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Efficient Adsorption of Copper and Nickel Ions from Aqueous Solution Using Sulfonated Poly (vinyl alcohol)/Chitosan/Arabic Gum as Adsorbent Membrane

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ABSTRACT

The described work concerns fabrication and characterization of adsorbent membranes based on sulfonated blend of polyvinyl alcohol/chitosan/Arabic gum (PVA/CS/AG) for removal of heavy metals from industrial wastes. The membranes were obtained via solution casting of PVA/CS/AG mixtures followed by sulfuric acid treatment. Structural details, crystallinity and thermal stability of the membrane were investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transformer infrared spectroscopy (FTIR) and thermographmetric analysis (TGA). In addition to physicochemical characterization, Ni^{2+} and Cu^{2+} uptake studies were also performed. The effect of pH, contact time, temperature and initial concentration of Ni^{2+} and Cu^{2+} ions were studied. The experimental sorption data was successfully fitted to Freudlich and Langmuir isotherms the results indicate that the affinity of the sulfonated PVA/CS/AG adsorbent membrane for Cu^{2+} ions sorption was higher than that for Ni^{2+} ions. The maximum adsorption efficiency of Ni^{2+} and Cu^{2+} were observed at pH 5.5 and 35°C, after 150 min. The study leads to the conclusion that the new adsorbent membranes based on sulfonated PVA/CS/AG blends offer high efficiency for the heavy metal ions adsorption.

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INTRODUCTION

The industrial effluents containing heavy metal pollutants are becoming one of the most serious environmental problems (Inyang *et al*. 2012). Wastes containing compounds of heavy metals such as copper, nickel, cadmium, zinc, etc. pose a risk to public health because of their toxicity, carcinogenicity, non-biodegradability as well as tendency to accumulate in living organisms ((Inyang *et al*. 2012; Mohan *et al*. 2015; Singh *et al*. 2011; Wang *et al*. 2015). The continued intake of Cu^{+2} by humans leads to necrotic changes in the liver and kidney, mucosal irritation; widespread capillary damage, depression, gastrointestinal irritation, and finally lung cancer ((Jiang *et al*. 2015; Mousavi *et al*. 2010)). The presence of Ni^{+2} in drinking water also causes numerous health iness harms. When Ni^{+2} concentration in drinking water exceeds it's a critical level, serious lung and kidney problems appear in addition to a gastrointestinal distress ((Borba *et al*. 2006; Joseph 2009; Lacerda *et al*. 2009; Waalkes 2000; Waalkes 2003), thus, the elimination of Ni^{+2} from wastewater and industrial effluents is a vital necessity (Rad *et al*. 2014). The main sources of heavy metal pollution are discharges from mining, metal plating, battery, paper and textile industries. Numerous methods have been used to remove heavy metal from wastewater, including membrane filtration, electrolysis, chemical precipitation, ion-exchange and adsorption (Fu and Wang 2011). Membrane filtration techniques can remove heavy metal ions with high efficiency, but the associated problems, such as high cost, process complexity, membrane fouling and low permeate flux have limited their use

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in heavy metal removal. Development of membrane separation systems based on inexpensive components is urgently needed.

The present work responds to this demand and regards fabrication and characterization of cost-effective adsorbent membranes for the removal of toxic nickel and copper contaminants.

To avoid the high cost of the membrane used in heavy metals removal, it is obligatory to substitute these high cost membranes to that synthesized using cost effective membranes prepared from low cost natural polymers blended with synthetic polymer.

The membranes are synthesized by sulfonation of films cast from mixtures of inexpensive polymers including chitosan (CS), Arabic gum (AG) and poly (vinyl alcohol) (PVA).

Chitosan is a deacetylated chitin and it is a copolymer of glucosamine and N-acetyl glucosamine. CS has many properties that have generated interest in its use such as biodegradability, biocompatibility and its nontoxicity (Crini *et al*. ; Özen *et al*. 2015; Wang and Chen 2014). CS has amine functional groups, which has strong affinity toward metal ions. These amine groups interact with the solution's metal ions in different ways, including the solution composition and its pH (Maleki *et al*. 2015).

Poly(vinyl alcohol) is a hydrophilic, semi crystalline synthetic polymer, which contains a large number of hydroxyl groups which can easily form hydrogen bonds with water molecules (Părpăriţă *et al*. 2014). PVA can interact with other organic and inorganic molecules, including heavy metal ions (Hallaji *et al*. 2015). The last component, Arabic gum is a branched-chain, complex polysaccharide forming either neutral or slightly acidic aqueous solutions (Ali *et al*. 2009). AG is considered a natural bio-sorbent with the capability to be used the removal of toxic metals from water (Dauqan and Abdullah 2013). The role of AG in the current work is to primarily improve the mechanical properties of blend membranes.

The aim of the present research was to design, and synthesis of sulfonated PVA/CS/AG adsorbent membranes and then to characterize their effectiveness in removal r removal of Ni^{2+} and Cu^{2+} ions from model aqueous solutions.

MATERIALS AND METHOD

2.1. Materials:

All chemicals and reagents used in the current experiments were analytical grade and used as received without further modification unless otherwise specified. Polyvinyl alcohol (PVA, M_w 72,000 g/mol) was purchased from Merck, Germany; Chitosan (CS, M_w161 g/mol, purity>90%) was supplied by Biobasic, Canada; Arabic gum (AG) was purchased from Panreac, Spain. Standard solution 1000 ppm Ni^{2+} was obtained from Panreac, Spain; standard solution 1000 ppm $Cu^{2+}$was purchased from Merck, Germany; sodium chloride, hydrochloric acid and sodium hydroxide were purchased from Fischer scientific, USA. All aqueous solutions were prepared with distilled water.

2.2. Methods:

2.2.1 Preparation of Sulfated PVA/CS/AG blend solution:

The solution of PVA, CS and AG was prepared as follow: Clear solution of 10 wt % of PVA was obtained by dissolving 10 g in 100 ml of distilled water at 80^{o}C for 5 h under magnetic stirring; CS solution was prepared by dissolving 3 g of CS in 100 ml of 2% acetic acid solution at room temperature with stirring overnight. The both solutions were combined together at a 60/40 PVA/CS ratio and the mixture was kept under continuous mechanical stirring at room temperature for 1 h. PVA/CS/AG blend solutions was prepared by adding specific amounts of AG (0.5,1,1.5,2,3%) to the above PVA/CS mixture at 35^{0}C under continuous stirring. Sulfonation was performed by addition of an aqueous 0.2 M H_2SO_4 solution. The final reactant solutions were cast as film in a plastic petri dish, where the films were dried for 24 h, washed thoroughly with using distilled water to remove unreacted materials, and then dried again for 24h.

3. Characterization of the membrane:

3.1. Membrane Water Uptake and Dimensional Changes:

The water uptake of the sulfonated S-PVA/CS/AD membranes was determined by weighing the sample before and after immersing them in distilled water at ambient temperature for 24 h The excess water was removed from the membrane surface with filter paper before the sample was weighed (Eldin *et al*. 2011b). Water uptake was calculated using Equation 2.

$$\boldsymbol{Water\ uptake} = \frac{\boldsymbol{W}_{\text{wet}} - \boldsymbol{W}_{\text{dry}}}{\boldsymbol{W}_{\text{dry}}} \times \mathbf{100}\% \qquad \text{Eq. 2}$$

Where W_{wet} and W_{dry} are the membrane weights before and after equilibration with deionized water.

The dimeniensional changes (DA %) of the membrane samples were measured after immersing the dry samples in distilled water for 24 h at room temperature. Equation 3 was used for the calculation.

$$DA\% = \frac{A - A_o}{A_o} \times 100 \qquad \text{Eq. 3}$$

Where A_0 and A are membranes area before and after equilibration with deionized water.

3.2. Membrane Roughness:

The surface roughness of the membranes was evaluated using a surface roughness tester (model: MattitoSJ-201P, Japan). The sensor of the instrument was carefully placed on the surface of the

membrane and then moved automatically. Due the sensitivity of the roughness instrument, each sample was measured six times, starting from different locations, and the results were averaged.

3.3. Mechanical properties of the membranes:

The mechanical properties (tensile strength and % elongation at break) of the sulfonated PVA/CS/AG membranes were determined using a tensile testing machine (Shimadzu, model: AG-I/ 50 N-10KN, Japan). Digimatic caliper was used for measuring the thickness and width of the samples before testing.

3.4. Ion-exchange capacity (IEC) of the membranes:

IEC is defined in millie quivalents of sulfonic groups per gram of dry membrane. About 0.1g sample of membrane was soaked in 20 mL of 2M NaCl aqueous solution at room temperature for 12 hr to replace the protons by sodium ions. The solution was then titrated with 0.1N NaOH solution and the amount of HCl released from the membrane sample was etermined in the presence of phenolphthalein as an indicator (Liu *et al*. 2003; Tsai *et al*. 2010). IEC was calculated using Equation 4.

$$\text{IEC} = \frac{\text{Volume of NaOH consumed} \times \text{Normality of NaOH}}{\text{Dry Weight of Sample}} \quad \text{(meq/g)}$$

Eq. 4

The DS is defined as the percentage of repeating units of the polymer that have been sulfonated by sulfuric acid. A high DS indicates a higher number of CS repeating units have been substituted worth SO_3H (Jaafar *et al*. 2007; Kim *et al*. 2015; Yee *et al*. 2013; Zaidi 2003). The DS was calculated from IEC using Equation 5, where molar mass of SO_3H group 81.07(g/mol):

$$\text{DS} = \frac{\mathbf{81.67} \times \boldsymbol{IEC}}{(1000 - 81.07 \times \text{IEC})} \qquad \text{Eq. 5}$$

3.5. Fourier Transform Infrared Spectroscopy (FTIR):

The presence of sulfate acid group in the membrane was identified by using FTIR spectroscopy (Shimadzu, R-8400 S, Japan) (Eldin *et al*. 2011a). The membrane was powdered and pressed with KBr into tablets which were then scanned in the range of 400-4000 cm^{-1}

3.6. Thermogravimetric Analysis (TGA):

TGA was used to determine the thermal degradation patterns of the membranes. The analyses were performed with selected sulfonated PVA/CS/AG membranes using thermogravimetric analyzer (Shimadzu TGA-50) (Abu-Saied *et al*. 2012; Mohy-Eldin *et al*. 2010).

3.7. X-ray Diffraction (XRD):

The crystalline structure of PVA, PVA/CS, PVA/CS/Ag and sulfonated PVA/CS/AG membranes was characterized using X-ray diffractometer (Shimatzu, XRD-6000) with a back monochromator and a Cu anticathode. Radial scans were recorded in the reflection-scanning mode with 2θ being changed from 0º to 120º (Zaidi 2003).

3.8. Scanning Electron Microscopy (SEM):

The surface morphology and internal structure of the selected PVA/CS/AG membranes were analyzed SEM (JEOL, JSM-6360LA, Japan). Before scanning, the sulfonated PVA/CS/AG membranes were dehydrated by freeze-dryer and coated with Au using an ion sputter coater (model: 11430, USA) (Hebeish *et al*. 2014).

3.9. Adsorption experiment:

3.9.1. Adsorption efficiency:

The adsorption efficiency of all the sulfonated PVA/CS/AG membranes in the removal of Ni^{2+} and Cu^{2+} ions was evaluated by immersing a specimen of each membrane with area of 2×2 cm^2 and thickness 0.25 ± 0.1 mm in a conical flask containing 20 ml aqueous solution containing either Ni^{2+} or Cu^{2+} ions. The effect of pH (2–6), contact time (30–180 min), temperature (25–55 ºC) and initial concentration of metal ions (10–100 ppm) were investigated. The concentrations of the metal ions in the solutions were determined by ICP spectrometer (VARIAN 700-ES). The adsorption efficiency percentage (AE %) of metal ions was calculated from Equation 5.

$$AE\ \% = \frac{C_o - C_e}{C_o} \times 100 \qquad \text{Eq. 5}$$

Where AE is metal ion adsorption efficiency %, C_o is initial concentration and C_e is final concentration.

3.9.2. Adsorption Isotherms:

To observe the mechanistic parameters related to the both heavy metal (nickel and copper) adsorption, the experimental results were analyzed by Freundlich and Langmuir isotherm models (Tsai *et al*. 2010). The Langmuir isotherm has been used by several workers for the sorption study of a variety of compounds. The model assumes uniform energies of adsorption onto a surface and no migration of adsorbate in the plane of the surface. It is assumed that the adsorption arises at specific homogeneous sites within the adsorbent. Equation 6 represents the linear form of the Langmuir isotherm and the nonlinear Langmuir isotherm is given by Equation 7.

$$\frac{C_e}{q_e} = \frac{1}{q_m k_l} + \frac{C_e}{q_m} \qquad \text{Eq. 6}$$

$$q_e = \frac{q_m k_l C_e}{1 + k_l C_e} \qquad \text{Eq.7}$$

where q_e indicates the adsorption capacity (mg/g) and C_e represents the equilibrium concentration of the adsorbate (mg/L). q_m denotes

the maximum adsorption capacity of adsorbents (mg/g) and k_l represents the Langmuir adsorption constant (L/mg).

The Freundlich isotherm is an empirical equation describing heterogeneous systems. The Freundlich Equation 8 is a nonlinear version and Equation 9 is linearized Freundlich isotherm:

$$q_e = k_f C_e^{\frac{1}{n}} \quad \text{Eq .8}$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad \text{Eq.9}$$

Where k_f is Freundlich constant, which indicates to adsorption capacity and $\frac{1}{n}$ is the Freundlich constant, which quantifies the adsorption strength.

3.9.3. Kinetic study:

Pseudo second order model is described by Equation 10:

$$q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t} \quad \text{Eq. 10}$$

Where $k_2$is the rate constant of the pseudo-second-order sorption (g/(mg min)), q_e is the amount of Cu and Ni adsorbed (mg/g) at equilibrium and q_t is the amount adsorption (mg/g) at time t (min)

RESULTS AND DISCUSSION

PVA/CS/AG membranes and sulfonated PVA/CS/AG adsorbent membranes were fabricated via solution casting and solvent evaporation Sulfonation of the PVA/CS/AG solutions was performed with sulfuric acids, prior to membrane casting, as decribed in Section 2.2.2. The membranes were characterized using the FTIR spectroscopy, TGA, SEM and XRD diffraction and the results are presented in the following sections.

3.10. Membranes characterization:

3.10.1. Water uptake of the sulfonated PVA/CS/AG membranes:

Water uptakes of the sulfonated membranes are displayed in Table 1. The obtained data indicates that the membrane hydration level increased with increasing concentration of AG. Water uptake of PVA/CS membrane with 0.5 % AG was 112% and increased to 140 % along with increasing the AG concentration to 3.0 %. It can be concluded that the addition of increasing amounts of AG to PVA/CS mixtures increases the hydrophilicity of the resultant sulfonated membrane.

3.10.2. Surface roughness of membranes:

The surface roughness data of sulfonated PVA/CS/AG membranes are shown in Table 1. The roughness decreased from 1.13 mm to 0.95 mm when concentration of AG was increased from 0.5 % to 3 %, respectively. The decrease of surface roughness may be attributed to the increased hydrophlicity of AG and the resultant increase of membrane water sorption.

Table 1: Water uptake, roughness, dimensional changes, IEC and SD of sulfonated PVA/CS/AG membranes.

Membrane ID	Water uptake (%)	Dimension Change (%)	Roughness (mm)	IEC (meq/g)	SD (%)
PVA/CS/AG-1	112.00	28.40	1.13	1.97	18.87
PVA/CS/AG-2	125.00	32.00	1.12	2.09	20.29
PVA/CS/AG-3	125.18	36.00	1.19	2.81	29.28
PVA/CS/AG-4	127.00	44.00	1.05	2.80	29.14
PVA/CS/AG-5	140.00	60.40	0.95	2.79	29.01

3.10.3. Dimensional changes of sulfonated PVA/CS/AG membranes:

The dimensional changes of the sulfonated PVA/CS/AG membranes are outlined in table 1. The data indicate that areal swelling of the PVA/CS/AG membranes increased from 28.4 % to 60.4 % when the AG content was raised from 0.5 % to 3 % respectively. A strong correlation between the water uptake and the dimensional changes (areal swelling) of the sulfonated membranes was observed.

3.10.4. Mechanical properties of the sulfonated PVA/CS/AG membranes:

The mechanical properties (tensile strength and elongation at break) of the sulfonated membranes were compared with that of PVA, PVA/CS, PVA/CS/AG cast membranes; all the measurements were done on rectangular strips. Tensile strength is defined as the maximum stress developed in a film during a tensile testing before the sample breaks, and elongation at break quantifies the capacity of the sample to stretch. Table 2 shows the resultant mechanical data for the PVA, PVA/CS, and PVA/CS/AG and sulfonated PVA/CS/AG dry films. It can be observed that, as expected, the tensile strength and elongation at break of the PVA/CS blend was improved compared to that of the pristine CS as a result of addition of PVA which has higher tensile strength and elongation-at-break. The percent elongation at break and tensile strengths of the sulfonated PVS/CS/AG membranes increased as the amount of AG was increased. The highest value of tensile strength (52.8 N/mm^2) was observed in PVA/CS/AG-5 membrane which contained 3% AG. This indicates that, the increase of the AG content induced greater elasticity and strength of the PVA/CS/AG membranes

Table 2: Tensile strength of the sulfonated PVA/CS/AG membranes and their components.

Membrane ID	Max_Stress (N/mm2)	Max_ Strain (%)
PVA	52.50	81.00
CS	26.67	11.25
PVA/CS	31.58	29.50
PVA/CS/AG-1	39.81	35.50
PVA/CS/AG-2	42.45	36.05
PVA/CS/AG-3	46.31	36.65
PVA/CS/AG-4	48.95	37.25
PVA/CS/AG-5	52.80	37.60

3.10.5. Ion-exchange capacity and Degree of sulfonation:

IEC and SD results are shown in Table 1. The data indicate that, both the IEC and SD increased as the AG content was increasing until the plateau was reached. PVA/CS/AG-3 membrane showed the highest IEC value (2.81 meq/g).

3.10.6. Fourier Transform Infrared Spectroscopy:

FTIR spectroscopy was used to detect characteristic vibrations of functional groups within the blends. Figure 1X shows FTIR spectra of PVA/CS/AG films and of the sulfonated PVA/CS/AG membrane. The following vibrations were identified in the spectra of the PVA/CS/AG film. PVA and CS exhibited characteristic broad bands of OH group at 3568-3037 cm^{-1}, bands at 2914 cm^{-1} could be ascribed as the a symmetric stretching of CH_2 group (Liu *et al*. 2003), The bands at 1236 cm^{-1} and 1159 cm^{-1} are due to the CH_2 and CH wagging vibrations respectively (Eldin *et al*. 2011a). CS displayed characteristic broad band of CH_3 group and CH_3-O at 1037 cm^{-1}, bands of NH_2 group and O-C-NH_2 group can be observed at 1614 cm^{-1}.

The bands at 1712 - 1780 cm-1 are characteristic bands of the carbonyl group. The characteristic bands around 3400–3500 cm-1 is assigned to the N–H stretch for primary and secondary amine of CS. For the sulfonated PVA/CS/AG membrane, the presence of many peaks at 709, 1066 and 1163 cm-1 could be associated with the SO3H symmetric and asymmetric stretching vibrations, which correlates well with the data found in the literature (Hebeish *et al*. 2014 , Espinoza *et al*. 2012).

3.10.7. Thermogravimetric Analysis:

TGA provided detailed information on the thermal stability of the membranes. The relevant thermograms recorded at a heating rate of 20°C/min are shown in Figure 1Y. It can be noticed that the CS sample had two different stages of weight loss. The first stage positioned between 40 and 130 ^{o}C could be associated with to the loss of adsorbed and bound water. The second stage, beginning at 180 ^{0}C and continued up to 400 ^{0}C, during which there was 44% weight loss, could be ascribed to the thermal degradation of CS (Liu *et al*. 2003). PVA, on the other hand, exhibited a three-step degradation pattern. The first step began around 80 °C up to 170 °C and was attributed to the evaporation of loosely bound water of hydration. The second step, which was a major mass loss (76%) appearing between 260 °C and 380 °C could be related to the thermal degradation of PVA. Finally, in the third step, there was a small weight loss observed (12 %) in the range of 430 ^{o}C - 480 ^{o}C, which was probably associated with the polymer backbone fragmentation. Similar observations have been reported in literature. Regarding the thermal stability of PVA/CS/AG film, the three-stage weight loss at 50–130°C, 180–340°C and 370–480°C was evident. PVA/CS/AG-3 membrane exhibited three weight loss stages at 50–130^{o}C, 180–340^{o}C and 420–480°C, followed by the final decomposition that began around 480°C associated with the structural complete decomposition of the polymer. It can be seen that CS membrane had higher water content compared to PVA membrane. At 400^{0}C, CS membrane lost 57.57% of its weight, PVA membrane lost 78.17% of its weight, and PVA/CS/AG membrane lost 58.78% of its weight whereas sulfonated PVA/CS/AG-3 membrane lost 64.28% of its weight.

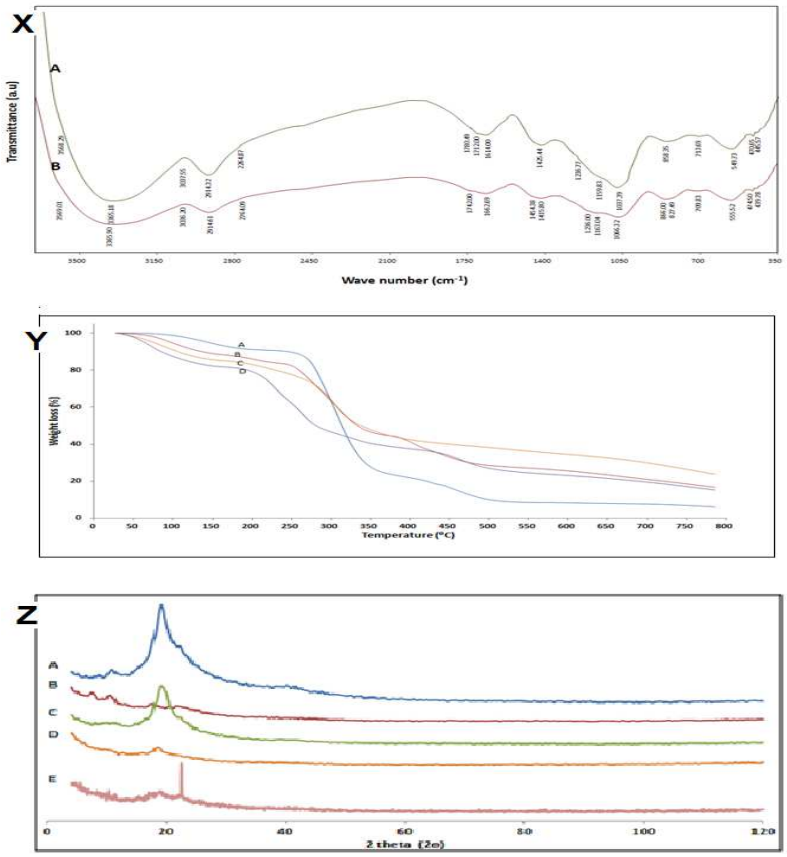

Fig. 1: X) FTIR analysis of A) PVA/CS/AG membrane and B) sulfonated PVA/CS/AG-3 membrane, Y) Thermograms of films cast from (A) PVA, (B) PVA/CS/AG blend, (C) CS, and (D) sulfonated PVA/CS/AG-3 membrane, Z) XRD diffractograms of cast films from (A) PVA, (B) CS, (C) PVA/CS, (D) PVA/CS/AG, and (E) Sulfonated PVA/CS/AG-3 membrane.

From the recorded thermograms. It was also evident that the sulfonated PVA/CS/AG membranes had good thermal stability up to 200°C so it can be concluded that AG served as a stabilizing agent for the sulfonated membrane.

4.1.8 X-ray diffraction:

The crystalline structure of the films cast from PVA, CS, PVA/CS, /PVA/CS/AG and sulfonated PVA/CS/AG was analyzed using XRD.

Selected diffractograms are shown in Figure 1Z. PVA membrane had two characteristic crystalline peaks at 2θ = 11.2° and 19.2° which are also reported by other researchers.

The presence of distinct three peaks at 9.0º, 11.2º and 19.0º in the CS diffractogram can be also treated as a typical fingerprint of this polymer semi-crystallinity. The analysis of the PVA/CS membrane diffraction pattern leads to the conclusion that the crystallinity of PVA was decreased after blending with CS.

4.1.9 Scanning Electron Microscopy (SEM):

The surface and the cross-sectional morphology of PVA, CS, PVA/CS/AG and sulfonated PVA/CS/AG membranes was analyzed using SEM. The micrographs of surfaces and cross-sections of the sulfonated PVA/CS/AG membrane and PVA, CS, PVA/CS and PVA/CS/AG films are shown in figure 2. It was noticed that PVA and CS films have smooth and homogeneous surface (Figure 2A and B). Likewise the surface the PVA/CS blends is also homogeneous, with no apparent pores or domains, indicating good compatibility between CS and PVA (Figure 2C and D). The formation of homogeneous blends of CS and PVA was mostly caused by the presence of hydrogen bonds between the functional groups of the blended component (–OH and $–NH_2$ groups in CS, and –OH groups in PVA).

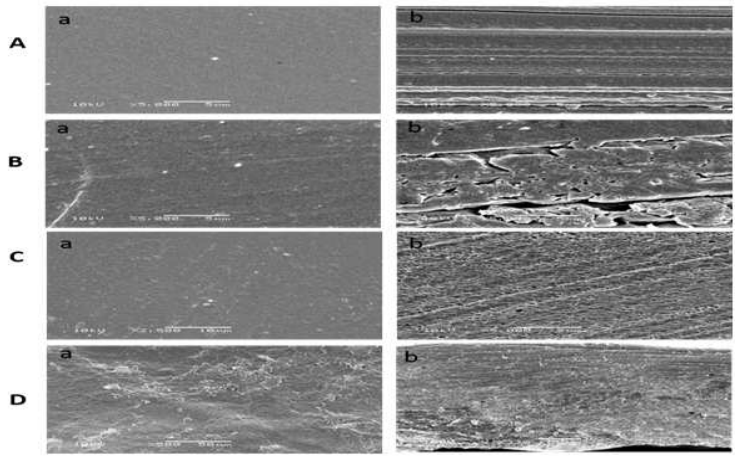

Fig. 2: SEM micrographs of: (a) surface and (b) cross-section of membranes from (A) PVA, (B) CS, (C) PVA/C/AG blend and (D) sulfonated PVA/CS/AG-3 blend.

4.2 Adsorption of Ni^{2+} and Cu^{2+} ions by sulfonated PVA/CS/AG membranes:

In order to evaluate the adsorption performance of the different types of the prepared membranes, the adsorption experiments were performed at pH 5 for 120 min, under continuous magnetic stirring at room temperature. Dilute hydrochloric acid and sodium hydroxide solutions were used to adjust pH value to 5. The adsorption data is shown in Figure 3a. The following adsorption order was observed: PVA<CS<PVA/CS/AG<sulfonated PVA/CS/AG. The adsorption efficiency of the membranes for Cu^{2+} ions was higher than that for Ni^{2+} ions. The photograph of the sulfonated PVA/CS/AG-3 membrane before and after the metal ions adsorption is shown in Figure 3b. Before the adsorption, the membrane appears colorless. After the adsorption experiment, the membrane becomes bluish-black, due to the presence of the metal ions.

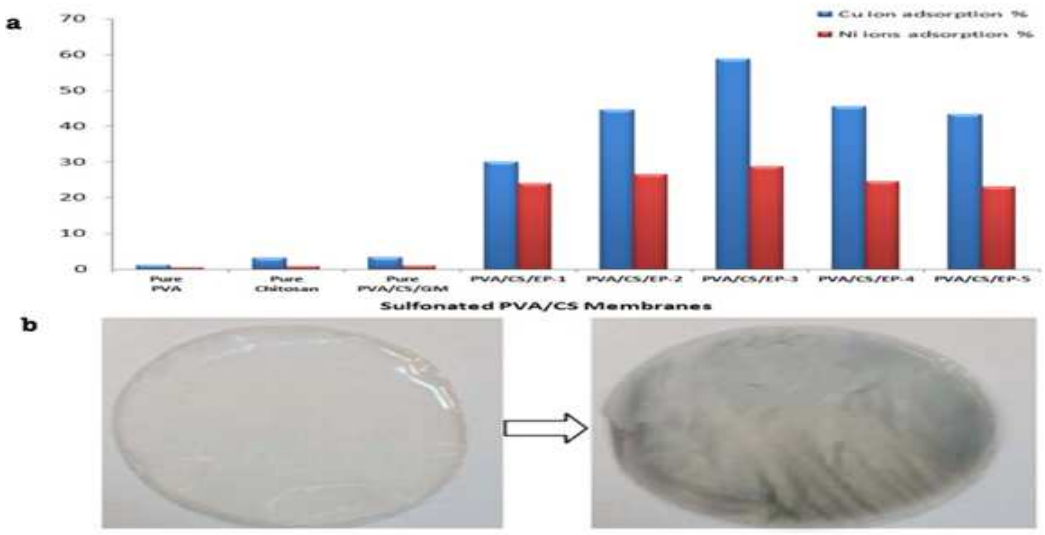

Fig. 3: a) Adsorption % from the aqueous solution containing 50 ppm of both Ni^{2+} and Cu^{2+} by: PVA membrane, CS membrane, PVA/CS/AG membrane and sulfonated PVA/CS/AG membranes; b)Photograph of the sulfonated PVA/CS/AG-3 membrane before and after adsorption.

4.2.1.
Effects of pH and contact time:

The sulfonated PVA/CS/AG-3 membrane showed the highest adsorption efficiency and therefore it was selected for further adsorption studies.

It is well known that pH of the adsorption environment is one of the most important process parameters due to its impact on the solubility of metal ion species and on the extent of ionization of the adsorbent functional groups.

The effect of pH (2-6 range) on the metal ion adsorption from the 50 ppm (Ni^{2+}, Cu^{2+}) aqueous solution by PVA/CS/AG-3 membrane was investigated and the results are shown in Figure 4a. The experiment was carried out for 120 min at 25^{o}C. The pH was adjusted by adding appropriate amounts

of dilute hydrochloric acid and sodium hydroxide solutions. It can be observed that the pH value has a significant influence on the adsorption of the heavy metal ions. Maximum Ni^{2+} and Cu^{2+} adsorption occurred in pH range of 5.5–6. Further increase of pH beyond the value of 6 resulted in precipitation of Ni and Cu salts (Espinoza *et al*. 2012). The maximum ion removal with PVA/CS/AG-3 membrane was found to be 65 and 32 % for Cu^{2+} and Ni^{2+}, respectively, at pH 5.5.

The contact time during the batch adsorption process is another important parameter, in addition to solution pH, especially when taking into account the economics of the water treatment processes.

Figure 4b shows the effect of contact time on the Ni^{2+} and Cu^{2+} ions removal from the 50 ppm feed kept at pH of 5.5 and 25 ^{0}C, under continuous mechanical stirring. Six different contact times were investigated: 30, 60, 90, 120, 150 and 180 min.

Based on Figure 4b, the percentage of ions removed increased with increasing contact time for both the ion types until the plateau was reached at around 120 min, which indicated saturation of all the available adsorption sites Further sorption experiments were carried out using 150 min contact time.

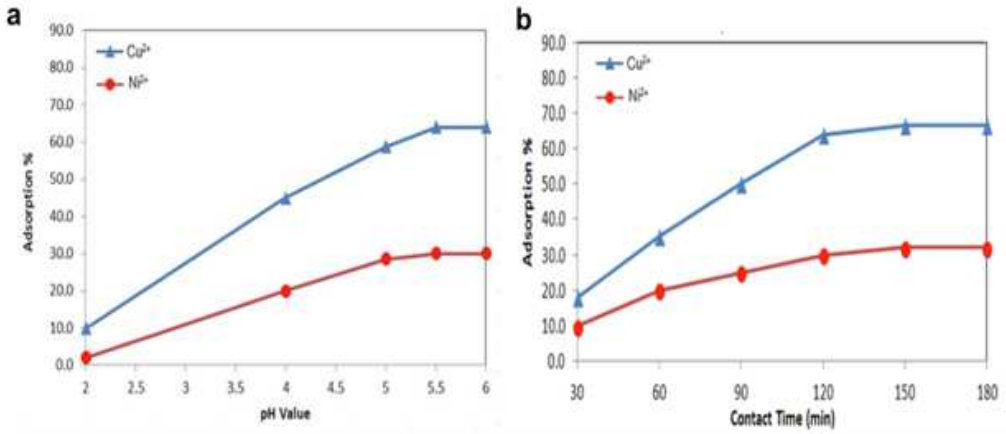

Fig. 4: Dependence of adsorption % from feed of 50 ppm Ni^{+2} and Cu^{+2} by PVA/CS/AG-3 membrane on a) pH (2–6) and b) contact time (30 -180 min).

4.2.2. Effect of Temperature and Metal ion concentration:

The effect of temperature on the adsorption of Ni^{2+} and Cu^{2+} ions by PVA/CS/AG-3 membrane was investigated at 25, 30, 35, 45 and 55 ^{0}C. The pH and contact time were 5.5 and 150 min., respectively for all the experiments; the solutions were magnetically stirred. Figure 5a shows the effect of solution temperature on the adsorption efficiency. Between 25^{o}C and 35^{o}C the adsorption increased slightly to level-off above 35^{o}C. Increasing the temperature of solutions increased the mobility of metal ions and also increased membrane swelling, thus, enabling faster ion penetration and more exhaustive site occupation within the membrane (Wang and Chen 2014; Crini *et al*.; Maleki *et al*. 2015). Therefore, temperature of 35^{0}C was selected an equilibrium temperature for further experiments.

The effect of adsorbate ion concentration was investigated using solutions containing 10, 20, 40, 50, 60, 80 and 100 ppm of Cu^{+2}, and Ni^{+2}. During testing, the solutions were stirred magnetically and kept at pH of 5.5 and temperature of 35^{o}C. The contact time was 150 min. The results are shown in Figure 5b.

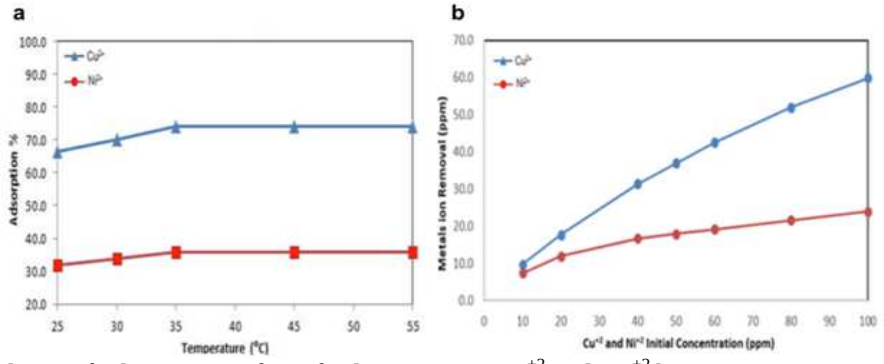

Fig. 5: Dependence of adsorption % from feeds containing Ni^{+2} and Cu^{+2} by PVA/CS/AG-3 membrane on a) temperature (50 ppm initial metal ion concentration) and b) metal ion concentration.

It is evident that the amount ion removal was higher for Cu^{+2} compared to that of Ni^{+2}, at the same concentration. This could be attributed to the difference in their chemical affinity towards the chemical functional group within the PVA/CS/AG-3 adsorbent membrane.

4.3 Adsorption Isotherms and Kinetic Study:

The Langmuir isotherm is typically used to model the adsorption process for sorbents where the adsorption is localized in a monolayer, and each adsorption site has the same adsorptive power. It is also assumed that there is no interaction between the adsorbate molecules. On the other side, the Freundlich isotherm is used to model the multilayer adsorption on a heterogeneous surface.

The plots of Ce/qe versus Ce for the adsorption of Cu^{+2} and Ni^{+2} on PVA/CS/AG-3 adsorbent membranes are shown in Figure 6a. The linear regression fit of the experimental data appears good and supports the validity of the Langmuir isotherm model.

The nonlinear regression of experimental data using Langmuir isotherm model is shown in Figure 6b. The predicted results well validated experimental data, as observed the results deliberated so far designate a higher adsorption of Cu (60 mg/g) at equilibrium concentration about (40 mg/l) compared to Ni (24 mg/g) at about (78 mg/l) equilibrium concentration for the experimental conditions and Langmuir isotherm model.

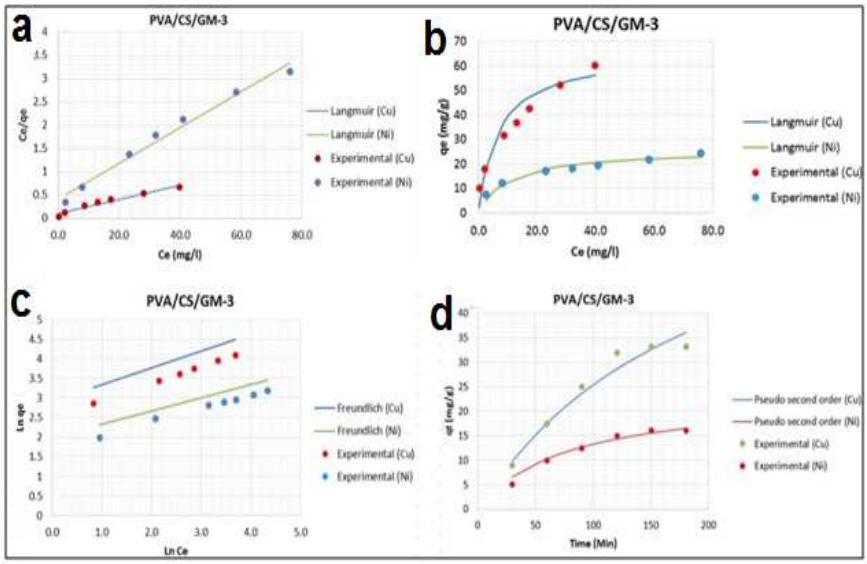

Fig. 6: a) Linear regression and b) Nonlinear regression, for Langmuir isotherm model of Cu^{2+} and Ni^{2+} adsorption into PVA/CS/AG-3 membrane, c) Linear regression for Freundlich isotherm model for adsorption of Cu^{2+} and Ni^{2+} into PVA/CS/AG-3 membrane, d) The contact time effect on adsorption of Cu^{2+} and Ni^{2+} into PVA/CS/AG-3 membrane.

The linear regression with Freundlich isotherm model for adsorption both of Cu^{2+} and Ni^{2+} onto PVA/CS/AG-3 membrane is presented in Figure 6c. As expected, the fit is not as good as with the Langmuir model, which then appears more appropriate for the sorption kinetics analysis (Özen *et al*. 2015). Figure 6d shows the contact time effect on adsorption of Cu^{+2} and Ni^{+2} onto the PVA/CS/AG-3 membrane. The solid points in the figure designate experimental data and the lines represent the results predicted by pseudo-second order kinetic model. The equilibrium adsorption capacity qe (mg/g), and the second order constant k_2 (g/mg· min) were calculated from the slope and intercept the plot of qt versus t. Good fitting is obtained for adsorption of both Cu^{+2} and Ni^{+2} into the PVA/CS/AG-3 membrane.

Conclusions:

In the current research work, sulfonated PVA/CS/AG adsorbent membranes were fabricated by addition of sulfuric acid to the aqueous solution of the three polymer mixture followed by film casting and solvent evaporation. The resultant membrane was characterized by using physico-chemical techniques. FTIR confirmed the creation of sulfonic groups within the adsorbent membrane. XRD and TGA confirmed the retention of crystallinity and the high thermal stability of the membranes. The surface morphology of the membranes was characterized using SEM and membranes' water uptake, dimensional changes after immersion in water and IEC was also determined. The results showed that the addition of AG led to increase of the hydrophilicity and improvemen of the mechanical characteristics of the sulfonated PVA/CS/AG membranes. The sulfonated membranes were used as low-cost adsorbent for the

removal of Cu^{+2} and Ni^{+2} from aqueous solutions. It was determined that the amount of Cu^{+2} and Ni^{+2} removed from the adsorbate solution changed with initial Cu^{+2} and Ni^{+2} concentration, contact time and temperature. The optimum conditions for the best removal were found to be at 35 °C, pH 5.5 and 150 min. contact time. The removal efficiency for Cu^{+2} and Ni^{+2} was decreased with increasing adsorbate concentration up to 100 ppm, and reached 65 and 26 % from 100 ppm of Cu^{+2} and Ni^{+2} respectively. The adsorption data were studied using Freundlich and Langmuir isotherms. The kinetics of adsorption process was well defined by pseudo-second-order model equation while pseudo-first-order model equation failed to properly fit the experimental results. In summary, new adsorbent membranes from sulfonated PVA/CS/AG blends were conveniently prepared. The membranes showed high adsorption capacity and suitability for effective metal ions removal from aqueous solutions. This new membranes may provide new possibilities for the applications in remediation of industrial wastewaters.

REFERENCES

Abu-Saied, M.A., K.A. Khalil, S.S. Al-Deyab, 2012. Preparation and Characterization of Poly Vinyl Acetate Nanofiber Doping Copper Meta International Journal of Electrochemical Science, 2019-2027

Ali, B.H., A. Ziada, G. Blunden, 2009. Biological effects of gum arabic: a review of some recent research Food and chemical toxicology : an international journal published for the British Industrial Biological Research Association, 47: 1-8 doi:10.1016/j.fct.2008.07.001

Borba, C.E., R. Guirardello, E.A. Silva, M.T. Veit, C.R.G. Tavares, 2006. Removal of nickel(II) ions from aqueous solution by biosorption in a fixed bed column: Experimental and theoretical breakthrough curves Biochemical Engineering Journal, 30: 184-191 doi:http://dx.doi.org/10.1016/j.bej.2006.04.001

Crini, G., N. Morin-Crini, N. Fatin-Rouge, S. Déon, 2014. Fievet P. Metal removal from aqueous media by polymer-assisted ultrafiltration with chitosan Arabian Journal of Chemistry doi:http://dx.doi.org/10.1016/j.arabjc.2014.05.020

Dauqan, E., A. Abdullah, 2013. Utilization of Gum Arabic for Industries and Human Health, American Journal of Applied Sciences, 10: 1270-1279

Eldin, M.S.M., M.A. Abu-Saied, A.A. Elzatahry, K.M. El-Khatib, E.A. Hassan, M.M. El-Sabbah, 2011a. Novel Acid-Base Poly vinyl chloride-Doped Ortho-Phosphoric Acid Membranes for Fuel Cell Applications International Journal of Electrochemical Science, 6: 5417 – 5429.

Eldin, M.S.M., A.A. Elzatahry, K.M. El-Khatib, E.A. Hassan, M.M. El-Sabbah, M.A. Abu-Saied, 2011b. Novel grafted nafion membranes for proton-exchange membrane fuel cell applications Journal of Applied Polymer Science, 119: 120-133 doi:10.1002/app.32613

Espinoza, E., R. Escudero, F.J. Tavera, 2012. Waste Water Treatment by Precipitating Copper, Lead And Nickel Species Research Journal of Recent Sciences, 1: 1-61.

Fu, F., Q. Wang, 2011. Removal of heavy metal ions from wastewaters: A review Journal of Environmental Management, 92: 407-418 doi:http://dx.doi.org/10.1016/j.jenvman.2010.11.011

Hallaji, H., A.R. Keshtkar, M.A. Moosavian, 2015. A novel electrospun PVA/ZnO nanofiber adsorbent for U(VI), Cu(II) and Ni(II) removal from aqueous solution Journal of the Taiwan Institute of Chemical Engineers 46:109-118 doi:http://dx.doi.org/10.1016/j.jtice.2014.09.007

Hebeish, A., M.H. El-Rafie, A.M. Rabie, M.A. El-Sheikh, M.E. El-Naggar, 2014. Ultra-microstructural features of perborate oxidized starch Journal of Applied Polymer Science, 131: n/a-n/a doi:10.1002/app.40170

Inyang, M., B. Gao, Y. Yao, Y. Xue, A.R. Zimmerman, P. Pullammanappallil, X. Cao, 2012. Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass Bioresource Technology, 110: 50-56 doi:http://dx.doi.org/10.1016/j.biortech.2012.01.072

Jaafar, J., A.F. Ismail, A. Mustafa, 2007. Physicochemical study of poly(ether ether ketone) electrolyte membranes sulfonated with mixtures of fuming sulfuric acid and sulfuric acid for direct methanol fuel cell application Materials Science and Engineering: A., 460–461: 475-484 doi:http://dx.doi.org/10.1016/j.msea.2007.02.095

Jiang, T., 2015. Adsorption behavior of copper ions from aqueous solution onto graphene oxide–CdS composite Chemical Engineering Journal, 259: 603-610.
doi:http://dx.doi.org/10.1016/j.cej.2014.08.022

Joseph, P., 2009. Mechanisms of cadmium carcinogenesis Toxicology and Applied Pharmacology, 238: 272-279. doi:http://dx.doi.org/10.1016/j.taap.2009.01.011

Kim, N.H., A.K. Mishra, D.Y. Kim, J.H. Lee, 2015. Synthesis of sulfonated poly(ether ether ketone)/layered double hydroxide nanocomposite membranes for fuel cell applications Chemical Engineering Journal, 272: 119-127. doi:http://dx.doi.org/10.1016/j.cej.2015.03.026

Lacerda, V.G., A.B. Mageste, I.J.B. Santos, L.H.M. da Silva, M.D.C.H. da Silva, 2009. Separation of Cd and Ni from Ni–Cd batteries by an environmentally safe methodology employing aqueous two-phase systems Journal of Power Sources, 193: 908-913. doi:http://dx.doi.org/10.1016/j.jpowsour.2009.05.004

Liu, F., B. Yi, D. Xing, J. Yu, H. Zhang, 2003. Nafion/PTFE composite membranes for fuel cell applications Journal of Membrane Science, 212: 213-223. doi:http://dx.doi.org/10.1016/S0376-7388(02)00503-3

Maleki, A., E. Pajootan, B. Hayati, 2015. Ethyl acrylate grafted chitosan for heavy metal removal from wastewater: Equilibrium, kinetic and thermodynamic studies Journal of the Taiwan Institute of Chemical Engineers, 51: 127-134. doi:http://dx.doi.org/10.1016/j.jtice.2015.01.004

Mohan, D., P. Singh, A. Sarswat, P.H. Steele, C.U. Pittman Jr., 2015. Lead sorptive removal using magnetic and nonmagnetic fast pyrolysis energy cane biochars Journal of Colloid and Interface Science, 448: 238-250. doi:http://dx.doi.org/10.1016/j.jcis.2014.12.030

Mohy-Eldin, M.S., M.F. Elkady, M.A. Abu-Saied, A.M.A. Rahman, E.A. Soliman, A.A. Elzatahry, M.E. Youssef, 2010. Removal of cadmium ions from synthetic aqueous solutions with a novel nanosulfonated poly(glycidyl methacrylate) cation exchanger: Kinetic and equilibrium studies Journal of Applied Polymer Science, 118: 3111-3122. doi:10.1002/app.32587

Mousavi, H.Z., A. Hosseinifar, V. Jahed, 2010. Removal of Cu (II) From Wastewater by Waste Tire Rubber Ash Journal of the Serbian Chemical Society, 75: 845–853.

Özen, R., N.A. Sayar, S. Durmaz-Sam, A.A. Sayar, 2015. A sigmoidal model for biosorption of heavy metal cations from aqueous media Mathematical Biosciences 265:40-46 doi:http://dx.doi.org/10.1016/j.mbs.2015.04.007

Părpăriţă, E., N. Cheaburu Cătălina, F. Paţachia Silvia, C. Vasile, 2014. Polyvinyl alcohol/chitosan/montmorillonite nanocomposites preparation by freeze/thaw cycles and characterization, 22. doi:10.2478/achi-2014-0008

Rad, L.R., A. Momeni, B.F. Ghazani, M. Irani, M. Mahmoudi, B. Noghreh, 2014. Removal of Ni2+ and Cd2+ ions from aqueous solutions using electrospun PVA/zeolite nanofibrous adsorbent Chemical Engineering Journal, 256: 119-127. doi:http://dx.doi.org/10.1016/j.cej.2014.06.066

Singh, R., N. Gautam, A. Mishra, R. Gupta, 2011. Heavy metals and living systems: An overview Indian Journal of Pharmacology, 43: 246-253. doi:10.4103/0253-7613.81505

Tsai, C.E., C.W. Lin, B.J. Hwang, 2010. A novel crosslinking strategy for preparing poly(vinyl alcohol)-based proton-conducting membranes with high sulfonation Journal of Power Sources, 195: 2166-2173. doi:http://dx.doi.org/10.1016/j.jpowsour.2009.10.055

Waalkes, M.P., 2000. Cadmium carcinogenesis in review Journal of Inorganic Biochemistry, 79: 241-244 doi:http://dx.doi.org/10.1016/S0162-0134(00)00009-X

Waalkes, M.P., 2003. Cadmium carcinogenesis Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis, 533: 107-120. doi:http://dx.doi.org/10.1016/j.mrfmmm.2003.07.011

Wang, H., B. Gao, S. Wang, J. Fang, Y. Xue, K. Yang, 2015. Removal of Pb(II), Cu(II), and Cd(II) from aqueous solutions by biochar derived from KMnO4 treated hickory wood Bioresource Technology, 197: 356-362 doi:http://dx.doi.org/10.1016/j.biortech.2015.08.132

Wang, J., C. Chen, 2014. Chitosan-based biosorbents: Modification and application for biosorption of heavy metals and radionuclides Bioresource Technology, 160: 129-141. doi:http://dx.doi.org/10.1016/j.biortech.2013.12.110

Yee, R., K. Zhang, B. Ladewig, 2013. The Effects of Sulfonated Poly(ether ether ketone) Ion Exchange Preparation Conditions on Membrane Properties Membranes, 3: 182-195

Zaidi, S., 2003. Polymer Sulfonation - A Versatile Route To Prepare ProtonConducting, Membrane Material For Advanced Technologies ARABIAN JOURNAL FOR SCIENCE AND ENGINEERING 28:183-194.