

Synthesis and characterization of ceramic/carbon nanotubes composite adsorptive membrane for copper ion removal from water

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Abstract—We prepared a novel adsorptive membrane by implanting carbon nanotubes (CNTs) in pore channels of ceramic (α -alumina) support via chemical vapor deposition (CVD) method using cyclohexanol and ferrocene as carbon precursor and catalyst, respectively. Optimization of CNTs growth conditions resulted in uniform distribution of the CNTs in the pore channels of the support. The optimized CNTs-ceramic membrane was oxidized with concentrated nitric acid, and chitosan was employed for filling intertube-CNT gaps. The modified CNTs-ceramic membrane was used for copper ion removal from water, and the effects of the modification steps (oxidation and filling intertube-CNT gaps with chitosan) and pH on permeation flux and rejection of the prepared adsorptive membrane were investigated. Moreover, static adsorption was also investigated and Langmuir and Freundlich isotherms and two kinetics models were used to describe adsorption behavior of copper ions by the prepared adsorptive membrane.

Keywords: Carbon Nanotubes (CNTs), Ceramic (α -Alumina) Support, Adsorptive Membrane, Copper Ions Removal from Water

INTRODUCTION

Toxicity of heavy metal ions in water toward aquatic-life, plants, animals, human beings and the environment has been a major concern for many years. Heavy metal ions are not degraded biologically like organic pollutants. Due to adsorption and therefore possible accumulation of heavy metal ions in organisms, their presence in water is a public health problem. With rapid industrial development and competitive use of fresh water in many parts of the world, water contaminated by heavy metal ions has become recently a much more serious concern. Therefore, heavy metal ions removal from water is an important subject today [1-3].

Copper as one of the most important toxic heavy metals has many applications. Copper contamination in water occurs mainly from metal cleaning and plating bath, paper and pulp, fertilizers, refineries, and wood preservatives. Copper can cause serious problems such as stomach intestinal distress, kidney damage, anemia and even coma and eventual death. Permissible limit of copper ions in drinking water is 1.3 mg/l (according to the Safe Drinking Water Act). Therefore, it is important to develop technologies that can be industrially used for copper ion removal from effluents [4-6].

Several conventional methods, e.g. chemical precipitation, ion exchange and adsorption columns, have been applied for heavy metal ions removal from effluents. Compared to the conventional methods, adsorption membrane filtration (AMF) process with several advantages such as excellent removal efficiency, higher flow rate, lower pressure drop, faster kinetics, longer life, smaller foot-

prints and easier scale up have appeared as powerful technique for heavy metal ions removal from effluents [5-14].

Carbon nanotubes (CNTs) are relatively new adsorbents for wastewater treatment. Nowadays, application of CNTs with extraordinary properties such as extremely porous and hollow structure, uniform pore size distribution, high affinity for heavy metal ions, large specific area, good antifouling nature, biocompatibility, biodegradability and functionalization capability by various surface functional groups have gained great importance in the separation of heavy metal ions from effluents as adsorbent. Also, due to excellent affinity of CNTs toward heavy metal ions, CNTs application in adsorptive membrane preparation is expanding [3,15-27]. As reported [9], CNTs have demonstrated superior affinity toward copper ions, compared to other divalent heavy metal ions.

Recently, the powder of CNTs has been used as adsorbent in adsorption processes. On industrial scale, when powder of CNTs is used as adsorbent, mixing of the CNTs with waste water with ultrasonic agitation is not economically and technically possible. Also, after adsorption process, it is difficult to completely remove powder of CNTs from treated water without the centrifuging process. Also, separation of the CNTs from treated water by filtration is difficult because the filter may be quickly blocked by the CNTs. With accumulating evidence of toxicity of CNTs, there are serious concerns over their health and environmental risks once released to the environment. Also, adsorption of toxic substances by CNTs may enhance toxicity of CNTs and this further affects transfer of toxic substances to the environment. Therefore, economical waste water treatment without CNTs leakage into water is preferable.

Chitosan (CS) is a biopolymer derived by deacetylation of chitin, an abundant biopolymer obtained mainly from shellfish waste as a byproduct of the seafood industry. Chitosan, a natural amino-

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polysaccharide polymer, with excellent properties such as high hydrophilicity, good film and fiber forming ability, normal chemical resistance, wide availability and biocompatibility and its abundant functional groups (as reactive sites), has great importance for preparation of adsorptive membranes. Chitosan has both amino (-NH₂) and hydroxyl (-OH) functional groups in its structure, and hence has excellent adsorption capacities for a number of metal ions. These characteristics allow chitosan to find wide applications as a material in water purification [27-32].

The aim of the present work is to prepare a novel adsorptive membrane for removal of copper ions from water by CNTs implanting into the pore channels of a ceramic (α -alumina) support by chemical vapor deposition (CVD) method using cyclohexanol and ferrocene as carbon precursor and catalyst, respectively. The implanted CNTs are oxidized with concentrated nitric acid at room temperature and chitosan is employed for filling intertube-CNT gaps. Static adsorption of the prepared adsorptive membrane is also investigated. Langmuir and Freundlich isotherms and pseudo-first-order and pseudo-second-order kinetic models are used to describe adsorption behavior of copper ions by the prepared adsorptive membrane.

EXPERIMENTAL

1. CNTs Implanting in Alumina Pore Channels

A schematic diagram of experimental CVD set-up is shown in Fig. 1. Details of the CVD system are presented elsewhere [3,33, 34]. The CVD system consisted of a horizontal stainless steel tube housed in a one-stage cylindrical furnace. A flask containing a known quantity of cyclohexanol (~10 g) (purity \geq 98%, Fluka) as carbon source was connected to the reactor nearby the nitrogen inlet. Nitrogen was used as carrier gas. Ceramic porous supports (α -alumina disks with 20 mm diameter and 2 mm thick) were used as substrates. The substrates had an average pore diameter of 1 μ m and

porosity of about 40%. They were placed in the middle of reactor. A known quantity of ferrocene (purity \geq 98%, B.D.H) as catalyst was placed inside the reactor between the nitrogen inlet and the substrates. An oil bath was used for carbon source evaporation.

At first, in order to get rid of residual air, the reactor was purged with nitrogen and then the furnace was heated to the preset temperature. It was reported that ferrocene is thermally stable up to 454 °C and above this temperature it begins to decompose by releasing hydrogen [35]. With increasing the furnace temperature, ferrocene was sublimed gradually and the iron atoms were decomposed from ferrocene vapor and begun to deposit on the surface and in the pore channels of the alumina substrate to form iron nanoparticles. When the reactor was heated to the preset temperature, the flask containing cyclohexanol was placed in the oil bath (at 250 °C) for immediate vaporization process. The produced vapor was carried by nitrogen towards the high temperature zone of the reactor where the substrates were situated. Pyrolysis of the vapor took place and the CNTs were synthesized on the substrate surface and in the substrate pores. Pressure inside the reactor was kept constant during the reaction. When the experiment was completed, the furnace was switched off and allowed to cool naturally.

Several experiments were carried out at different CNTs growth conditions such as reaction time, reaction temperature, ferrocene content, nitrogen flow rate and reactor pressure in order to obtain a uniform distribution of CNTs in the pore channels of ceramic porous support. Finally, it was obtained that the best values of the CNTs growth conditions (optimum conditions) are: reaction time=60 min; ferrocene content=1 g; nitrogen flow rate=400 cm³min⁻¹; reactor pressure=5 bar and reaction temperature=750 °C.

2. Oxidation of the Implanted CNTs in the Alumina Pore Channels

The CNTs-ceramic membrane prepared under the optimum conditions was immersed in concentrated nitric acid (65%, Merck) for one day and then washed using deionized water several times

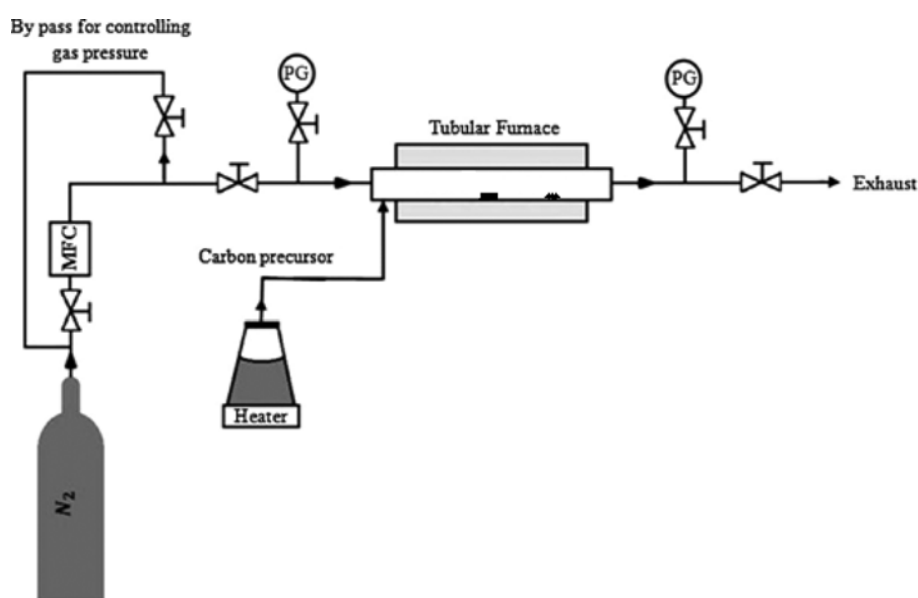


Fig. 1. Schematic diagram of the experimental CVD setup.

until pH of the washing water showed no change, then dried at 110 °C for 24 h.

3. Filling of Intertube-CNT Gaps with Chitosan

Chitosan (CS) ($MW_{ave}=190000-310000$, Aldrich) polymeric solution (2 wt%) was prepared by dissolving distinct amount of chitosan powder in 1% (v/v) acetic acid solution with stirring at room temperature for 24 h. The prepared oxidized CNTs-ceramic membrane was dipped in the polymer solution for 15 min and then removed and placed on a glass plate. The excess solution and air bubbles were removed by a roller. The samples were dried at ambient temperature for one day and then annealed at 90 °C for one hour.

4. Membrane Characterization

Scanning electron microscope (SEM, Philips: XL30) was used for analysis of the substrate and the prepared CNTs-ceramic membrane morphologies. Nanostructure of the CNTs was determined by transmission electron microscope (TEM, Philips: CM200).

5. Permeation Test

Analytical grade of $Cu(NO_3)_2 \cdot 3H_2O$ (Merck) and deionized water were used to prepare feed stock solutions of copper ions. Copper ion concentration range was 20-100 mg/l. A dead-end cell (100 ml volume) with a membrane area of about 3 cm² was used for permeation tests. The cell was equipped with a pressure gauge. Pressurized nitrogen was used to force the feed through the membrane. A schematic of the dead-end system is shown in Fig. 2. Permeate samples were collected over a given period and weighed. A conductometer (CRISON, GLP 32) was employed to determine copper ion concentration. The experiments were carried out at 25 °C and nitrogen pressure of 4 bar.

Permeation flux was calculated using the following equation:

$$J = \frac{m}{A \cdot t} \quad (1)$$

where J is permeation flux (kg/m²·h), m is permeate mass (kg), A is the effective membrane area (m²) and t is the permeation time (h).

The rejection was calculated using the following equation:

$$Rej(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where C_p and C_f are copper ion concentration in permeate and feed (mg/l), respectively.

6. Static Adsorption

Static adsorption of copper ions onto the prepared membrane

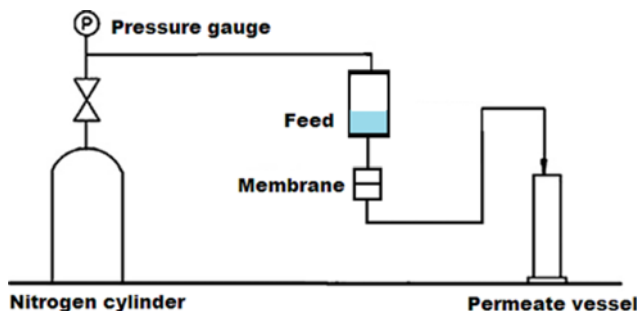


Fig. 2. Schematic of the dead-end filtration system.

samples was measured using the batch procedure. 50 mg of the prepared adsorptive membrane was soaked in 50 ml of copper ions solution (with concentration of 20, 40, 60, 80 and 100 mg/l, pH 7, 25 °C) for 24 h. A conductometer (CRISON, GLP 32) was employed to determine copper ions concentration. Adsorption capacity of the prepared membrane samples was calculated using the following equation:

$$q_e = \frac{V \times (C_i - C_f)}{W} \quad (3)$$

where q_e is equilibrium adsorbed amount of copper ions by the membrane (mg/g), V is volume of copper ions solution (l), C_i and C_f are initial and final copper ions concentration (mg/l), respectively and W is mass of the adsorptive membrane sample (g).

7. Batch Kinetics Studies

Kinetics studies were performed at initial copper ion concentration of 100 mg/l, and the procedure was identical to that of the static adsorption experiments. The aqueous samples were taken at pre-set time intervals and the copper ion concentration was similarly measured. Adsorption amount at time (t), q_t (mg/g), was calculated using the following equation:

$$q_t = \frac{V \times (C_i - C_t)}{W} \quad (4)$$

where C_t (mg/l) is copper ions concentration at time (t).

RESULTS AND DISCUSSION

1. Membrane Characterization

Figs. 3(a) and 3(b) show the virgin ceramic support and the CNTs-ceramic membrane prepared under the optimum CNTs growth conditions, respectively. As could be observed, at the optimum CNTs growth conditions, color of the ceramic support (white) was changed to color of the CNTs (black) and a uniform distribution of the CNTs in the pore channels of the ceramic membrane was obtained. It should be mentioned that no leakage of CNTs into water was observed after immersing the prepared CNTs-ceramic membrane in water for 24 h.

SEM images of the virgin ceramic support and the CNTs-ceramic membrane prepared under the optimum CNTs growth conditions are shown in Fig. 4. A uniform distribution of CNTs in the pore channels of the ceramic membrane was obtained. CNTs implanted into the ceramic membrane lead to fill of the ceramic membrane pores, producing large amount of adsorption sites.

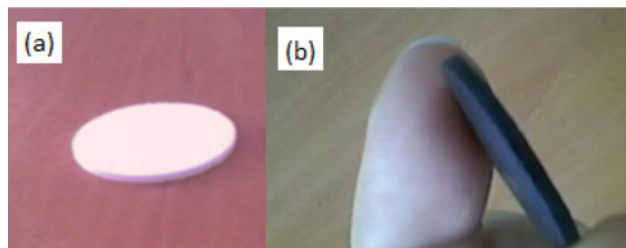


Fig. 3. An overview image of (a) the virgin ceramic support and (b) the CNTs-ceramic membrane.

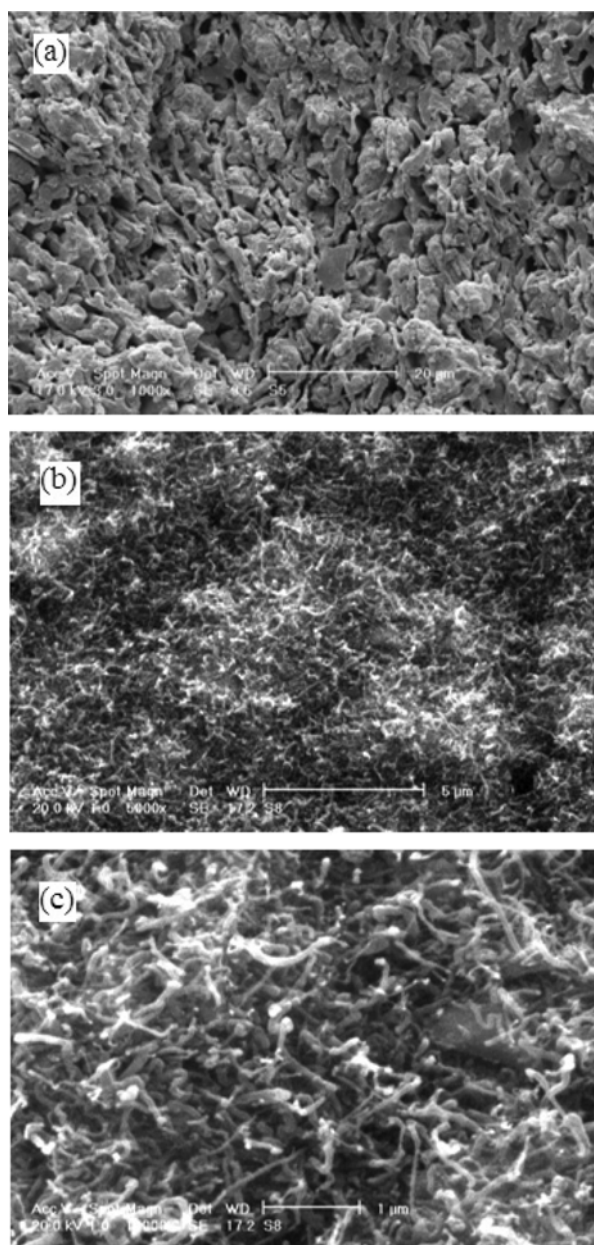


Fig. 4. SEM images of (a) the virgin ceramic support, (b) the CNTs-ceramic membrane and (c) the CNTs-ceramic membrane (high resolution).

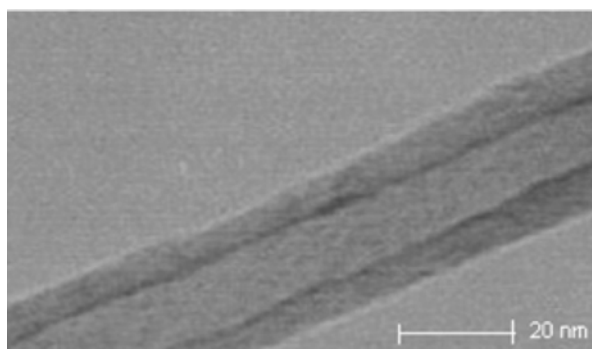


Fig. 5. TEM image of a typical CNT.

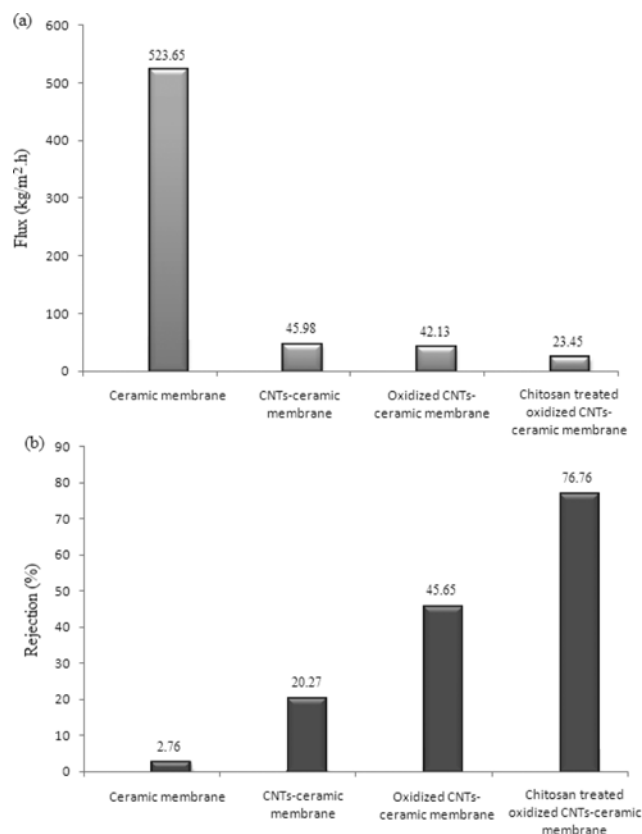


Fig. 6. Effects of the modification steps on (a) permeation flux and (b) rejection of the prepared CNTs-ceramic membrane.

Fig. 5 shows a TEM image of an implanted CNT in pore channels of the ceramic support with inner tube diameter of about 10 nm and outer tube diameter of about 30-40 nm, respectively.

2. Membrane Performance

Fig. 6 shows the influence of the modification steps, including CNTs implanting, oxidation of implanted CNTs and filling inter-tube-CNT gaps with chitosan on permeation flux and rejection of the prepared CNTs-ceramic membrane. These experiments were performed at initial pH of 6 for initial period of 10 min. The results demonstrated that CNTs implanting significantly decreases permeation flux of the ceramic membrane, while increases rejection. This is because CNTs implanting reduces the membrane pore void fraction, which consequently increases the membrane resistance, and as a result permeation flux decreases. However, this membrane cannot considerably reject copper ions. Oxidation of the implanted CNTs resulted in severe increasing rejection but permeation flux did not significantly change. Increasing rejection in this step is due to the functional groups of the oxidized CNTs and their interactions with copper ions [37-40]. As mentioned, oxidation of CNTs can offer a great number of acidic functional groups on external surface of CNTs. These functional groups provide a large number of chemical adsorption sites and thereby increase adsorption capacity of CNTs. These functional groups react with and adsorb copper ions from water. This improves rejection capability of the membrane. However, the membrane void fraction does not significantly change after oxidation of the implanted CNTs. The oxidized CNTs-

ceramic membrane after filling the intertube-CNT gaps with chitosan, due to the reduced porosity, exhibited lower permeation flux and higher rejection. The latter is partly due to presence of functional groups of the oxidized CNTs and chitosan in the pore channels of membrane. As mentioned, chitosan has both amino (-NH₂) and hydroxyl (-OH) functional groups in its structure. Hence, it has excellent adsorption capacities for a number of metal ions such as copper ions. The functional groups of chitosan can provide a large number of chemical adsorption sites and thereby can increase adsorption capacity of copper ions of the prepared adsorptive membrane. Interaction between copper ions and the functional groups of the prepared adsorptive membrane (functional groups of chitosan and functional groups of oxidized CNTs) is the major mechanism of the prepared membrane separation. Also, filling the intertube-CNT gaps of prepared membrane with chitosan, due to the reduced membrane porosity and membrane pore void fraction can also improve rejection (copper ions removal from water).

To prove that the main mechanism of the prepared membrane separation is adsorption, static adsorption experiments were also conducted. Adsorption capacities of the membranes after each modification step are compared in Fig. 7. The observed trend is in good agreement with the rejection results confirming the separation mechanism is adsorption.

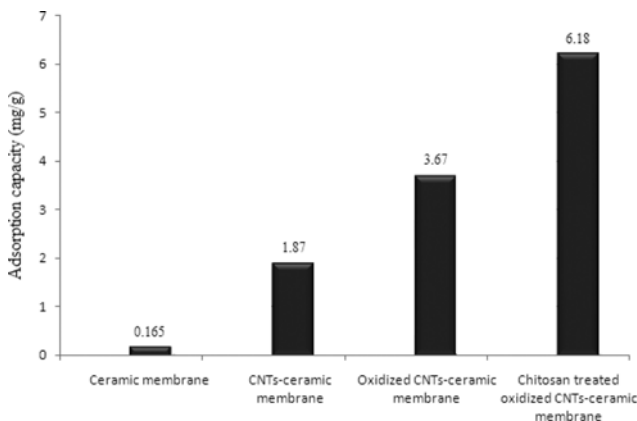


Fig. 7. Adsorption capacities of the membranes after each modification step.

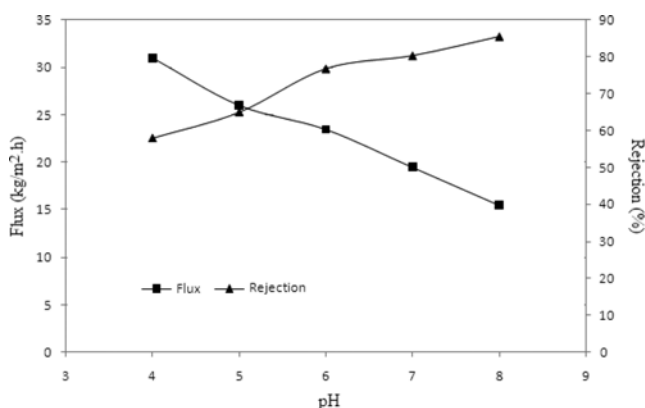


Fig. 8. Effect of pH on rejection of copper ions and permeation flux of the prepared adsorptive membrane.

3. Effect of pH on Membrane Performance

Fig. 8 elucidates the effect of pH on rejection of copper ions and permeation flux of the CNTs-ceramic membrane after modification. Increasing pH, improves adsorption of copper ions. This is mainly due to the changes in surface charge of CNTs and hydrolysis degree of copper ions. Copper ions are available in the forms of Cu²⁺, Cu(OH)⁺, Cu(OH)₂, Cu(OH)₃⁻ and Cu(OH)₄²⁻ at different pH values [10,41]. At low pH, copper ions are available in the form of Cu²⁺. With increasing pH, the amount of copper ions in the form of Cu²⁺ decreases and that of other forms of copper ions with negative charges increase. Thus, at lower pH, the copper ions rejection is low and this may be partly attributed to the competition between H⁺ and Cu²⁺ ions on the adsorption sites (the functional groups) of CNTs and chitosan in the membrane pores. At higher pH, the CNTs surface is more negatively charged, which causes higher electrostatic attraction of copper ions [42]. Then, at higher pH, the copper ion adsorption on the adsorption sites increases. With increasing the copper ion adsorption on the adsorption sites of the prepared adsorptive membrane, the membrane pore void fraction is reduced, and this consequently increases the membrane resistance and as a result permeation flux decreases.

4. Adsorption Isotherms

The experimental data for copper ions adsorption onto the prepared adsorptive membrane were analyzed using the Freundlich and the Langmuir isotherm models.

The linear form of Langmuir isotherm can be expressed by the following equation:

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

where q_m is the maximum adsorption capacity, in mg/g, and K_L is the Langmuir constant.

The equilibrium parameter can be expressed by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

where C_0 is the highest initial copper ions concentration, in mg/l. The value of R_L indicates the type of isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The linear form of Freundlich isotherm can be expressed by the following equation:

$$\log q_e = n \log C_e + \log K_F \quad (7)$$

where K_F and n are the Freundlich parameters related to adsorption capacity and adsorption intensity, respectively. Value of $n < 1$ represents a favorable adsorption condition.

The calculated Langmuir and Freundlich parameters are listed in Table 1. As can be observed, the calculated equilibrium parameters, R_L , lie within the favorable limit between 0 and 1. The q_m value calculated using the Langmuir isotherm is 7.04 mg/g, which is consistent with the experimental value. The K_F values calculated using the Freundlich model are large, indicating that the prepared adsorptive membrane has high affinity toward copper ions. Deviation of the n values from unity indicates a non-linear adsorption that takes place on heterogeneous surfaces [1,26,43]. As observed in Table 1,

Table 1. Parameters of the Langmuir and the Freundlich isotherm models for adsorption of copper ions onto the prepared adsorptive membrane

Adsorptive membranes	Langmuir isotherm				Freundlich isotherm		
	q_m (mg/g)	K_L (L/mg)	R_L	R^2	n	K_F (L/mg)	R^2
Chitosan treated oxidized CNTs-ceramic membrane	7.04	0.00063	0.63	0.98	0.85	1.2	0.99

Table 2. Parameters of the pseudo-first-order and the pseudo-second-order kinetics models for adsorption of copper ions onto the prepared adsorptive membrane

Adsorptive membrane	Initial cons. (mg/l)	$q_{e, exp}$	Pseudo-first-order kinetics model			Pseudo-second-order kinetics model		
			q_e	k_1	R^2	q_e	$k_2 \cdot 10^{-3}$	R^2
Chitosan treated oxidized CNTs-ceramic membrane	100	6.18	8.34	0.67	0.92	6.54	3.54	0.98

based on the correlation coefficient (R^2) values, both the Langmuir ($R^2=0.98$) and the Freundlich ($R^2=0.99$) isotherm models match well the experimental data. Several researchers also reported that the metal ions sorption onto the CNTs can be described by both the Langmuir and the Freundlich isotherm models [16,19,44].

5. Adsorption Kinetics

To analyze the adsorption kinetics of copper ions, two kinetics models, including the pseudo-first-order and the pseudo-second-order models were applied to fit the experimental data obtained at 100 mg/l initial copper ions concentration.

The linear form of pseudo-first-order and pseudo-second-order kinetics models can be expressed by the following equations, respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where k_1 and k_2 are the adsorption rate constants of the first and the second order kinetic models, in min^{-1} and $\text{l/mg}\cdot\text{min}$, respectively.

The calculated kinetics parameters for adsorption of copper ions onto the prepared adsorptive membrane at initial copper ions concentration of 100 mg/l are listed in Table 2. As can be observed, the correlation coefficients (R^2) of the pseudo-second-order kinetics model are higher than those of the pseudo-first-order kinetics model. Also, the experimental q_e values are closer to the q_e value calculated using the pseudo-second-order kinetics model. Consistency of the experimental data with the pseudo-second-order kinetics model indicates that the rate-limiting step may be chemical adsorption (chemisorption). In chemical adsorption, it is assumed that adsorption capacity is proportional to the number of active sites (functional groups) incorporated on the adsorbent surface [45-47].

Using the prepared membrane in this work as an adsorptive membrane with fixed implanted CNTs in pore channels of the ceramic (α -alumina) support eliminates problems of agitating and removing of the CNTs with and from water before and after adsorption. Also, using the prepared adsorptive membrane, economical

waste water treatment without CNT leakage into water is feasible. As a result, the prepared membrane in this work with high practical potential can be recommended as an economical and effective adsorptive membrane for heavy metal ion removal from waste water at industrial scale. Also, this adsorptive membrane can be scaled up and prepared at industrial scale simply, because its preparation method is simple and does not have any expensive instruments.

CONCLUSION

We prepared a novel adsorptive membrane for copper ions removal from water by implanting carbon nanotubes (CNTs) in pore channels of a ceramic (α -alumina) support. Chemical vapor deposition (CVD) was used for CNTs implanting into the pore channels of the ceramic support using cyclohexanol and ferrocene as carbon precursor and catalyst, respectively. After optimization of the growth conditions of CNTs synthesis, the best CNTs-ceramic membrane was oxidized with concentrated nitric acid at room temperature and chitosan was employed for filling intertube-CNT gaps. The results demonstrated that increasing pH improves adsorption of copper ions, and this may be due to changes in the surface charge of CNTs and the degree of copper ionization. The prepared CNTs-ceramic membrane after oxidation with nitric acid exhibited higher rejection of copper ions due to the incorporated functional groups on the CNTs external surface. These functional groups can react and adsorb copper ions from water. Oxidized CNTs-ceramic membrane after filling intertube-CNT gaps with chitosan exhibited lower flux and higher rejection. The latter is partly due to the presence of adsorption groups of oxidized CNTs and functional group of chitosan in the pore channels. Adsorption behavior of copper ions onto the prepared adsorptive membrane does match well both with the Langmuir and the Freundlich isotherm models. The results demonstrated that kinetics of adsorption does match well with the pseudo-second-order kinetics model. Further research is required to prepare a membrane with higher rejection and adsorption efficiency.

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