Assessment of the produced grafted nylon-6 non woven fabrics as ion-exchangers in wastewater treatment

Samy Elsebaie Shalaby^{a,*}, Naser Gad Ahmed Al-Balakocy^a, Samiha Mohamed Abo El-Ola^a, Margarita Konstantinovna Beliakova^b

^aProtenic and Manmade Fibres Department, Textile Research Division, National Research Centre (NRC), Dokki, Cairo, Egypt, email: samyshalaby40@yahoo.com (S.E. Shalaby), nasergad@yahoo.com (N.G.A. Al-Balakocy), samiham_2000@yahoo.com (S.M. Abo EL-Ola)

^bPreparation & Finishing of Cellulosic Fibres Department, Textile Research Division, National Research Centre (NRC), Dokki, Cairo, Egypt, email: margritabilyakova@gmail.com (M.K. Beliakova)

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ABSTRACT

The present work aims to assess: (a) The effectiveness of nylon nonwoven fabrics containing antimicrobial substance and grafted with PMAA, PDMAEMA and the blended fabric containing the above mentioned two types of nonwoven fabrics for metal ions (Cu^{2+} , Pb²⁺) and chromate (Cr_2O_7)² recovery from wastewater; (b) The amount of the ion-exchanger used; and (c) The desired quality of product water (breakthrough point) on the operating capacity of textile under investigation. The main objective of this study is to investigate the possibilities of the final effluent in order to comply with the National Environmental Regularity standard for wastewater discharge into the public sewage network. The Cu²⁺and Pb²⁺ removal efficiency by the above mention textile types was studied by batch adsorption and column runs methods. It was found, in case of applying batch adsorption method that, the maximum removal of Cu²⁺ (92%) takes place when nylon grafted with PMAA nonwoven fabric was used. The application of blended nonwoven grafted with PMAA and PDMAEMA fabric paves the way for high sorption (79%) of Cu^{2+} from wastewater. The Cu^{2+} removal with grafted with PDMAEMA nonwoven fabric slightly increased relative to control fabric. The maximum ion removal % of Pb2+ (80–82%) was attained upon using all three types of grafted textiles, irrespective of the types of grafted polymer. Column method was used for determination of Cu²⁺ and Pb²⁺ removal efficiency by using the three types of grafted nylon-6 nonwoven fabrics. The copper and lead free effluents, breakthrough points and breakthrough capacities for the ion-exchangers under investigation were obtained Chromate removal efficiency by using Nylon non woven antimicrobial fabrics grafted with PDMAEMA was studied. For this anion exchanger fabric chromate free effluent, chromate breakthrough point and breakthrough capacity were also obtained.

Keywords: Nylon non woven fabrics; Antimicrobial; Grafting; PMAA; PDMAEMA; Ion exchanger; Water filtration

1. Introduction

Recent research in the area of heavy metal removal has focused on the development of materials with increased affinity, capacity, and selectivity for the target metals [1–3].

Karrs et al. [4] have concluded that in the wastewater treatment and the subsequent metal salt recovery, the ion exchange method is more effective than evaporation, precipitations, or reverse osmosis. Therefore, selective textile fiber can be used for reducing the amount of metal wastes, especially in small scale industries operating in communal areas where there is need to find easy and reliable methods for wastewater treatment.

*Corresponding author.

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During recent years attention has been paid to exchangers with amino- or imino-acid as ligand groups. The presence and arrangement of the carboxyl groups and the tertiary nitrogen atom confer upon the textile a strong preference for complexing copper and other heavy metal cations [5].

Many short-term laboratory and pilot-scale studies are routinely undertaken now to evaluate the viability of ion exchange processes in treating specific wastewater contaminated with heavy metals. They help to provide a good level of confidence in commercializing the ion exchange process for copper removal. This reflects the importance of the present work.

Practical applications of ion exchange processes generally involve utilizing the ion exchanger in a column. The most common columnar ion exchange process is a fixed bed process, whereby the aqueous stream to be treated is passed through a stationary bed of ion exchange materials. A properly operated fixed ion exchange column can achieve nearly complete separation of the aqueous contaminant from the solution, and is well suited to operating as a continuous treatment unit. Furthermore, using an ion-exchange column nearly completely utilizes the exchange capacity of the ion exchanger and allows for efficient and effective exchanger regeneration [6].

Operating capacity or effective capacity is the actual useful capacity of the textile for exchanging ions from a solution flowing through a fixed bed of textile particles under specified conditions. It may be defined as the capacity of a textile bed when the solute being removed from the feed solution exceeds some arbitrarily selected level [7].

Recently development of laboratory conditions for establishment of know-how for the production of ion exchanger nylon-6 was carried out. Adjustment and adaption of these conditions to suit the production of those fibers on pilot scale was achieved. The preparation of nylon-6 fibers as ion-exchange material based on grafting of antimicrobial nylon-6 fibers with PMAA and DMAEMA using $Cu²⁺-K₂S₂O₈$ redox system was carried out. Assessment the application of the produced fibers as ion-exchanger was evaluated for adsorption of heavy metals from aqueous solutions. The effect of adsorption parameters such as pH, duration, initial ion concentration and the adsorption temperature on the degree of extraction (R%) and adsorption capacity (SC mg/g) was calculated. The grafted fibers showed high efficiency for adsorption of $Cu²⁺$, $Pb²⁺$ as cations and SO_4^{-2} , $Cr_2O_7^{-2}$ as anions [8,9].

The present work aims to use bench scale sorption and column runs to assess:

- (a) The effectiveness of different types of textile non woven fabrics for metal and chromate recovery,
- (b)The amount of the ion-exchanger used, and
- (c) The desired quality of the product water (breakthrough point) on the operating capacity of textiles under investigation.

2. Experimental

2.1. Materials and reagents

• The following types of produced nylon non woven fabrics were examined as ion exchangers:

• Lead, copper and chromium salts used throughout the work were of analytical reagent grade (Merck). Standard stock solutions for each metal ions were prepared in deionized water using $Pb(NO₃)₂$, $CuSO₄$:5H₂O and K₂Cr₂O₇:7H₂O freshly prepared daily-diluted solutions were used.

2.2. Methods

2.2.1. Fixation of AS on nylon fibers

Preparation of nylon fibers containing antimicrobial substrate (AS) was carried out according to the method described by Shalaby et al. [10].

2.2.2. Grafting process

Nylon fibers containing antimicrobial substrate (AS) was grafted with PMAA and PDMAEMA according to the method described by Shalaby et al. [10].

2.2.3. Production of non woven fabrics

Preparation of non woven fabrics containing antimicrobial substrate (AS) was carried out according to the method described by Shalaby et al. [8].

2.2.4. Synthetic wastewater preparation

The laboratory-scale experimental studies were conducted using synthetic wastewater prepared using deionized water with different 5 mg/l concentrations for copper(II), lead(II) and Cr(VI). Duplicate column runs were applied for all experiments. All glassware and plastic containers were washed with 15% nitric acid solution and rinsed thoroughly with water.

2.2.5. Sorption of heavy metals ions

Sorption of heavy metals ions was carried using the following methods:

a. Batch sorption experiments

The batch sorption studies was carried out by contacting the different types of non woven nylon-6 fabrics with each metal ions in a glass tube at pH (5 \pm 0.1) for Pb (II) and Cu(II) and pH (4 ± 0.1) for Cr (VI) according to our previous studies [8]. Studies were conducted at room temperature $(25 \pm 0.1^{\circ}\text{C})$ using the same size of each fabric (5×6 cm) and was added in 100 ml of metal ions solution to verify the efficiency of these fabrics on the sorption of heavy metals [Cu(II), Pb(II) and Cr(VI)] ions. Each experiment was conducted in a mechanical shaker at 200 rpm for 60 min. All samples were filtered through Whatman filter paper (No. 41) and the metal ions concentration was determined in the filtrate. To distinguish between possible metal precipitation and actual metal sorption, controls were used without sorbent materials.

All the experiments were carried out in triplicate. The percent relative standard deviation of the measurements was calculated and considered acceptable if the value was lower than 5%; otherwise, the data were discarded.

The percentage of each metal ion removed by different types of fibers during the series of batch investigations was determined using the following Eq. (1):

$$
Removal(\%) = \frac{C_o - C_f}{C_o} \tag{1}
$$

where C_{ρ} and C_{f} are the initial and equilibrium concentration (mg/l) of metal ion in solution, respectively. The concentrations of metal ion in all samples were digested and analyzed according to "Standard Methods" [11].

b. Column runs for synthesized textiles

Bench scale single fixed-bed column runs were performed with 2.292 cm diameter (d) and columns containing textile of 22.0 ml bed height (L) ; so the corresponding volume of the textiles bed is equal to 90.7 cm³ ($\pi r^2/4 \times L$). The column runs were carried out at room temperature (25 ± 2°C) by using positive-displacement pumps with constant-flow rate for each run.

The textiles were washed with deionized water, and 22.0 ml of sample solution was passed through the column at a flow of 13.33 ml/min. This step was carried out for equilibration of the textile with respect to major cation of water as well as pH to avoid compositional and pH changes upon passage the waste through the column.

2.3. Volumetric loading rate for column runs for all types of *nonwoven nylon fabrics*

Volumetric loading rate for column runs for all types of non woven nylon fabrics is usually expressed in bed volumes (*bv*) of treated solution per unit time or the volume of solution treated per volume of textile in a unit time (ml of effluents per minute per ml of textile). In essence, it defines the length of time the solution is in contact with the textile [12] at volumetric loading rates 0.147 ml/min/ml of textile. (0.7998 l/h volumetric flow rates) was used as shown in Eq. (2).

$$
Bed volume(bv) = \frac{Volume of wastewater to be treated}{Volume of textile}
$$
 (2)

The main contributing parameters for measuring the efficiency of the exchanger process using the textiles under investigations, based on the experimental results, are determined by both of breakthrough and elution curves.

- (i) The breakthrough curves: are obtained by passing the wastewater through the column and the effluent samples were manually and consequently collected every 2.205 bed volumes (*bv*) (200.0 ml per textile bed volume 90.7 ml) for chemical analysis. This process is continued until the effluent is approximately of the same composition as the influent of the column.
- (ii) Regeneration Runs (elution curves): The exhausted bed textiles were washed with deionized water and copper ions were eluted with 0.2 N HCl for chelating cation exchange textiles with volumetric flow rate 0.15 l/h (0.02756 ml/min/ml of textile volumetric loading rate). The effluent regenerated solutions were collected continuously every 2.0 bed volumes (*bv*) (200 ml per textile bed volume 90.7 ml) for chemical analysis. Finally, after elution, the bed textiles were rinsed with enough deionized water to produce an effluent of pH 5.0 to 7.0 with the same flow rate for elution after that the textile bed volume was reactivation by soaking it in 0.5 N sodium hydroxide for 24 h.
- (iii) Breakthrough (textile) capacity: was measured by monitoring metal ion concentrations according to Egyptian regulatory standards for wastewater discharge into the public sewage network (Ministerial decree 4/2000 for discharge into public sewerage system). The breakthrough (textile) capacity is calculated by multiplying the treated bed volume (*bv*) by ion concentration in the influent at the moment of metal ion leakage [13].
- (iv) The empty bed contact time (EBCT) is generally expressed as the ratio of the empty textile bed volume of the column (90.7 cm^3) to the volumetric flow rate (ml/min) [14].

2.4. Instrumentation

2.4.1. Knick digital pH meter model "646" (Germany)

The metal concentrations were measured using Atomic Absorption spectrometer Varian Spectra AA (220) with graphite furnace accessory and equipped with deuterium arc background corrector.

2.5. Analytical methods

2.5.1. pH measurement

pH was measured with a combined glass electrode. The electrode was calibrated at room temperature with three standard buffers of pH 4, 7 and 10. Calibration was checked periodically and adjusted if necessary.

2.5.2. Heavy metals determination

The concentrations of heavy metals ions in all samples were digested and analyzed according to "Standard Methods" [11]. Metal ions were performed on an Atomic Absorption Spectrometer. For each series of measurements absorption cal-

Table 1

ibration curve constructed was composed of a blank and three or more standards. External reference standards from Merck, Germany and quality control sample from US EPA were used to confirm the instrument metal concentration reading.

3. Results and discussion

3.1. Heavy metals removal using cationic exchangers based on nylon non woven fabrics

3.1.1. Copper

Since copper metal is insoluble, most copper enters the water system by copper salts such as chloride, sulfate, and nitrate. Such salts are used in the electroplating industries, and photography. Wastes from rinse tanks and filter cleanouts also find their way into the sanitary system [15].

Electrolysis copper plating has been employed extensively for printed circuits, plating on plastics and other industrial applications. The treatment of rinse water from electrolysis copper baths has become more of an issue since rules and regulations on waste discharge have become more stringent. The ideal treatment for this rinse water must be effective and, of course, economical [16].

Copper ions, as pollutant, do not accumulate in the human body. In massive amounts, though, copper can cause illness or even death. The most serious effect of copper, in the sanitary sewer system and subsequent discharge into bodies of waters, is its destruction of bacteria in treatment plants. Without the optimum numbers of bacteria a treatment facility cannot properly treat sewage for which it was designed [15].

The presence of copper in water supply, although not constituting a hazard to health, may interfere with the intended domestic uses of water. Copper concentration should not exceed 1.0 mg/l and this value was recommended as guideline value by WHO [17]. However, WHO [18] recommended a provisional health-based guideline value of 2 mg/l (rounded figure). The main objective of this study is to investigate the possibilities of the final effluent in order to comply with the Egyptian Environmental Regularity Standard for wastewater discharge into the public sewage network (Law 93 of 1962, amended by the Minister of Housing Decree 44/2000; sets limits for reuse of treated wastewater in agricultural purposes and sets limits for effluent discharges to the public sewer).

The copper removal efficiency by using the above mentioned textile types (1, 2, 3, 4, 5) of nylon-6 nonwoven fabrics was studied by batch adsorption and column runs methods.

Batch adsorption experiments were conducted with the same size of nylon nonwoven fabrics with 100 ml of initial concentration 5.25 mg/l of copper II ions. Each sample was agitated in a rotary shaker at 200 rpm for 60 min. The obtained results are listed in Table 1 from which one can conclude the following:

1 The maximum removal of Cu(II) (92%) takes place when [Nylon→T(AS)→grafted PMAA 40%] non woven fabric was used for the ions adsorption. This may be attributed to the ionic attraction between the COO¯ groups (active centres) of the grafted nylon and Cu+2 ions.

Removal of Cu(II) by nylon non woven fabrics using batch sorption method

Sorption conditions [Cu(II)], 5.25 mg/l; pH, 5; Temperature, 25°C; Size of each non woven fabric, 5×6 cm².

- 2 The application of blended non woven fabric consisting from 50% Wt/Wt of [Nylon→T $(AS) \rightarrow$ grafted PMAA (40%)] and 50% Wt/Wt of [Nylon-6→T(AS)→grafted PDMAEMA (20%)] fibers also paves the way for high sorption (79%) of Cu(II) ions from wastewater. This means that, grafting nylon fibers with PMAA increases the ability of the produced from them nonwoven fabrics to adsorb Cu(II) ions.
- 3 The opposite holds true when $[N$ ylon \rightarrow T(AS)→grafted PDMAEMA (20%)] was used for sorption process. It was found that such treatment slightly increases the copper removal relative to the control nonwoven fabrics.

Columns method was used for determination of copper removal efficiency by using cation exchangers based on nylon→(AS)→grafted with PMAA (40%) or PDMAEMA (20%)] and the blended fabric of the above mentioned two types of nonwoven fabrics. The determination was carried out under the same operating conditions with initial copper concentration of 5 mg/l at PH 5.0 and 0.147 ml/min/ml textile fiber volumetric loading rate. The obtained results are listed in Tables 2–4 and shown in Figs. 1–3. These results are pointed to the following:

- 1 For the three types of used nylon non woven fabrics copper free effluent could be obtained until 114.66 [Table 2-Fig. 1] and 26.46 [Table 3-Fig. 2], and 97.023 [Table 4-Fig. 3] bed volumes (*bv*), respectively.
- 2 Copper breakthrough point occurred at concentration 1.5 mg/l of the effluent concentration with breakthrough capacities of 0.5733 (Table 2), 0.132 (Table 3) and 0.4859 cu/l textile for three activated nonwoven fabrics, respectively.

Table 2 Copper removal using [Nylon→T(AS)→grafted with PMAA 40%] nonwoven fabric at pH 5.0

No.	Volume (m _l)	(a) Bed volume (bv)	Volumetric flow rate $= 13.33$ ml/min	
			$EBCT = 6.8$ min	
			Conc. $(mgCu/l)$	C/C_{0}
1	200	2.205	0.0010	0.0002
\mathcal{P}	8000	88.203	0.0010	0.0002
3	10000	110.254	0.940	0.1880
4	$*10400$	114.664	1.460	0.2920
5	12000	132.304	2.450	0.4900
6	14000	154.355	3.330	0.6660
7	16000	176.406	3.890	0.7780
8	17000	187.431	4.190	0.8380
9	18000	198.456	4.340	0.8680
10	19000	209.482	5.000	1.0000

(a) Bed volume = Volume/(textile bed volume 90.7 ml; Initial concentration (C₀) 5.0 mg/l; *Breakthrough capacity at 1.5 mg/l = *bv* × C₀/1000 ~ 0.5734g Cu/l textile at 13.33 ml/min; EBCT = Empty bed contact time ratio of bed volume to volumetric flow rate = $90.7 / 13.33$.

Table 3

Copper removal using [Nylon→T(AS)→grafted with PDMAEMA 20%] nonwoven fabric at pH 5.0

No.	Volume (m _l)	(a)Bed volume (bv)	Volumetric flow rate $= 13.33$ ml/ min $EBCT = 6.8$ min	
			Conc. (mg Cu/l)	C/C_0
1	200	2.205	0.0010	0.0002
$\overline{2}$	600	6.615	0.0010	0.0002
3	1000	11.025	0.184	0.0368
4	2000	22.051	1.4	0.2800
5	$*2400$	26.461	1.5	0.3000
6	3000	33.076	2.5	0.5000
7	5000	55.127	3.7	0.7400
8	9000	99.228	4.7	0.9400
9	10400	114.664	5.00	1.0000
10	11000	121.279	5.00	1.0000

(a) Bed volume = Volume/(textile bed volume 90.7 ml; Initial concentration (C_0) 5.0 mg/l; *Breakthrough capacity at 1.5 mg/l = *bv* × *C*⁰ /1000 ~0.132g Cu/l textile at 13.33 ml/min.; EBCT = Empty bed contact time ratio of bed volume to volumetric flow rate = 90.7 /13.33.

3.2. Regeneration of cation exchanger [Nylon→*T(AS)*→*grafted with PMAA (40%)] non woven fabric*

The high efficiency for three times of regeneration for recovering the copper ions (Cu(II)) from the textile fiber beds were obtained by using 0.5 N hydrochloric acid, as shown in Table 5 and Fig. 4. The regeneration was effi-

Table 4

Copper removal using blended nonwoven fabric consisting of (50%) Wt/Wt [Nylon→T(AS)→grafted with PMAA 40%] and 50%) Wt/Wt [Nylon→T(AS)→grafted with PDMAEMA 20%] (at pH 5.0)

No.	Volume (m _l)	(a)Bed volume (bv)		Volumetric flow rate = 13.33 ml/ min	
			$EBCT = 6.8$ min		
			Conc. (mg Cu/l)	C/C_{0}	
1	200	2.205	0.001	0.0002	
$\overline{2}$	6000	66.152	0.001	0.0002	
5	*8800	97.023	1.56	0.3120	
6	11000	121.279	2.57	0.5140	
7	13000	143.330	3.37	0.6740	
8	18000	198.456	4.340	0.8680	
9	18600	205.072	4.600	0.9200	
10	19000	209.482	5.000	1.0000	

(a) Bed volume = Volume/(textile bed volume 90.7 ml; Initial concentration (C₀) 5.0 mg/l; *Breakthrough capacity at 1.5 mg/l = *bv* × C₀/1000 ~0.485gCu/l textile at 13.33 ml/min; EBCT = Empty bed contact time ratio of bed volume to volumetric flow rate = 90.7 /13.33.

Fig. 1. Copper removal using [Nylon→T(AS)→grafted with PMAA 40%] nonwoven fabric.

Fig. 2. Copper removal using [Nylon→T(AS)→grafted with PD-MAEMA 20%] nonwoven fabric.

Fig. 3. Copper removal using blended nonwoven fabric consisting of (50%) Wt/Wt [Nylon→T(AS)→grafted with PMAA 40%] and (50%) Wt/Wt [Nylon→T(AS)→grafted with PDMAEMA 20%].

Table 5

Recovery of Copper from an exhausted cation exchange columns of [Nylon→T(AS)→grafted with PMAA 40%] nonwoven fabrics

Volume	(a)Bed volume	Copper (mg/l)			
(m _l)	(bv)	Batch 1	Batch 2	Batch 3	
50	0.55	60.30	59.90	59.30	
100	1.10	160.20	159.40	158.70	
150	1.65	40.90	39.90	39.50	
200	2.21	9.30	8.90	8.70	
250	2.76	3.30	3.10	2.90	
300	3.31	1.50	1.35	1.30	
350	3.86	0.50	0.39	0.27	
400	4.41	0.20	0.14	0.12	
450	4.96	0.10	0.09	0.09	
500	5.51	0.10	0.08	0.07	

Fig. 4 Recovery of Copper from an exhausted cation exchange columns of [Nylon→T(AS)→grafted with PMAA 40%] nonwoven fabrics

ciently continued until the effluent concentration reaches 0.1 mg/l for the exhausted columns of copper using \sim 5 bv of regenerant for textile fiber beds at $0.1\overline{5}$ l/h volumetric flow rate. Regeneration process for textile fiber beds was in agreement with the report issued by US EPA (10), which concludes that, for the cation exchange process firstly being converted to hydrogen then to the sodium form.

3.3. Lead

3.3.1. Lead removal using [Nylon→*T(AS)*→*grafted with PMAA (40%)] non woven fabrics*

Many serious environmental problems were raised from the presence of heavy metals in the industrial waste water attributed to their non-biodegradable properties and toxicity [19]. Exposure to toxic heavy metals, such as Pb (II) ions, even at low concentration led to a wide range of spectrum health problems, such as convulsions, capillary, hepatic and renal damage. Precipitation, membrane processes, electrolytic recovery, liquid-liquid extraction, ion exchange and adsorption are techniques employed to the removal of heavy metals [20–22]. These techniques are ineffective or expensive, especially when the heavy metal ions are present in high concentration in the polluted media. Biosorption occurs due to physico-chemical interactions of metal ions with active groups such as carboxylic, phosphate, sulfate, amino, amide and hydroxyl groups [23,24].

In the present part the lead removal efficiency by using Nylon non woven fabric was determined by batch adsorption and column runs methods.

The results of the determination of lead removal percent using batch adsorption method are listed in Table 6. Based on these data one can conclude that, the maximum ion removal percentage of lead ions (80–82%) was attained in case of using nylon non woven fabrics grafted either with PMAA or with PDMAEMA and also when using its blended mixtures. This was noticed irrespective of the type of the grafted polymer.

In case of applying the column runs method the determination was carried out under the same operat-

Table 6

Removal of Pb(II) by nylon non woven fabrics using batch sorption method

	No. Type of non woven nylon-6 fabric	Equilibrium concentration (mg/l)	Metal ion removal $\binom{0}{0}$
1	Nylon (blank)	5.00	44.4
2	N ylon \rightarrow T(AS)	4.50	50.0
3	$Nylon \rightarrow T(AS) \rightarrow$ grafted with $PMAA$ 40%	1.68	81.3
4	$Nylon \rightarrow T(AS) \rightarrow$ grafted with PDMAEMA 20%	1.8	80.0
5	$(50\%) Wt/Wt$ [Nylon \rightarrow T(AS) \rightarrow grafted with PMAA 40%] and (50%) Wt/ Wt [Nylon \rightarrow T(AS) \rightarrow grafted with PDMAEMA 20%]	1.66	81.6

Sorption conditions

[Pb (II)], 9 mg/l; pH, 5; Temperature, 25°C; Size of each nonwoven fabric, 5×6 cm².

ing conditions with initial lead concentration of 5.3 mg/l (C_0) , at pH 5.0 and 0.147 ml/min/ml textile fiber volumetric loading rate. The results listed in (Table 7) and Fig. 5 show that for the activated textile fiber lead free effluent could be obtained until 138.920 *bv*, where lead breakthrough point occurred at concentration 1.0 mg/l of the influent concentration with breakthrough capacities of 0.736 g Pb/l textile.

3.3.2. Anion removal using anionic exchangers based on grafted nylon non woven fabrics

3.3.2.1. Chromate recovery

Recent studies provide voluminous data regarding mutagenicity and animal carcinogenicity of various chromium compounds [24]. As a result, there is a growing concern about chromium ultimate effect on the environment. The chromate discharge limits are being subjected to more stringent regulatory control in every industrialized country [26].

Table 7

Lead removal using [Nylon→T(AS)→Grafted with PMAA 40%] nonwoven fabrics at pH 5.0

No.	Volume (m _l)	(a)Bed volume (bv)	Volumetric flow rate $=$ 13.33 ml/ min	
			$EBCT = 6.8$ min	
			Conc. $(mgPb/l)$	C/C_{0}
1	200	2.205	0.001	0.0002
$\overline{2}$	9000	99.228	0.001	0.0002
3	10000	110.254	0.100	0.0189
4	12000	132.304	0.690	0.1302
5	12600	138.920	1.000	0.1887
6	13200	145.535	2.100	0.3962
7	14200	156.560	3.200	0.6038
8	16000	176.406	4.400	0.8302
9	17600	194.046	5.200	0.9811
10	17800	196.251	5.300	1.0000

a) Bed volume = Volume/(textile bed volume 90.7 ml; Initial concentration (*C*⁰) 5.8 mg/l;* Breakthrough capacity at 1.0 mg/l = *bv* × *C*⁰ /1000 ~ 0.7363g Pb/l textile at 13.33 ml/min; EBCT = Empty bed contact time ratio of bed volume to volumetric flow rate = 90.7/13.33.

Fig. 5. Lead removal using [Nylon→T(AS)→Grafted with PMAA 40%] nonwoven fabrics.

Several authors [27–29] have successful attempts to apply an anion exchange process primarily to recover and reuse chromate from metal-finishing industries. Many short-term laboratory and pilot-scale studies are routinely undertaken now to evaluate the viability of ion exchange processes in treating wastewater contaminated with chromate. They help to provide a good level of confidence in commercializing the ion exchange process for chromate removal [30].

In the present part the chromate removal efficiency by using nylon nonwoven antimicrobial fabrics grafted with PDMAEMA under the same operating conditions with initial chromate concentration of 5.8 mg/l (C_0) , at pH 4.0 and 0.147 ml/min/ml textile fiber volumetric loading rate was investigated. The results [Table 8-Fig. 6] showed that, for the anion exchanger nylon grafted non woven fabric chromate free effluent could be obtained until 39.691 *bv*, where

Table 8

Chromate removal using [Nylon→T(AS)→Grafted with PDMAEMA 20%] nonwoven fabric at pH 4.0

No.	Volume (m _l)	(a)Bed volume (bv)	Volumetric flow rate $=$ 13.33 ml/ min	
			$EBCT = 6.8$ min	
			Conc.	C/C_0
			(mg Cr(VI)/I)	
1	200	2.205	0.001	0.0002
$\overline{2}$	800	8.820	0.050	0.0086
3	2600	28.666	0.060	0.0103
$\overline{4}$	3400	37.486	0.140	0.0241
5	3600	39.691	0.500	0.0862
6	4400	48.512	1.299	0.2240
7	10000	110.254	2.20	0.3793
8	24000	264.609	3.20	0.5517
9	27000	297.685	3.50	0.6034
10	28000	308.710	4.00	0.6897

(a) Bed volume = Volume/(textile bed volume 90.7 ml; Initial concentration (C_0) 5.8 mg/l; *Breakthrough capacity at $0.5 \text{ mg}/1 = bv \times$ $C_0/1000 \sim 0.230$ g Cr(VI)/l textile at 13.33 ml/min; EBCT = Empty bed contact time ratio of bed volume to volumetric flow rate = 90.7 /13.33.

Fig. 6. Chromate removal using [Nylon→T(AS)→Grafted with PDMAEM 20%] nonwoven fabric.

chromate breakthrough point occurred at concentration 0.5 mg/l of the influent concentration with breakthrough capacities of 0.230 g Cr(VI)/l textile. This may be as a result of protonation the tertiary a mine in grafted nylon with PDMAEMA at acidic medium, so the ionic attractions with the chromate anions increased significantly.

Our results substantiated by the fact that, at higher volumetric flow rate, the contact time between the activated textile fiber and the liquid phase in the fiber bed is shorter therefore, operating at a lower volumetric flow rate will generally lead to greater breakthrough capacity per unit volume of fiber bed.

4. Conclusion

Ion-exchange non woven fabrics based on antimicrobial nylon-6 fibers grafted with PMAA and DMAEMA using $Cu^{2+}K_{2}S_{2}O_{8}$ redox system have been prepared. The effectiveness of the grafted with PMAA,PDMAEMA and the blended fabric containing the above mentioned two types of nonwoven fabrics for metal (Cu^{2+}, Pb^{2+}) and chromate $(\text{Cr}_2\text{O}_7)^2$ recovery from wastewater was investigated.

The Cu^{2+} and Pb^{2+} removal efficiencies by the above mention textile types were studied by batch adsorption and column runs methods. It was found, in case of applying batch adsorption method, that, the maximum removal of Cu2+ (92%) takes place when nylon grafted with PMAA nonwoven fabric was used. This may be attributed to the ionic attraction between the COO¯ groups (active centres) of the grafted nylon and Cu⁺² ions. The application of blended nonwoven grafted with PMAA and PDMAEMA fabrics paves the way for high sorption $(79%)$ of $Cu²⁺$ from wastewater. The Cu²⁺removal with grafted with PDMAEMA nonwoven fabric slightly increased relative to control fabric. The maximum ion removal % of Pb^{2+} (80–82%) was attained upon using all three types of grafted textiles, irrespective of the types of grafted polymer.

Columns method was used for determination of copper removal efficiency for the grafted with PMAA, PDMAEMA and the blended fabric consisting of the above mentioned two types of nonwoven fabrics. The obtained results revealed that, for the three types of used nylon nonwoven fabrics copper free effluent could be obtained until 114.66, 26.46 and 97.023 bed volumes (*bv*), respectively. In addition it was found that, copper breakthrough point occurred at concentration 1.5 mg/l of the effluent concentration with breakthrough capacities of 0.573, 0.132 and 0.486 Cu/l textile for three activated non woven fabrics, respectively.

Nylon grafted with PMAA nonwoven fabric was used for determination of lead removal efficiency. The obtained results showed that, for the activated textile fiber lead free effluent could be obtained until 138.920 *bv*, where lead breakthrough point occurred at concentration 1.0 mg/l of the influent concentration with breakthrough capacities of 0.736 g Pb/l textile.

The chromate removal efficiency by using nylon nonwoven antimicrobial fabric grafted with PDMAEMA was investigated. The results showed that, for the anion exchanger nylon grafted non woven fabric chromate free effluent could be obtained until 39.691 *bv*, where chromate breakthrough point occurred at concentration 0.5 mg/L of the influent concentration with breakthrough capacities of 0.230 g Cr(VI)/l textile. This may be as a result of protonation the tertiary a mine in grafted nylon with PDMAEMA at acidic medium, then ionic attractions with the chromate anions increase significantly.

Generally, The grafted fibers showed high efficiency for adsorption of Cu²⁺, Pb²⁺ cations and Cr₂O₇² anions.

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