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Article

Development of Sulfonated Nanocomposites Ion Exchange Resin for Removal of Sodium Ions from Saline Water

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Abstract: A stable composite cation exchange adsorbent for the treatment of sodium metal ions has been synthesized by suspension polymerization method. Kinetic study, Ion exchange capacity, pH titration, distribution studies were also carried out to determine the primary ion-exchange characteristics of the composite cation exchange adsorbent material. The material shows exchange capacity of 4.22meq g^{-1} (for Na^+ ions).pH titration data reveal its bifunctional behavior. The distribution coefficient values (K_d) of metal ions have been determined in water Colum systems. On the basis of K_d values the composite cation exchange material was selective for sodium ions. The composite cation exchanger is applied for the treatment of saline water and synthetic mixture successfully and can be used as a conducting material.

Keywords: water, sodium, cations, desalination

1. Introduction

In the 21st century, recognition of a potential water shortage and the unpredictable impact of global warming on overall water scarcity posits that the first and second decades should be referred to as the "water crisis decades" [1]. This shortage can be partially attributed to global population growth, limited natural resources, and increased industrial activities [2]. Consequently, to resolve the water scarcity problem in many regions around the world, seawater is no longer merely a marginal water resource for resource-limited countries. In a recent global industry forecast [2], from as recent as three years ago the global desalination industry can be seen to be rapidly expanding, and this is just the beginning stage of desalination market

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expansion.

A number of organic and inorganic ion-exchangers have been developed but there are certain limitations existing with them. The main drawbacks associated with organic ion-exchangers are of poor mechanical strength and low thermal stability under high radiation conditions while inorganic ion-exchangers are not suitable for column applications. Hence, in order to overcome all the above limitations, composite ion-exchangers have been synthesized by incorporating organic polymer with the matrix of inorganic precipitate. The composite materials show better exchange capacity, granule metric properties, reproducibility, and chemical stability along with thermal stability and also possess better selectivity for heavy metals compared to pure inorganic and organic materials. These composite ion-exchange materials can also be used as a catalyst ion-exchanger [3], ion selective electrode [4]and also finds a large number of applications in pollution control and water treatment [4]. CNTs are categorized as single-walled nanotubes (SWCNTs), double-walled CNTs (DW-CNTs), triple-walled CNTs, and multi-walled nanotubes (MWNTs). The electronic properies significantly vary depending on the chirality and the number of graphene walls [5].However, the insolubility and weak dispersibility of CNTs in common solvents and matrices' have limited their applications. An effective method to improve dispersion of nanotubes the modification of CNTs by polymers. The modification of CNTs may be divided into two categories on the basis of either non-covalent or covalent bonding between the CNTs and the polymer. Non-covalent modification of CNTs is the physical adsorption and/or wrapping of polymers to the surface of the CNTs. Covalent modification of CNTs is the covalent chemical bonding (grafting) of polymer chains to CNTs, which process dramatically improves the interfacial interactions between nanotubes and the polymer matrix. Interfacial interaction is one of the most critical issues in polymer/CNT composites [6].

A typical procedure for the preparation of a PS/CNT composite is as follows [7] CNTs are dispersed in toluene using an ultrasonic wand dismembrator. The CNT suspensions are then admixed with toluene solutions of PS to yield PS/CNT solutions. These mixtures are further homogenized in an ultrasonic bath. Thin composite films are then produced from these solutions using two different techniques, film casting and spin casting. A typical procedure for film casting is as follows: Solution is poured into a fat-bottomed glass culture dish, and the toluene is allowed to evaporate[8]. Thin uniform films are obtained and dried in a vacuum oven. A typical procedure for spin casting is as follows: PS/CNT solutions are deposited at the center of a rotating disk and spun on a Spin Coater. Thin films are formed and the flms are subsequently dried in a vacuum oven. Safadi et al. [9] reported on the basic relationships between processing conditions and the mechanical and electrical properties of MWCNT reinforced PS composites. The presence of 2.5 vol% MWCNTs approximately doubles the tensile modulus, and transforms the flm from insulating to conductive. Andrews et al. investigated the dispersion of nanotubes in polymer matrices to derive new and advanced engineering materials. The nanotube concentration at which conductivity was initiated varied with the host polymer. In PP, this concentrations was as low as 0.05 vol%, while higher concentrations were

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required for PS, and particularly for ABS. Xie et al. [10]prepared SWCNTs with high covalent bonding density of polymer layers by a "grafting to" approach. Only0.06 wt% of SWCNTs resulted in 82% and 78% increases in tensile strength and elastic modulus of polymer composites, respectively, indicating an efficient interfacial stress transfer between SWCNTs and polymer. The present work describes synthesis, characterization, analytical applications and conducting behavior of PSDVB nano composite as cation exchanger for sodium ions.

2. Experimental

2.1. Adsorption Isotherm Studies

The cation exchange resin PS-DVB-P-MWCNTs used in this study are generally used for the removal of hardness metals from water and wastewater. All the chemicals used were of analytical grade. A stock solution of Na^+ (500 ppm) was prepared by dissolving 1.83 g of $NaNO_3$ (Aldrich, USA) in distilled water. The stock solution was diluted as required to obtain standard solutions containing 5 to 30 mg/l of sodium. One hundred ml of sodium solution of a desired concentration[1], adjusted to a desired pH, was taken in reagent bottles of 300 ml capacity and known amounts of ion exchange resins were added. The solution pH was adjusted by using dilute hydrochloric acid or sodium hydroxide solutions. The solutions were agitated for a predetermined period at 25±1 ^{o}C in a shaking incubator (Vision Scientific Co., Ltd., KMC 8480S). The resins were separated and the filtrate was analyzed by an atomic absorption spectrometer (Perkin Elmer, AAS-3110) for sodium content. Series of different initial concentrations of sodium while maintaining the resin dosage at constant level.

2.3. pH Effect

10 mg/l copper and ion exchange resins PS-DVB and PS-DVB-P-MWCNTs each of dose of 500 mg/100 ml were used. In order to correct for any adsorption of sodium on the container surface, control experiments were conducted without resins. It was found that no adsorption occurred by the container walls. In addition, all mixing vessels were kept sealed throughout the duration of each isotherm test to minimize dissolution of gaseous species in the atmosphere [11].

2.3. Kinetic Experiments

A known weight of resin dosage and sodium concentration in the range of 10-20 mg/dm^3 where mixed. After regular intervals of time, suitable aliquots were analyzed for sodium concentration and recorded[1]. The rate constants were calculated by using the conventional rate expression. This synthetic solution was used for the adsorption study with ion exchange resins. For the study of adsorbent dosage, the sample was used at solution pH and agitated with different dosage of ion exchange resins for 24 hrs.

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3. Results and Discussion

There has been constant improvement in ion exchange materials since the first use of natural and synthetic inorganic products. Denser resins PS-DVB become more developed for heavy duty industrial applications by addition of nanomaterial (CNTs) to produced PS-DVB-P-MWCNTs nanocomposites resins. Such products are more resistant to degradation by oxidizing agents such as chlorine and withstand physical stresses that fracture lighter duty. They remove alkalinity by exchanging their hydrogen ions for the cations associated with the chlorides ion (calcium, magnesium, and sodium chlorides). Because of almost100% utilization of the regenerate acid, chemical operating costs will be at a minimum, and there will be little excess acid to produce objectionable waste effluents.

3.1. Kinetic Studies

The kinetic study of cation exchange resins were carried out using patch process to measure the ability of resins towered the individually counters ions[12]. Figure 1 shows that in higher concentrations the rate of cation exchange resin containing pristine MWCNTs exchange of sodium ions, and higher at low concentration taking into consideration that the rate of cation exchange resin containing pristine MWCNTs is higher than that in copolymer resins (PS-DVB), in low concentrations the exchange rate is also following the same rank[1].

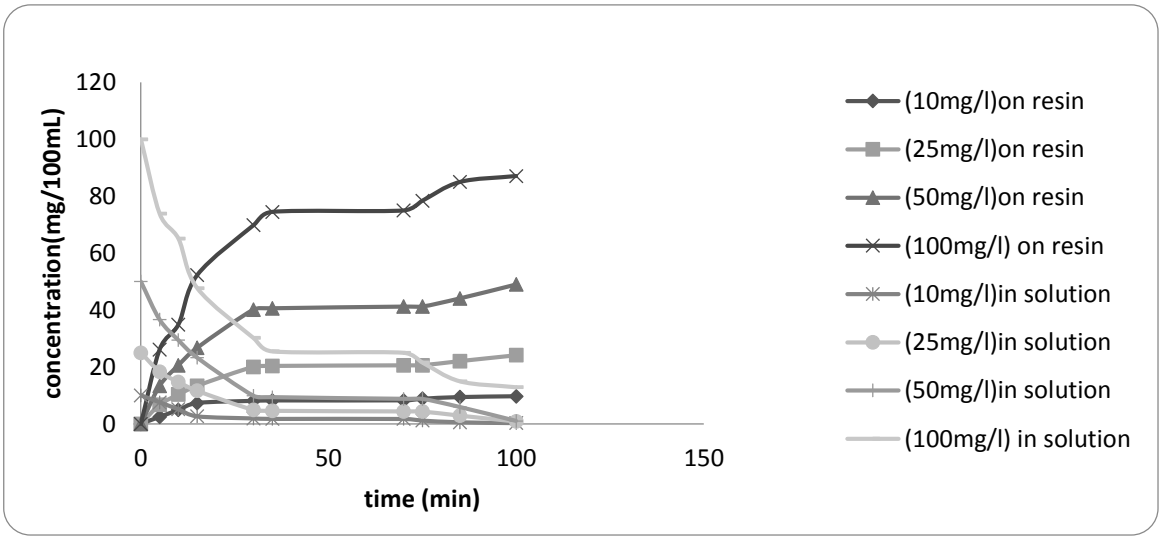

Figure 1. Na^+ uptake using sulfonated PS-DVB-P-MWCNTs resin

3.2. Exchange Capacity of Prepared Cation Exchange Resins

During the titration of prepared resins (PS-DVBMWCNTs SO_3H) with 0.01mol L^{-1} NaOH solutions in methanol it's observed that the cationic exchange capacity of PS-DVB P-MWCNTs particles are highly increased in the prepared resins containing P-MWCNTs achieved cationic exchange capacity values to 446.6meq./100-g. Although the sulfonated PS-DVB –P-MWCNTs containing only 1% of its weight CNTs

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as showed in Table 1.

Table 1. The main characteristics of the investigated cation exchange resins

Cations	Exchange Capacity (mEq./g)	Particle size	Thermal Stability
PS-DVB-P-MWCNTs	4.25	50-150Mm	600

3.3. Effect of Initial pH of Solution on Metals Ions Removal by Resins

Initial pH plays an important role for the adsorption of metals ions on the SPS-DVB-P-MWCNTs resin beads. The removal efficiency of metals removal in aqueous solution was evaluated in a batch system at constant temperature of 30 ^{0}C and initial concentration of 100 mg /L, and varying pH from 1 to 9, with addition of 0.1mg of SPS-DVB-P-MWCNTs resin in the batch system. Adsorption percentage of the SPS-DVB -P- MWCNTs depends on the pH value presented in Figures 2, in this respect, SPS- DVB-P-MWCNTs resin show a high selectivity for the metal ions at high pH. It's shown also that the plateau portion appear at basic pH, this means that the metals complexation at basic pH is carried out by the hydroxyl groups, meaning the surface of resin is more negatively charged at basic media due to high OH ions present in the solution which attracts more positively charged metal ions [11].

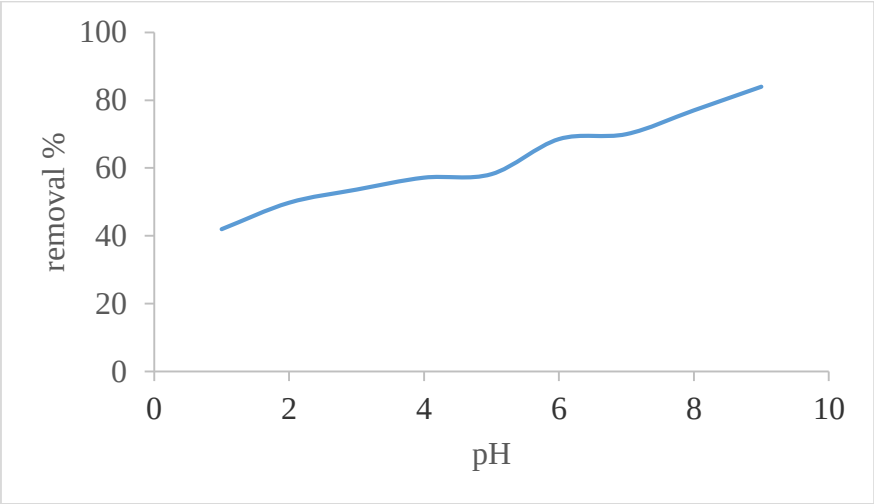

Figure 2. Study the pH effect on cation exchange capacity for SPS-DVB -P-MWCNTs resin

In order to realize the practical use of CNTs in environmental protection applications, the reversibility, which decides the cost of adsorption to some extent, must be considered. Figure 2 shows the Na^{+}, metals ion adsorption curves with different pH values of solution from 1to 9. It is apparent that the Na^{+}, ions adsorption increases with the increase of pH value of the solution[11]. The adsorption percentage is almost zero at pH 1 of solution, while the adsorption percentage increases till pH 9 and eventually reaches 82%, 49%, 85% for Na^{+}, respectively. These results show that the Na^{+}, adsorbed by MWCNTs can be easily take place, thus the SPS-DVB -P-MWCNTs can be employed repeatedly in Na^{+} metal removal from saline water.

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3.4. Distribution Coefficient (K_d) Values for Metal Ions in Presence of (copolymer or Nanocomposites) Resins

Measurement of distribution coefficient of metal ions over a wide range of condition is a good way to avoid choosing eluting conditions for column separations by a strictly trial and error method. The batch distribution coefficient K_d is defined as:

$$K_d = \frac{\text{mmole of metal ion on resin}}{\text{mmole of metal ion in solution}} \times \frac{\text{vol. of metal ion solution}}{\text{wt. of dry resin}}$$

Although this distribution coefficient is measured on a batch basis, it can be used to predict elution behavior of metal ions eluted from an ion exchange column. To separate two substances, conditions should be selected such that the distribution coefficient of one of them is low (preferably 1 or less) so that it elution from the column will be rapid, while the distribution coefficient of the other substance under the same conditions should be as large as possible (more than 10 times) so that this substance will be tightly held by the resin. The Effect of different concentrations and pH on metal ion uptake by the synthesized SPS-DVB-O-MWCNTs resin was studied. The K_d values of the metal ions were studied as a function of pH and concentration of electrolyte solution. The results are presented in Table 2 and indicated that at all electrolyte concentrations and entire pH range, the K_d values increase with increasing electrolyte concentrations. Finally, to achieve higher metal ions removal, large ΔK_d values should be selected on the same experimental conditions[4].

Table 2. The Distribution coefficient of metals on the sulfonated PS-DVB-P-MWCNTs resins

resin weight	V solution	con(Na) (mg/100mL) on resin	in solution	K_d
0.1	100	2.51	0.48	5244
0.1	100	1.25	1.74	722
0.1	100	1.49	1.50	990
0.1	100	2.31	0.68	3349
0.1	100	1.71	1.28	1334
0.1	100	2.05	0.94	2178
0.1	100	1.7	1.25	1391
0.1	100	1.6	1.391	1156
0.1	100	2.1	0.9	2333

4. Conclusion

Ion exchange resins have been identified as potentially and efficient materials for use in the treatment of water contaminated with selected ions that Doman in sea water or produced water. It's found

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that the addition of pristine MWCNTs to polystyrene divinylbenzene resin to form nano composite structure improved the mechanical properties of these resin and their ability to exchange sodium ions in sea water with high capacity of exchange. The kinetics of ions uptake is applied to select the optimum operating conditions for the full-scale batch process. The effect of pH on PS-DVB/MWCNT dosage or resin dosage towered the selected ions adsorption show that the increase of ions adsorption capacity of PS-DVB/MWCNT resin containing MWCNTs is greater than that of copolymer without MWCNTs.

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