Functional Analysis of Selected Ion Electrically Conductive Hydrogel: Production and Applications in Seawater Treatment


Abstract: Seawater desalination is becoming a crucial intervention for mitigating water shortage in numerous Middle East countries. Desalination technology is associated with various technological challenges that should be resolved to maintain plant sustainability and performance. For instance, seawater hardness is recognized as a challenge for recent large scale desalination plants. Optional technologies including chemical treatment, adsorption and membrane filtration have been developed for hardness removal and recovery of Ca and Mg. This paper addresses the development and application of a new conductive polymeric hydrogel composite exhibiting electrically tunable characteristics. A comprehensive review on the preparation of conductive hydrogel and its application for water treatment is first presented. The newly developed hydrogel composite comprises treated zeolite, polyacrylate, polyaniline, hydrolyzed polyacrylamide and special processing aids. The characteristics of the composite have been determined via scanning electron microscopy, Fourier transform infrared spectroscopy and electric conductivity measurements in addition to swelling ratio. Impact of composition and processing conditions on conventional and electrochemically enhanced adsorption experiments have been presented and analyzed. Electro-regeneration has been also explored. The promising features of this hydrogel in composite are elucidated by the removal and recovery of hardness causing elements in simulated seawater and brines. It is concluded that the developed hydrogel is initially qualified for upstream seawater softening. Additional endeavors are still needed for downstream brine management to overcome apparent osmotic effects.

Keywords: acrylic acid; adsorption; conductive hydrogel; seawater; polyaniline; zeolite.

I. INTRODUCTION

The removal of hardness from seawater is an essential pretreatment stage for desalination technology. Widely adopted options for hardness removal are chemical treatment, adsorption and membrane filtration. Adsorption is being highly favored because of its simplicity and low cost. Polymer hydrogels are 3-dimensional cross linked polymers which are capable of adsorption[1]. There is growing research interest on preparation of tailored hydrogels as hybrid, zeolite and conductive composites hydrogels for water treatment. Jing et al. (2013) reviewed the removal of metal cations, anions and dyes in addition to various other pollutants utilizing hybrid hydrogels [2]. Naik et al. (2018) studied the effect of zeolites together with hydrogels to remove dyes from wastewater in addition to controlled fertilizer release and other biomedical applications[3]. Conducting polymers (CPs) are characterized by having electrical and electrochemical properties approaching that of metals and semiconductors. Due to their good characteristics, processing conditions and tunable conductivity, CPs are gaining wide scientific and practical applications [4]. Specifically, Polyaniline PANI, has many advantages as a conductive polymer according to its electrochemical properties, simple synthesis method has thus been adopted for several applications. Fabrication of PANI is normally undertaken using chemical oxidation or electrochemical polymerization. Polyaniline is prepared by polymerization reaction comprising mixing aqueous solution of aniline hydrochloride with adding ammonium peroxysulphate, PANI hydrochloride is precipitated then filtered and dried [5]. Moreover, PANI based conducting polymer composite hydrogel has been investigated for water treatment [6-9]. It also imparts its conductive properties to a well-tailored polymer prints fulfilling minimum level of conductivity while characterized by a suitable level of interaction. The composite preparation method may be incorporated by blending, coating, and in situ polymerization[10].

Polyaniline in the emeraldine base (EB) form has been dispersed in chitosan then blend films were obtained using solution casting[11]. Polyaniline was also prepared in situ within the hydrogel matrix. Polyacrylate (PAC) / PANI composite were prepared by absorbing aniline in the substrate of polyacrylate followed by aniline polymerization. The resulting hydrogel had electrical conductivity of 2.33 mS.cm$^{-1}$[8,12-13]. Also, Abu-Thabit et al. (2014) and Tang et al. (2008) reported the preparation of polyamide / polyaniline conductive hydrogel with a similar approach by first preparing poly acrylamide hydrogel and polyaniline was introduced to the polymeric network through prolonged oxidative polymerization[8-9]. Taşdelen (2018) prepared polyaniline, kaolin and polycrylamide by introducing kaolin into polyacrylamide/ hydrogel network. Aniline was then introduced in polycrylamide/ hydrogel network and polymerized using free radical technique.
The produced hydrogel had electrical conductivity of $1.1 \times 10^{-2}$ S cm$^{-1}$, enhance mechanical, electrical properties and adsorption ability [13]. Prabhakar et al. (2014) also reported the preparation of poly (acrylate-co- acrylamide) / polyacrylamide hydrogel by introducing aniline in poly (acrylate-co-acrylamide) hydrogel matrix followed by polymerization of aniline. The electrical conductivity of the prepared hydrogel was 0.81 mS cm$^{-1}$[14]. Regarding Ca and Mg removal using composite hydrogels, Sorour et al. (2018) prepared zeolite and kaolin based acrylate hydrogel composites using microwave and ultrasonic irradiation techniques to be used for adsorption from saline solutions. The Mg adsorption capacity ranged between 63-108 mg/g[15]. Lower adsorption capacities from saline solutions were observed using kaolin based polysaccharide hydrogels chitosan[16].

Based on the findings of numerous investigations[17] electric current is used to enable easy desorption of adsorbed ions with minimal consumption of chemical regenerants. Due to the variation of the binding energy to the adsorptive platform, tuning of the supplied electric energy is thus necessary to enable exploration of preferential (sequential) desorption for recovery purposes. In this work, a conductive hydrogel based on polyaniline / polyacrylate composite with treated zeolite has been developed with electrically tunable characteristics. Impact of composition and processing conditions on characteristics and performance of the adsorptive gel is presented and analyzed.

II. MATERIALS AND METHODS

a. Materials

Aniline monomer (El Nasr Pharmaceutical Chemicals Co.), acrylic acid (AA) with molecular weight 72.06 g/mol (Research Lab) and acrylamide (Am) (Baker Chemical Co., USA) were used as starting monomers for the preparation of the conductive hydrogel composite. Ammonium persulfate (APS) and potassium persulfate (KPS) were supplied from Merck, Germany as an oxidant and initiator. Methylene bisacrylamide (MBA) as a cross linker was supplied from Fluka-Germany and sodium dodecyl sulfate sodium salt as dispersing agent was supplied from Merck. Sodium, calcium and magnesium chlorides were used for the preparation of synthetic brine solutions. Hydrochloric acid and sodium hydroxide were used for washing and pH adjustment. In house prepared zeolite was used in the composite matrix[15]. All experiments were performed using double distilled water.

b. Preparation of Polyaniline (PANI)

The chemical polymerization of aniline was conducted using ammonium per sulfate(APS) as an oxidant according to Stejskal, 2002[5]. First, 1 M aniline monomer was added to 2 M HCL and stirred in a water bath shaker (Julabo, SW-20C) at 0–2°C then, 1.25 M APS was added gradually and the polymerization reaction was continued for 24 hr. till the dark green PANI precipitate was formed and separated by centrifugation followed by washing with 0.2 M HCL and 0.2 M with acetone. Then, the produced polymer was washed using double distilled water until obtaining clear filtrate.

c. Preparation of polyacrylate/zeolite composite conductive hydrogel

A control sample of polyacrylate/zeolite composite hydrogel without polyaniline(C) was prepared as previously described by Sorour et al., (2018)[15]. Briefly, acrylic acid was neutralized using sodium hydroxide. Further, 5% freshly prepared acrylamide crystals were added to the neutralized acrylic acid, the crystals were prepared by dissolving acrylamide monomer in excess amount of cold acetone where, the solution was then cooled to 10°C until crystals were obtained and dried[18]. Sodium dodecyl sulphate, acrylamide and treated zeolite "13 X" were then added. The reaction was conducted at 70°C in an ultrasonic water bath (Tru-sweep cleaner, Crest Ultasonics Cor, USA). The produced hydrogel was washed with distilled water and ethanol to remove the excess homopolymer, cut into small pieces.

Five samples were then prepared at different PANI concentrations by adding PANI with different weight ratios (0.04-0.2 gm/gm mixture). The mixture was subjected to sonication for 30 min, followed by 24 hr. shaking at 210 rpm (SCILOGEX SK-O330-Pro). The produced hydrogel composite was filtered and vacuum dried (Memmert Vacuum drying oven VO500) at 60°C until constant weight was achieved. The control sample free of PANI (C) and the other five samples at different weight ratios of PANI (0.04, 0.05, 0.067, 0.1 and 0.2) are denoted by PANI 0.04, PANI 0.05, PANI 0.067, PANI 0.1 and PANI 0.2, respectively.

d. Characterization

The structure of the prepared conductive hydrogel composites were characterized via Fourier transform infrared spectroscopy (FTIR) using FT/IR-6100 type A Jasco Japan TGS detector with the absorbance technique ranging from 500 to 4000 cm$^{-1}$ with scanning speed of 2 mm/s. The surface morphology of the prepared hydrogel samples was studied using a scanning electron microscope (SEM) model QUANTA FEG 250.

e. Conductivity Measurement

Electrical conductivity of the prepared hydrogel has been determined at ambient temperature using 2401 Source Meter (Keithley Instruments) with 4-point probes. Resistance has been determined with the 4-point probes and conductivity was calculated using the next equation[13].

$$\rho = \frac{\pi t}{\ln(2A/t)}$$

Where: $\rho$ is resistivity, $V$: the voltage, $I$: the current and $t$: sample thickness (approximately 1mm in this study). The electrical conductivity ($\sigma$) is the inverse of the resistivity or $\sigma=1/\rho$. The compressive stress-strain measurements were performed using a universal tester (LOYD LRX, Poole, UK) performing uniaxial compression test [19-26].

2.6 Swelling water ratio (SWR)

An amount of dry hydrogel was soaked in distilled water for 24 h and filtered using stainless steel strainer to remove the excess surface water. The swollen hydrogel has been weighed twice before and after swelling. SWR has been calculated by the following equation[27].

Retrieval Number: F8015038620202906BEIESP
DOI:10.35940/ijrte.F8015.038620
Published By: Blue Eyes Intelligence Engineering & Sciences Publication
Where, $W_s$ and $W_d$ are the weights of the swollen and dry samples, respectively. SWR was calculated as grams of absorbed water per grams of dry hydrogel (g/g).

## 2.7 Adsorption and regeneration studies

Synthetic brine was prepared using sodium, calcium and magnesium chloride salts to simulate Red Sea desalination brine with Na, Ca, and Mg concentrations 24000, 800 and 2600 mg/L, respectively[28]. Adsorption experiments were undertaken conventionally and also applying an electric field. Hardness ions adsorption capacities were evaluated using batch-mode conventional technique at pH 8. The solution pH was adjusted using either hydrochloric acid or sodium carbonate via a pH meter HANNA apparatus model-211. 1 g of pre-swollen hydrogel was added to a specific volume of saline solution in appropriate flasks. The flasks were sealed and constantly shaken using a shaker (SCILOGEX SK-0330-Pro) with a constant agitation rate (150 rpm) and at room temperature for equilibration for 24 h. Solid liquid separation was conducted by filtration using a Whatman filter paper no. 4. The liquid was then analyzed to determine the concentration of Ca and Mg in solution using an atomic absorption flame spectrometer (GBC) Avanta. Same experiments were conducted applying DC current: 2.5 volt and 0.03 A for 90 min at pH 6.5.

The adsorption capacity ($Q$) has been evaluated using the following equation[29]:

$$Q = V \times \frac{C_e - C_i}{m}$$  

Where: $Q$: the amount of metal ions adsorbed in (mg/g of dry adsorbent), $V$: the volume of metal ions solution used (L), $C_i$ and $C_e$ are the initial and equilibrium ion concentrations (mg/L), respectively, and $m$ is the weight of dry adsorbent (g).

Regeneration experiments were conducted using HCl at pH 4 for 24 hours under shaking and for 1 hr applying an electric field at 2.5 volt and 0.02 A.

## III. RESULTS AND DISCUSSION

### f. FTIR

IR spectrum of PANI and PANI composite hydrogel samples is shown in Figure (1). The polyaniline showed the bands at 3439 cm$^{-1}$, 2923 and 2855 cm$^{-1}$ which are due to NH, C-H stretching aromatic. The absorption peaks observed at 1563 cm$^{-1}$, 1263 cm$^{-1}$ are attributed to C=C stretching in aromatic ring.

![FTIR spectra of the prepared conductive hydrogel composites](image)

The peak at 1455 is assigned to the benzenoid ring of polyaniline. The absorption band at 1293 cm$^{-1}$ confirms the C-N stretching of secondary aromatic amine. Moreover, the characteristic peaks at 1114 at 954 cm$^{-1}$, 799, 693 are assigned to p-di-substituted benzene ring. For the PAM composite hydrogel (CH), the peaks at 3430 cm$^{-1}$, 2926 cm$^{-1}$, 2857 cm$^{-1}$ are assigned to N-H bending of acrylamide and aliphatic asymmetrical C-H stretching of the acrylate group, respectively. The bands at 1630 cm$^{-1}$ and 1392 cm$^{-1}$ are assigned to asymmetrical and symmetrical carbonyl bonds (C=O) of the amide group CO-NH$_2$. For the PANI hydrogel composites, the absorption peaks at 3427 cm$^{-1}$ are due to N-H stretching, 1630-1636 cm$^{-1}$ is for the C=O bending for PAM (AM band 1 CO-NH$_2$), peak at 1452 cm$^{-1}$ is corresponding to C-N stretching. The absence of some peaks of polyaniline in polyaniline composite hydrogel samples are attributed to the formation of Hydrogen bonding between the Polyacrylamide composite hydrogel and the PANI. This result supports successful formation of PANI within the PAM composite hydrogel.

### g. SEM

Figure (2-a) is a typical granular PANI structure manifesting micro aggregation to flaky like structure with apparent differences of agglomerate sizes. Figure (2-b) is a typical image of zeolite after modification with apparent separation of particles to maintain a more or less spherical structure. On the other hand, the hydrogel particles may bridge together zeolite to constitute a different structure which is entirely dependent on hydrodynamics and duration of mixing as shown in Figures (2 c-h). The incorporation of PANI (the highly conductive component) seems to regulate the interaction of polycrystal, PANI and zeolite. No obvious significant phase separation is observed among the three components composing the entire hydrogel structure. This fact is confirmed by Figure (2-h) which is a typical almost homogeneous mix of the three components.
The conductivity of the hydrogel sample mainly depends upon the conducting material incorporated and the effective synthesis of conducting network which is related to the concentration of aniline. Since hydrogel has insulating property and conductivity increases with the formation of conducting polymer PANI inside the hydrogel matrix. The conductivity of the prepared hydrogel samples at different concentration of PANI is presented in Fig. (3). It is clearly that the conductivity of the hydrogel samples increased from 1.38 mS cm$^{-1}$ to 3.71 mS cm$^{-1}$ with increasing the ratio of PANI in the prepared hydrogel. This increase in conductivity could possibly be because of the presence of excess of PANI molecule available for polymerization and as a result, the longer chain is generated which gives more conductivity. It is observed that the conductivity of hydrogel increases slowly above a certain ratio of PANI concentration. This could be due to presence of an excess of PANI hydrochloride molecule inside the hydrogel matrix which restricts the proper movement of counter ion resulting slow increase in conductivity.

The dielectric measurements were performed between 0.1 Hz and 10 MHz via a Novocontrol high-resolution alpha analyzer. The investigated samples with thickness (about 1mm) were inserted between recently polished brass electrodes with a top electrode diameter of 10 mm to form a parallel-plate capacitor cell. The complex permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$) was measured using a sinusoidal voltage with amplitude 0.5 V over a 10$^{-2}$ – 10$^7$ Hz. The frequency dependence of the real part of complex conductivity, $\sigma'$, shows three different trends. The high frequency conductivity follows the well-known power law ($\sigma' = \sigma_0 \omega^s$) followed by the less-dependent frequency range of $\sigma'$ which characterizes the so called DC-conductivity. Further decrease of frequency shows a gradual- or even linear-decrease of $\sigma'$ with decreasing frequency. The later could be attributed to the accumulation of charge carriers at the interface between electrode and the conductive polymer usually called electrode polarization[19-26].

It is noticed from the Fig. (5) that the increase of absolute applied voltage increases gradually the DC-conductivity.
Figure (6) shows that the rate of DC conductivity increase is more reliable in case of pure polyaniline.

i. Swelling studies

SWR values in distilled water for the prepared hydrogel composites (PANI$_{0.04}$ and PANI$_{0.2}$) as well as the free PANI hydrogel are shown in Fig. (7). It is noticed that SWR decreases as a result of PANI addition up to 39%. It is worth mentioning that SWR of the free PANI composite hydrogel is higher than that reported by Sorour et al., 2018 for polyacrylate zeolite composite hydrogel[15], which implies the effect of the added polyacrylamide in the hydrogel.

Figure 7. SWR of the prepared hydrogel composites in distilled water

Electrochemically enhanced adsorption results are shown in Fig.(9). It is clear that increasing the PANI ratio decreases the adsorption capacity while retaining the Ca selectivity with lower performance than conventional adsorption.

Figure 9. Electro-enhanced adsorption of Ca & Mg using different ratios of PANI hydrogel

Exploratory regeneration experiments were conducted using HCl at pH 4 for 24 hours conventionally under shaking and for 1 hr under 2.5 volt and 0.02 A. Ca regeneration was 1.51% and 1.78%, respectively while the corresponding Mg values were 8.3% and 9.3%, respectively. This reveals the ability of electro-regeneration conducted in 1 hr to achieve the results obtained by conventional methods in 24 h. Efforts are underway to optimize and enhance the electro-regeneration results.

IV. CONCLUSIONS

PANI impregnated PAc/PAm/Zeolite conducting hydrogel has been synthesized. The aniline monomer was successfully polymerized and added within the composite much higher than magnesium, regardless of their initial concentrations

It is worth mentioning that Ca and Mg adsorption capacities from Red Sea RO brine onto alginate and chitosan grafted acrylamide hydrogels were 20 and 360 mg/g, respectively[29-30].

Further, alginate and chitosan grafted acrylamide-co-acrylic acid hydrogels and kaolin composite revealed Ca and Mg uptake from seawater of 18-19 mg/g and 22-45 mg/g, respectively [16]. Also, polyacrylate zeolite composite prepared using ultrasonic irradiation and tested for Mg removal from Mg enriched decalcified Red seawater showed 63 mg Mg/g [15,31].
hydrogel network as evident from SEM studies. Further, FTIR pattern shows that the PANI functional groups have been added to the pre-prepared hydrogel composite. The electrical conductivity of pure PANI and for the hydrogel samples with different PANI ratios have shown the maximum conductivity with max PANI weight ratio (PANI0.05). In addition, simulated sea water has been prepared. Hardness removal has been conducted using the prepared hydrogel samples by applying conventional and electro enhanced adsorption. The adsorption of Ca has a max value in the case of PANI0.05 , while, the adsorption of Mg was not effective. Exploratory regeneration experiments gave promising results. Further work is underway

REFERENCES


AUTHORS PROFILE

Corresponding Author : Dr. Marwa M Eid
Affiliation : Associated Professor, Chemical Engineering and Pilot Plant Department, Engineering Research Division, National Research Centre , Dokki,Cairo.
Email: dr.marwameid@gmail.com

Dr. Marwa has main experience in the field of chemical and engineering & polymers . She has more than 15 international publications and a member in several national and international research projects relevant to membrane science.

Prof. Dr. Mohamed Hassan Sorour
Affiliation : Chemical Engineering and Pilot Plant Department, Engineering Research Division, National Research Centre , Dokki, Cairo.
Mobile : 002 01000950048, Email: dmsorour@gmail.com
Dr. Sorour's main experience extends to membrane science and applications, desalination, water treatment, modeling, techno-economic studies in addition to biomedical. He is a main consultant or team member on several national and international research projects relevant to his fields of specialization. Dr. Sorour has more than 75 international publications , supervised several M.Sc. and Ph.D. Thesis and has published Patents. He also provided consultancy services to national organizations.

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Retrieval Number : F8015038620/202009BEIESP
DOI:10.35940/ijrte.F8015.038620
2877
Prof. Dr. Abdelghani M.G. Abulnour, Chemical Engineering and Pilot Plant Department, Engineering Research Division, National Research Centre, Dokki, Cairo.

Dr. Abulnour has been since 1994 a Research professor. His main field of specialization: Chemical engineering, chemical process design & analysis, water & wastewater treatment. He has participated in several projects as a principal investigator and as a member. The projects are related to synthesis and application of hydrogel, bioethanol production from agricultural residues, water and wastewater treatment systems. Dr. Abulnour has many international publications and supervised several M.Sc. and Ph.D. Thesis.

Prof. Dr. Shadia Ragheb Tewfik
Address: Home: 1 Ahmed Amin Street Dokki, Cairo
Office: Chemical Engineering and Pilot Plant Department, Engineering Research Division, National Research Centre, Dokki, Cairo.
Mobile: 002012 23239133, Email: shadiatewfik@yahoo.com

Dr. Tewfik has been since 1987 a Research Professor. Her main experience is in chemical and environmental engineering & techno-economic studies. She been the team leader of several national and international research projects relevant to membrane science, desalination, solid waste management, simulation and optimization. Dr. Tewfik has more than 30 international publications and supervised several M.Sc. and Ph.D. Thesis.

Dr. Hayam Fahim Shaalan is a Research Professor and the Head of Chemical Engineering Department in the National Research Centre from 2014 till now. She has over 60 publications, including articles in scientific journals and technical reports and four granted patents with the experience in tailored membrane based systems with its diversified applications in chemical and food industries in addition to process design and development of specialized polymeric systems.

is an associate professor in the Engineering Research Division, Egypt since 2016. Her research activities centers mostly in separation technologies and applications, modeling and simulation in chemical engineering. She has participated in several projects as a member and as a principal investigator. The projects were related to synthesis of composites and nano materials, hollow fiber membranes, salt recovery from brines, ethanol production and water treatment. She has more than seventeen international publications and two patents.