Removal of Heavy Metals from Wastewater by Adsorption and Membrane Processes: a Comparative Study

Nermen N. Maximous, George F. Nakhla and W. K. Wan

Abstract—This research aimed at investigating the Cr (III), Cd (II) and Pb (II) removal efficiencies by using the newly synthesized metal oxides/ polyethersulfone (PES), Al_2O_3/PES and ZrO_2/PES, membranes from synthetic wastewater and exploring fouling mechanisms. A Comparative study between the removal efficiencies of Cr (III), Cd (II) and Pb (II) from synthetic and natural wastewater by using adsorption onto agricultural by products and the newly synthesized Al_2O_3/PES and ZrO_2/PES membranes was conducted to assess the advantages and limitations of using the metal oxides/PES membranes for heavy metals removal. The results showed that about 99 % and 88 % removal efficiencies were achieved by the tested membranes for Pb (II) and Cr (III), respectively.

Keywords—Adsorption, metals removal, ultrafiltration membranes, wastewater

I. INTRODUCTION

DIFFERENT treatment techniques for wastewater laden with heavy metals have been developed in recent years both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Cr, Cd and Pb are among those hazardous materials that are most commonly found in industrial wastewaters, thus their removal is of utmost importance. The main techniques, which have been utilized to reduce the heavy metals content of effluents, include chemical precipitation [1], ion-exchange [2]-[4], adsorption [5], [6] membrane processes [7], [8] and electrolytic methods [9]. Although various treatments can be employed to remove heavy metals from contaminated wastewater, they have their inherent advantages and limitations in application.

Numerous approaches have been studied for the development of low-cost adsorbents. Babel and Kurniawan [10] reviewed the technical feasibility of various low-cost adsorbents for heavy metals removal and concluded that the use of low-cost adsorbents may contribute to the sustainability of the surrounding environment and offer promising benefits for commercial purpose in the future. Many researches showed effective adsorption of heavy metals using agricultural products and by-products such as walnut expeller meal, peanut skins, wool, tea leaves, coffee powder, sugar beet pulp [11], hazelnut shell activated carbon [12], pecan shell-based granular activated carbons [13] modified rice husk [14]-[16], rice husk activated carbon [17] and maize husk [18].

Membrane filtration has received considerable attention for the treatment of inorganics, since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis can be employed for heavy metal removal. Some significant findings were reported by Juang and Shiau [19], who studied the removal of Cu (II) and Zn (II) ions from synthetic wastewater using chitosan-enhanced membrane filtration. The results indicated that chitosan significantly enhanced metals removal by 6–10 times compared to using membrane alone. Technical parameters such as pH, ligand concentration, applied pressure and membrane pore size were found to significantly affect the rejection rate of metal ions. A major drawback of using ultrafiltration membranes is the relatively high operational cost due to membrane fouling.

Despite the limited research on the use of ultrafiltration membranes for heavy metals removal from wastewater, the use of inorganic-organic ultrafiltration membranes have not been studied for heavy metal removal (Cr, Cd and Pb) to this date. To fill this gap, the application of the newly synthesized metal oxide/polyethersulfone (PES) membranes [20] was investigated for heavy metals removal from synthetic wastewater. In order to assess the advantages and limitations in application, the removal efficiencies of Cr (III), Cd (II) and Pb (II) from synthetic wastewater using the newly synthesized membranes were compared to the removal efficiencies of the same tested metal ions from real wastewater using a low-cost adsorbent (maize leaves and rice husk) and a well known adsorbent (i.e., activated carbon).

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II. MATERIALS AND METHODS

A. Adsorption Studies

Adsorption equilibrium was determined using batch studies. A pre-determined weight of the dry adsorbent [activated carbon (AC) with average particle size of 0.45µm, both maize leaves (ML) and rice husk (RH) with particles range of 125-315 µm] was added, mixed with 30 ml of single metal solution (pH=5) and shaken at 25 ◦ C for 1 hr. For RH and ML, 0.5 ± 0.01 gm were used while for AC 1.0 ± 0.01 gm were used. The speed of agitation was kept constant for each run throughout the experiment to ensure equal mixing. The operational conditions were chosen based on our previous work [20]. Wastewater samples were collected from El-Umum drain (EMD) and El-Tabia pumping stations, Alexandria, Egypt. The samples were analyzed and the data are presented in Table I. Since the concentrations of heavy metals in these samples after adsorption were found to be out of the measurement range of the Atomic Absorption Spectrophotometer, the additive method in which a standard metal ion solution with a known concentration was added to the samples was used in order to increase the metal ion concentration to the detectable levels. The adsorption studies with the real wastewater were carried out using the same method described above.

TABLE I CHEMICAL CHARACTERISTICS OF THE REAL WASTEWATER SAMPLES

Parameters	El-Tabia	El-Umum
Water temperature ($^{\circ}$C)	19.9	24
pH	7.25	7.5
Salinity (‰)	1.5	3.5
D.O (ml O_2 /L)	0.85	1.9
DOC (mg/L)	47.0	15.1
Total Alkalinity (meq./L)	0.68	10
Ca^{2+}(mg/L)	88.4	122.5
Mg^{2+} (mg/L)	97.4	144.5
Ammonia (µg NH_3 – N/L)	42.0	30.3
Nitrite (µg NO_2 – N/L)	0.096	18.2
Phosphate (µg PO_4 – P/L)	28.5	4.4
Cr (III) spiked with 10 PPM Cr (III) solution	9 (6.89)[a]	9 (6.05)[a]
Cd (II) spiked with 10 PPM Cd(II) solution	9.51 (6.25)[a]	9.51 (5.38)[a]
Pb (II) spiked with 10 PPM Pb (II) solution	25.55(15.62)[a]	25.55(13.94)[a]

[a] The initial concentration (mg/L) of the tested metal in the wastewater samples

B. Membrane Preparation

Metal oxides/PES membranes were prepared using PES Radel A-100 (Solvay Advanced Polymers, Alpharetta, GA, USA), Al_2O_3 and ZrO_2 nanoparticles with particle size range of 48 nm and a surface area of 34 m^2 /g, and 40-50 nm and a surface area of 20-30 m^2 /g, respectively, (Sigma-Aldrich Canada Ltd.). Membranes were prepared by the phase inversion method [21]. The 5 % w/w metal oxides /PES membranes were prepared by dispersing the metal oxides nanoparticles in N-methyl pyrrolidone (NMP) solution, after which the solutions were sonicated at 60 ºC for 72 h to obtain uniform and homogeneous casting suspensions. Subsequently, 18 %wt. PES polymer was added and the mixture was sonicated again for a week. A 100 µm casting knife was used to cast the membranes onto a glass plate at room temperature. The nascent membrane was evaporated at 25±1 ºC for 15 s and then immersed in a deionized water coagulation bath maintained at 18±1 ºC for 2 min. To remove the remaining solvent from the membrane structure before testing, all prepared membranes were transferred to a water bath for 15-17 days at room temperature. The membranes characterization and performance with activated sludge filtration are mentioned else where [22], [23].

C. Ultrafiltration studies

Synthetic wastewater used in this study was prepared to match the real wastewater samples used in the adsorption studies. Table II presents the synthetic wastewater characteristics. Ammonia, nitrate and total alkalinity were measured using standard methods (APHA, 1998). pH was measured using Orion pH meter model 410A and a pH prob (VWR model SympHony). Alkaline metals (Ca^{+2}, Mg^{+2}, Na^{+1} and K^{+1}), anions (Cl^{-1} and SO^{-4}), phosphate and heavy metals (Cd, Cr and Pb) were analyzed by Inductive Coupled Plasma (ICP) (Vista-Pro, VARIAN) method No. 3120 Standards Methods (APHA, 1998).

TABLE II SYNTHETIC WASTEWATER CHARACTERISTICS

Parameters	Conc. ± S.D.
pH	6.9
Total Alkalinity (meq./L)	6 ± 1.6
Ammonia (mg NH_3 – N/L)	29.6 ± 1.8
Nitrate (mg NO_2 – N/L)	1230 ± 4.8
Ca^{2+}(mg/L)	121.5 ± 0.75
Mg^{2+} (mg/L)	274.9 ± 46
Na^{+1} (mg/L)	6447 ± 27
K^{+1} (mg/L)	159 ± 0.83
Cl^{-1} (mg/L)	6729 ± 47
SO_4^{-2} (mg/L)	504 ± 1.8
Phosphate (mg PO_4 – P/L)	0.78 ± 0.01
Cr (III)	7.4 ± 0.83
Cd (II)	9.01 ± 0.95
Pb (II)	10.93 ± 2.04

MINTEQ software (MINTEQA2, Version 3.11) was employed to specify the concentrations of precipitated and soluble material in the influent. Membrane filtration was carried out using a stirred batch cell (Model No.8050, Amicon) operated under constant trans-membrane pressure

(TMP) of 0.69 bar. The permeate flux was determined by monitoring the volume of permeate with time. The total membrane resistance was determined using the following equation:

$$J_p = TMP/(\eta . R_t) \qquad (1)$$

Where; J_p is the permeate flux (L/m^2. h), TMP = Trans membrane pressure (0.69 bar) and η= Viscosity of water at room temperature. The metal removal efficiency (% R) was calculated by the following equation:

$$\% R = (1 - C_{per}/C_{feed}) * 100 \qquad (2)$$

Where C_{per} is the concentration of metal ions in permeate and C_{feed} is the concentration of metal ions in the feed.

III. RESULTS AND DISCUSSIONS

A. Adsorption studies

The adsorption data of the single metal ion solutions have been analyzed with both Langmuir and Freundlich adsorption isotherms [24]. The sorption isotherm constants and correlation coefficients are presented in Table III. The data indicates that the adsorption of Cr (III) on AC, Cd (II) on RH or AC and Pb (II) on RH or ML are favorable with $1/n < 1$. Sorption isotherms were fit fairly well with both Langmuir and Freundlich models.

Table IV shows the removal capacities of Cr (III), Cd (II) and Pb (II) from wastewater containing a mixture of the three tested metals in the mass ratio of 1: 1: 2.5, respectively. The Table also shows the ability of a particular metal ion to compete with the other metal ions in solution for the adsorption sites on the sorbents.

TABLE IV THE ADSORPTION CAPACITIES FOR TESTED METAL IONS FROM FIELD

Sorbent/Metal	EMD	El-Tabia
	Adsorptive capacity (mg/g)	Adsorptive capacity (mg/g)
AC		
Cr (III)	0.26	0.25
Cd (II)	0.23	0.24
Pb (II)	0.71	0.74
ML		
Cr (III)	0.4	0.21
Cd (II)	0.31	0.27
Pb (II	1.38	1.24
RH		
Cr (III)	0.39	0.24
Cd (II)	0.37	0.38
Pb (II	1.45	1.39

SAMPLES [20]

The surface area of activated carbon used in this research was much higher than the low-cost adsorbents as it posses the highest weight used (1.0 ± 0.01 gm) among sorbents and the lowest particles size (0.45μm). Since it is well established that the higher the surface area, the higher the adsorption capacity, it was expected that the AC will have the highest metals removal capacities among the tested sorbents. However, as apparent from Table IV, the metals removal capacities (mg/g) for ML and RH were much higher than that of AC, which highlight the applicability of using ML and RH for the removal of Cr, Cd and Pb ions from real wastewater.

TABLE III LANGMUIR AND FREUNDLICH CONSTANTS [20]

Metal	Sorbent	Langmuir			Freundlich		
		Q$_{max}$	b	R^2	1/n	K	R^2
Cr(III)	**RH**	100	0.001	0.98	1.35	0.034	0.96
Cr (III)	**ML**	2.97	0.019	0.90	1.04	0.0407	0.84
Cr (III)	**AC**	3.26	0.685	0.98	0.55	1.0671	0.89
Cd (II)	**RH**	8.59	0.018	0.97	0.86	0.1775	0.92
Cd (II)	**ML**	200	0.001	0.96	1.16	0.0033	0.96
Cd (II)	**AC**	1.74	0.572	0.86	0.44	0.5979	0.87
Pb(II)	**RH**	8.36	0.049	0.99	0.69	0.509	0.99
Pb(II)	**ML**	66.7	0.005	0.93	0.82	0.3927	0.99
Pb(II)	**AC**	0.77	0.000	0.70	2.1	1.39	0.93

In the present study, the affinity of AC, ML and RH for tested metal ions from the real wastewater samples was Pb (II) > Cd (II) ≈ Cr (III). Different reasons have been given regarding the sorption affinity of biosorbent. According to Low et al [25], the amount adsorbed of the metal ions would depend on the equilibrium between sorption metal ions and biosorbent, nature of the metal ions and sorbent, the interaction and distribution of the reaction group on the biosorbent. The prevailing reason for the greater affinity of different sorbents for Pb (II) than other metals appears to be the relative stability of Pb-sorbent bond compared to that of Cd-sorbents or Cr-sorbents [15], and the higher Pb concentration in the solution than the other two tested metals.

B. Ultrafiltraion studies

Table V shows the metal removal efficiencies by the tested membranes. As apparent from the table, the metal removal efficiencies by the two tested membranes are comparable with the order of Pb > Cr > Cd. The ultrafiltartion study shows high selectivity to the removal of Pb with removal efficiencies of 99 %.

Table VI represents the equilibrium mass distribution by MINTEQ software. The software output indicates that 70 % of Pb was in a precipitate form however 99.9 % of $Cr (OH)_2^{+1}$ was in a precipitate form. This observation coupled with metal removal efficiencies indicates that the tested membranes were able to remove around 25 % of the soluble Pb ions.

TABLE V METAL REMOVAL EFFICIENCIES BY ULTRAFILTRATION

Metal	Initial Conc. (mg/L)	0.05 Al₂O₃/PES		0.05 ZrO₂/PES	
		Final Conc. (mg/L)	% removal	Final Conc. (mg/L)	% removal
Pb	10.93	0.07	**99.33**	0.06	**99.47**
Cd	9.01	7.82	13.24	8.02	10.96
Cr	7.35	1.22	**83.36**	0.84	**88.56**

TABLE VI EQUILIBRIUM MASS DISTRIBUTION BY MINTEQ

Component	Total dissolved (mole/L)	% dissolved	Total precipitate	% precipitated
Ca^{+2}	3.03E-03	100	0	0
Cd^{+2}	8.02E-05	100	0	0
Cl^{-1}	1.90E-01	100	0	0
CO_3^{-2}	3.02E-03	100	0	0
$Cr(OH)_2^{+1}$	1.47E-07	0.104	1.4E-04	99.9
Cr^{+2}	1.00E-16	100	0	0
CrO_4^{-2}	1.00E-16	100	0	0
H^{+1}	3.44E-03	100	0	0
K^{+1}	4.07E-03	100	0	0
Mg^{+2}	1.13E-02	100	0	0
Na^{+1}	2.81E-01	100	0	0
NH_4^{+1}	2.12E-03	100	0.00E+00	0
NO_3^{-1}	8.79E-02	100	0.00E+00	0
Pb^{+2}	1.60E-05	30	3.7E-05	70
PO_4^{-3}	6.74E-07	2.7	2. 5E-05	97
SO_4^{-2}	5.25E-03	100	0	0

To evaluate the performance and the operational cost of the tested membranes, the antifouling properties of the membranes were evaluated by membrane resistance (R_t) and permeability at (t) equal infinity (yº). The lowest membrane resistance (R_t) and the highest yº, meant best membrane recovery and consequently lowest operational cost. The membrane permeability at infinity was calculated by fitting the experimental data using Sigma Plot software version 10 (Systat Software, Inc., Canada). The data fit the exponential decay (3-parameters) equation (3) with R^2 of 0.90-0.99.

$$y = y^o + ae^{-bt} \qquad (3)$$

Where: y = permeability (L/m^2 h-bar), t = time (h), yº = permeability at (t) equal infinity and a, b are the regression constants.

Fig. 1 illustrates the experimental and calculated permeability data for the synthetic wastewater filtrations. As apparent from the graphs, the permeability data comprised of initial fouling (phase 1) resulting in a rapid permeability decline mainly due to the irreversible deposition of the inorganic precipitates , followed by pseudo steady-state (phase 2) in which the flux appears to stabilize, indicating that permeation drag and back transport have reached equilibrium. As little fouling still occurs during phase 2, this operation can be maintained during a certain filtration period, before cleaning of the membrane is required [26].
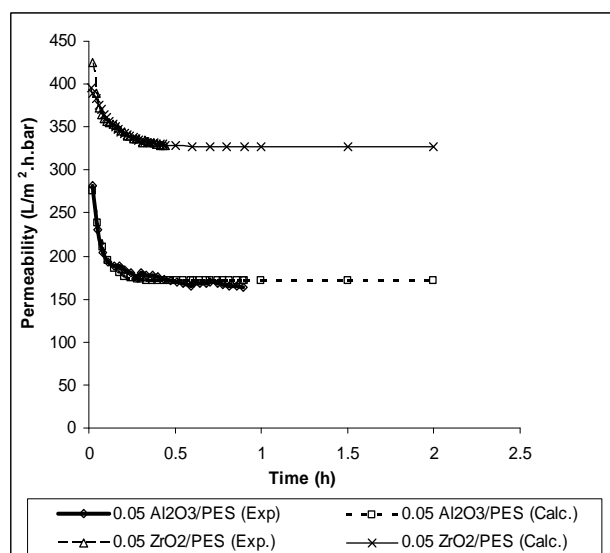

Fig. 1 Permeability data for tested membranes during synthetic wastewater filtration

Table VII shows the steady-state permeability (yº) values and membrane resistance (R_t) for tested membranes. As apparent from the table, the 0.05 ZrO_2/PES membranes have the lowest R_t (almost half that of the 0.05 Al_2O_3/PES membranes) and the highest permeability (yº) (twice that of the Al_2O_3/PES membranes) for the synthetic wastewater filtration. This indicates that 0.05 ZrO_2/PES membranes are superior in terms of membrane fouling and maintenance for wastewater laden with heavy metals filtrations.

TABLE VII PERMEABILITY AND MEMBRANE RESISTANCE FOR TESTED MEMBRANES

Parameters	0.05 ZrO_2/PES	0.05 Al_2O_3/PES
R_t	1.0 E+07	2.5 E+07
Pseudo steady-state permeability (yº) (L/ m^2 .bar - h)	326.7	171

IV. COMPARISON OF METAL TREATMENT TECHNOLOGIES

Table VIII summarizes the operational conditions and performance of the two aforementioned treatment techniques studied in the present work.

TABLE VIII OPERATIONAL CONDITIONS AND PERFORMANCES OF ADSORPTION AND ULTRAFILTRATION TREATMENT TECHNIQUES STUDIED IN THE PRESENT WORK

Operational conditions/ removal efficiencies	Adsorption			Ultrafiltration	
Power required	Agitation			TMP (0.69 bar)	
pH	5			6.9	
Metal selectivity	Pb			Pb	
Metal removal order	Pb (II) > Cd (II) ≈ Cr (III)			Pb > Cr (III) > Cd (II)	
% Pb (II) removal efficiency [a]	AC	ML	RH	Al_2O_3/PES	ZrO_2/PES
	98	85	93	99.3	99.5
% Cr (III) removal efficiency [a]	AC	ML	RH	Al_2O_3/PES	ZrO_2/PES
	95	56	58	83.4	88.6
% Cd (II) removal efficiency [a]	AC	ML	RH	Al_2O_3/PES	ZrO_2/PES
	83	50	66	13.2	11

[a] The % metals removal reported are the average of the % removal efficiencies of the two real wastewater samples [20]

As apparent from the table, the ultrafiltration results confirm that the novel Al_2O_3/PES and ZrO_2/PES membranes could be an excellent alternative for Pb (II) and Cr (III) removal from wastewater with removal efficiencies of 99 % and 88 %, respectively. Furthermore, the fact that this removal efficiencies have been achieved at pH of 7 and at low TMP (0.69 bar) add advantages to the newly synthesized membranes as they can be coupled with biological treatment in one facility. It is also important to emphasize that the aforementioned membranes were tested with activated sludge [22], [23] and the results showed lower flux decline; total resistance (R_t); cake resistance (R_c), and fouling resistance (R_f) compared to neat PES membranes.

On the other hand, despite that the Pb (II) and Cr (III) removal efficiencies by activated carbon at the optimum pH of 5 [20] are comparable to the removal efficiencies achieved by ultrafiltation at pH of 7, the frustrating aspects of this method are significant sludge production, the ever-increasing cost for landfill disposal of the resulting toxic sludge, and most importantly, the long-term environmental consequences [27], [28].

V. CONCLUSION

This study aimed at evaluating the applicability and the efficiency of the newly synthesized Al_2O_3/PES and ZrO_2/PES membranes for Pb (II), Cr (III) and Cd (II) metal ions from wastewater and to compare their results with a well established metal removal technique (i.e., adsorption). The major findings of this research are:

1) The tested ultrafiltration membranes showed above 99 % and 80 % removal efficiencies for Pb(II) and Cr (III), respectively. Furthermore, the operational conditions of neutral pH and low TMP (0.69) increase their applicability for coupling with biological treatment.

2) The adsorption studies showed that for the low-cost sorbents (RH and ML) and AC, the affinity for tested metal ions from real wastewater was Pb (II) > Cd (II) ≈ Cr (III).

3) The highly efficient low cost and the rapid uptake of ML and RH indicated that it could be a better alternative for the removal of Pb (II) from real wastewater by sorption process.

4) Comparing to the adsorption technique,, the smaller space requirement, the high Pb (II) and Cr (III) removal efficiencies, the better control of membrane fouling and consequently lower maintenance expenses are the major advantages of using the newly synthesized Al_2O_3/PES and ZrO_2/PES membranes for wastewater laden with heavy metals filtration

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