 5. A comperative study of dichromate selective membrane electrode based on various electroactive material with polyurethane-Al_2O_3.

Ref.	Electroactive Material	Response Time (s)	Linear Range	pH Range	Nernstian Slope (mv/decade)	Life Span (months)	Detection Limit
[16]	5,11,17, 23-tetra-tert-butyl-25, 27,-bis-(isoniazidyl-carbonylmetoxy)-26	15-20	10^{-1} to 10^{-7} mol L^{-1}	1	41.5	3 months	4.3×10^{-8} mol L^{-1}
[17]	Quinaldine Red	30	10^{-1} to 10^{-6} mol L^{-1}	<6	56.4	3 months	2.5×10^{-6} mol L^{-1}
[18]	SBA-15/Ionic Liquid/MWCNTs/ Graphite	23	10^{-1} to 10^{-6} mol L^{-1}	4	-	8 week	2.6×10^{-6} mol L^{-1}
This work	polyurethane-Al_2O_3	18-20	10^{-1} to 10^{-8} mol L^{-1}	2.0-4.0	30.36	12 months	1×10^{-9} mol L^{-1}



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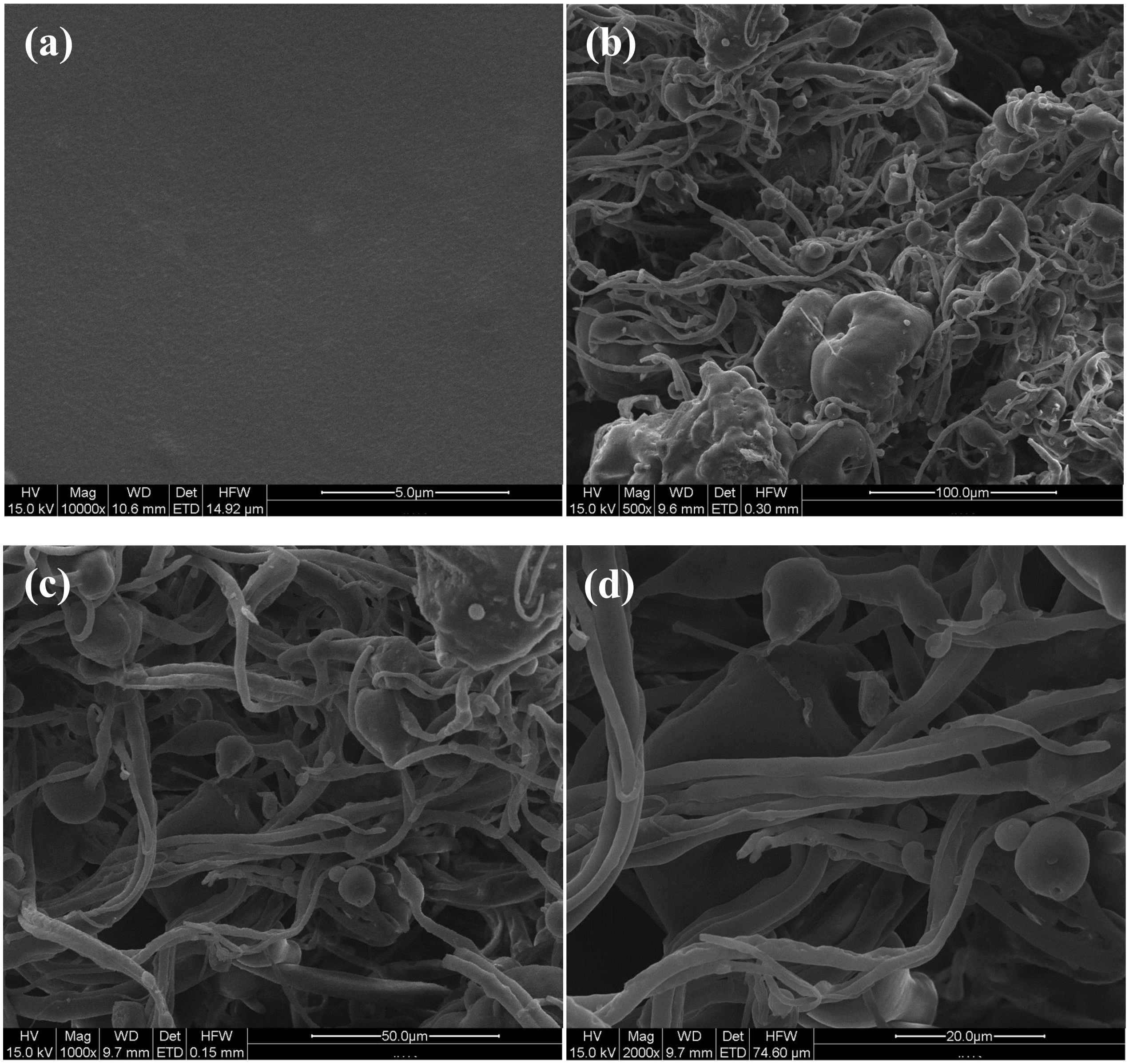

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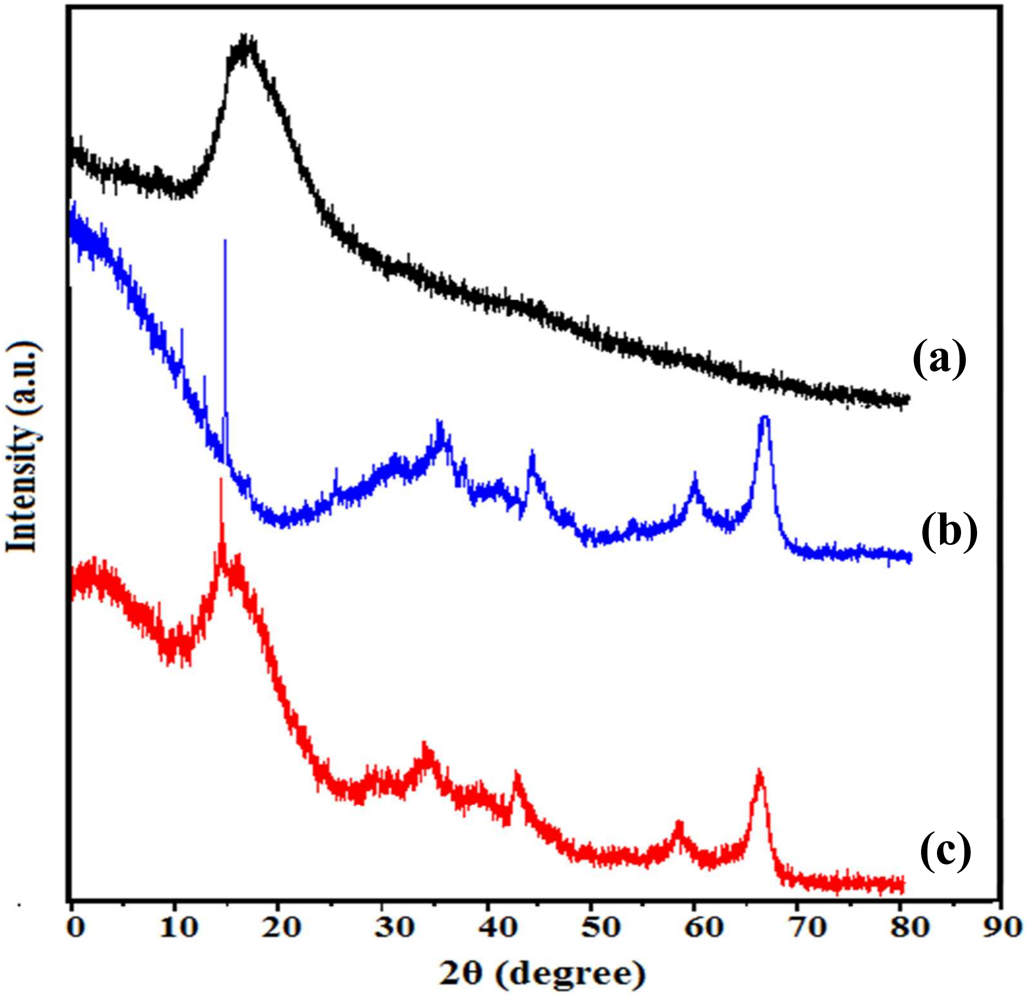

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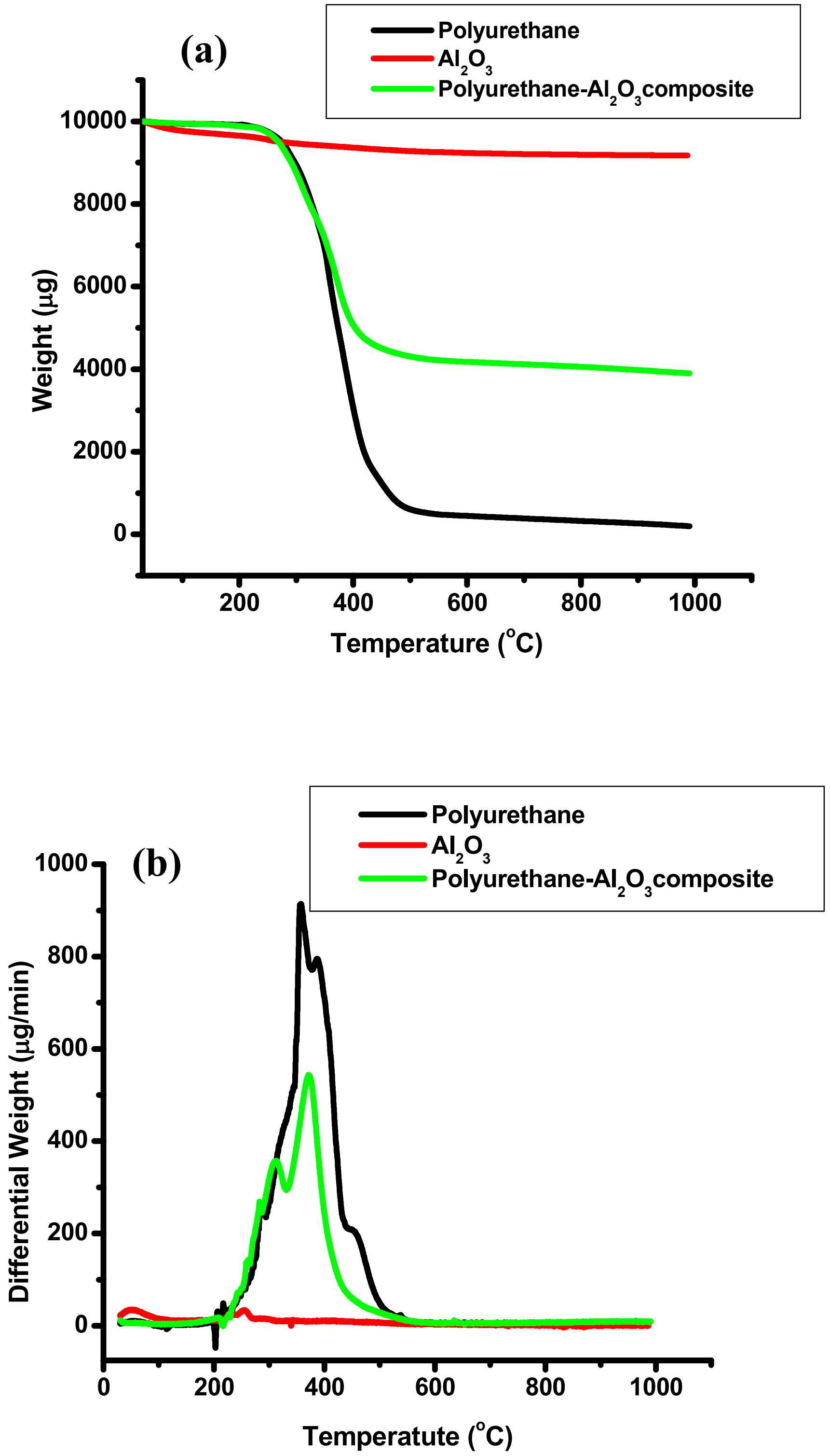

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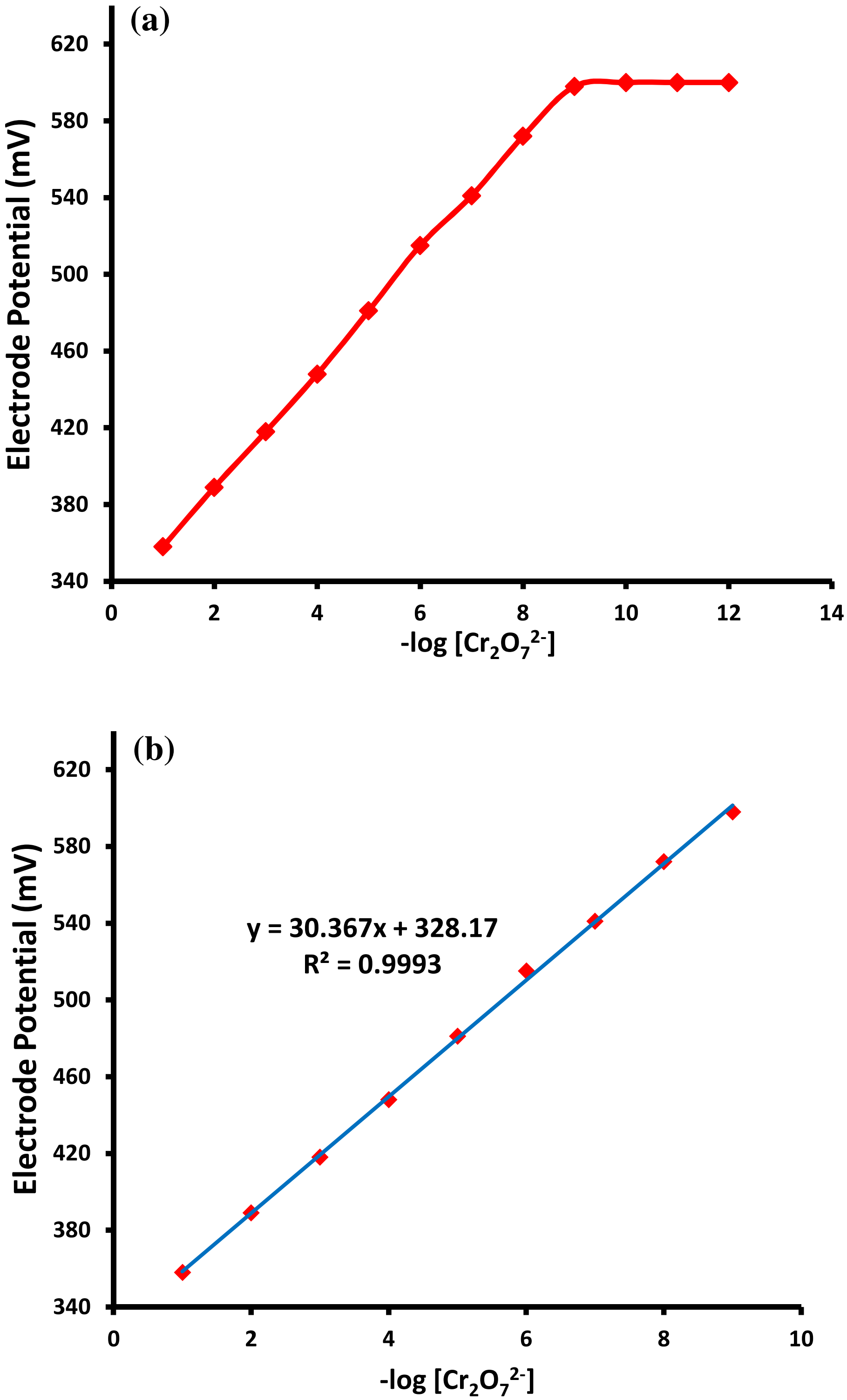

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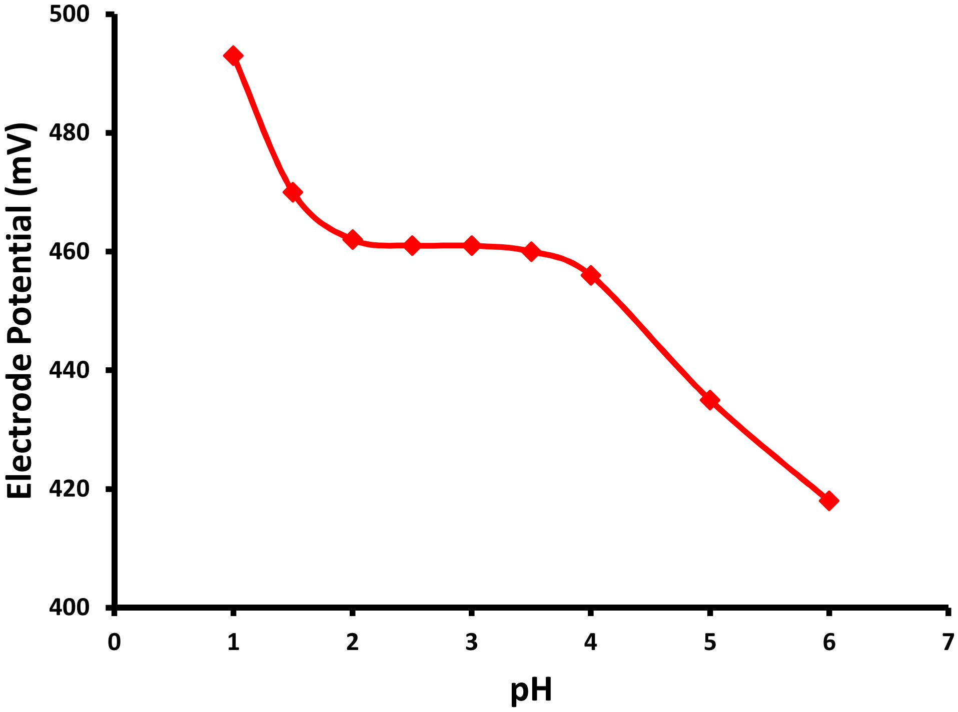

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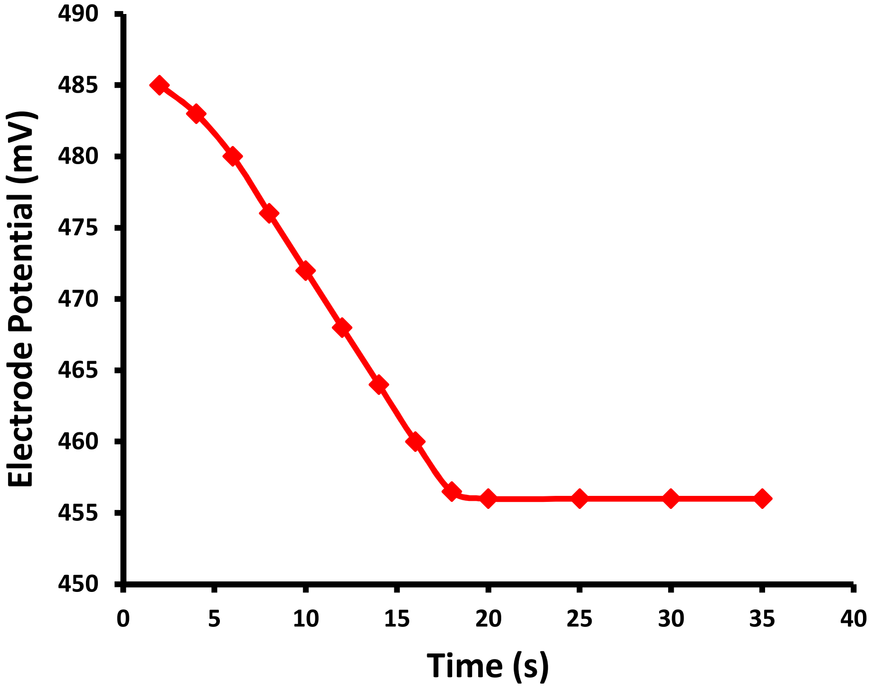

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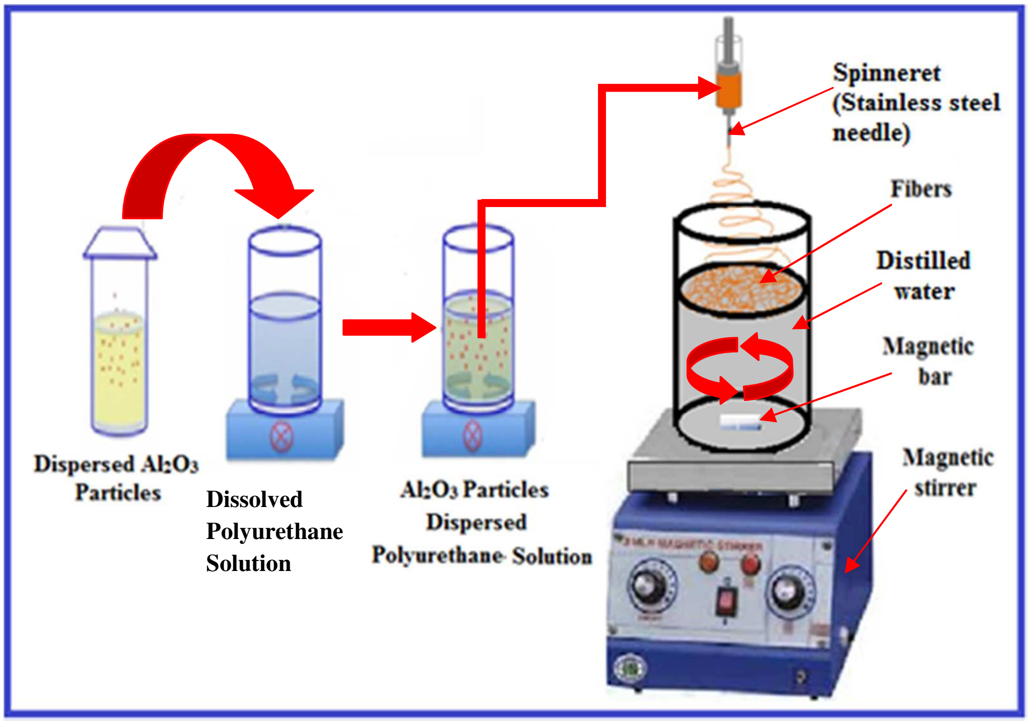
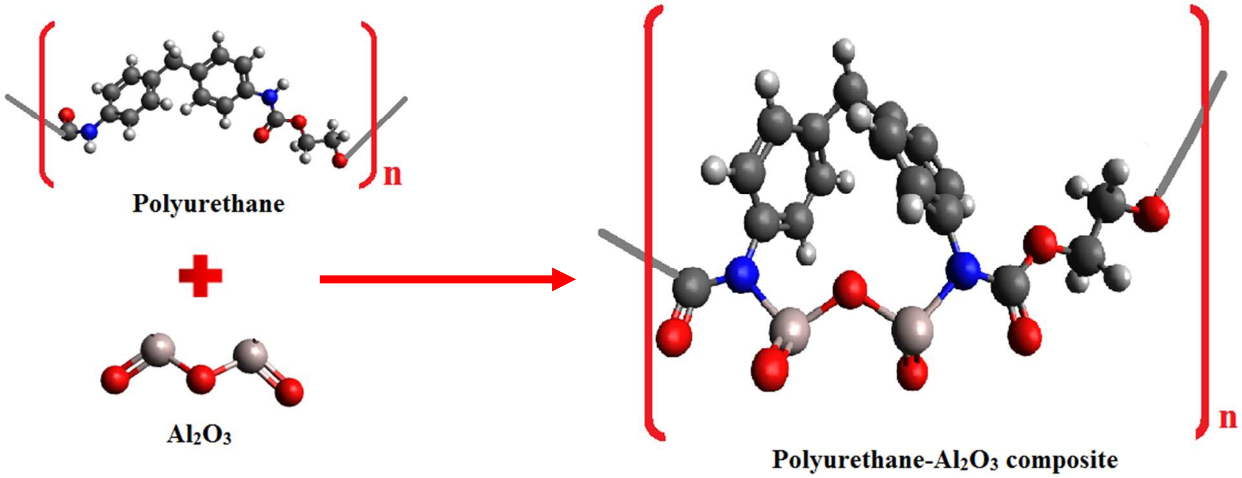


Scheme 1. Schematic diagram of the formation of polyurethane-Al_2O_3 anion-exchange fibrous composite.



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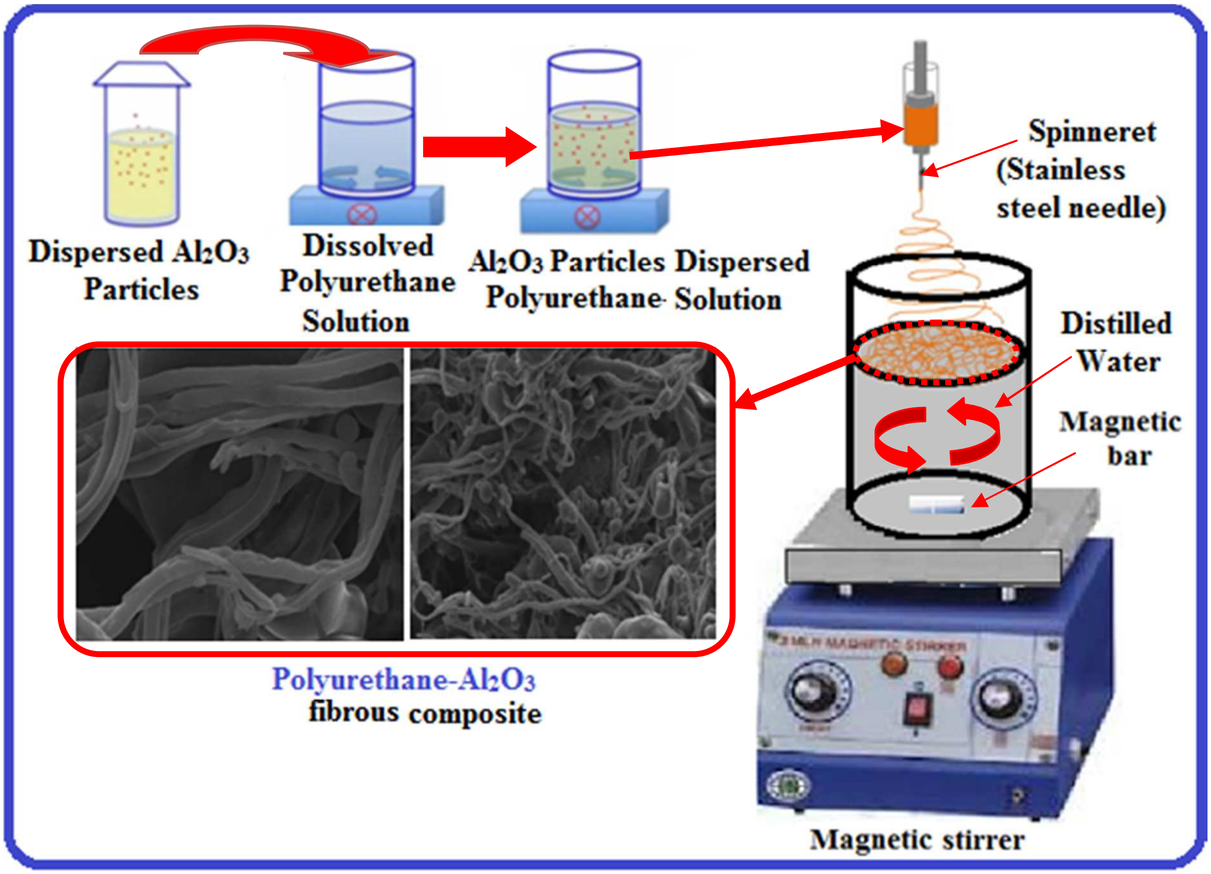
Graphical Abstract



Ion-selective electrode was developed by using polyurethane-Al_2O_3 organic-inorganic fibrous composite for the determination of Cr(VI) from water.