RESEARCH ARTICLE

Pre-irradiation grafting of acrylic acid and sodium styrene sulfonate on non-woven polyethylene fabric for heavy metal removal

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ABSTRACT

In present study acrylic acid (AAc) and sodium styrene sulfonate (SSS) were grafted onto non-woven polyethylene fabric using pre-irradiation method and the grafted adsorbent is employed for Cr(III) and Pb(II) adsorption. After irradiation of the non-woven polyethylene fabrics with 50 kGy radiation dose the grafting reaction was carried out at 80º C with monomer solution consisted of 30% AAc, 10% SSS and 4% NaCl in water. A high graft yield of 270% was achieved. Fourier Transform Infrared, Scanning Electron Microscopy and Thermo-gravimetric Analysis were used to analyze the adsorbent. Pb (II) and Cr (III) adsorption from synthetic aqueous solution was attempted by the grafted adsorbent. Adsorption study was accomplished by changing the contact time, pH and initial metal ion concentration. Contact time 48 h and initial metal concentration 1000 ppm were found optimum for all the metal ions studied. pH 6.2 and 5 was observed best for Pb (II) and Cr(III) adsorption respectively. Kinetic adsorption data fitted better with pseudo-second-order equation than pseudo-first-order. Good correlation of experimental data with Langmuir isotherm model suggested monolayer adsorption. Langmuir equation showed that the maximum adsorption capacity for Pb (II) was 38.46 mg g^{-1} and Cr (III) was 111.11 mg g^{-1}. Experiment on desorption of metal ions and reuse of the adsorbent depicted good results. Adsorbent also showed efficient adsorption of Cr(III) from real waste water. From all the findings it can be expected that the AAc-SSS grafted PE fabric can successfully eliminate Cr(III) and Pb(II) from industrial waste water.

Keywords: Heavy metal, acrylic acid, sodium styrene sulfonate, adsorption, wastewater

1. INTRODUCTION

Environmental contamination arise from discharge of toxic heavy metals in industrial wastewater is a severe global crisis we are experiencing these days. Environmental purity is now a days the major concern [1-2]. Heavy metals commonly generate from metal mineral treating, leather tanning, metallurgical process, glass manufacture, mining action, metal plating, and battery production etc. [3]. Compact structure and harmfulness made the heavy metals are different from other metals. Another alarming matter about heavy metal is their non- biodegradability. They are also unaffected by bacterial breakdown. Natural environment and human health suffer a humongous

danger due to the presence of these heavy metals in water. Because heavy metals have tendency to form complexes with organic matters that can be fatal at little quantities too. Noxious nature of heavy metals, their perseverance in environment and bioaccumulation extremely disturbs the food sequence [4]. After entering into the food chain heavy metals can influence various harmful biochemical reactions and after certain period they can also gather inside living organisms. Therefore, eliminating heavy metals from industrial effluent before their discharge into water stream has given utmost priority in different countries recently.

Harmful heavy metals that are usually inspected are Lead, Copper, Nickel, Cadmium, Mercury and Chromium. Among these, Lead and Chromium are the

groundwater pollutants that are generally discharged from different industries. Leather industry that is one of the major industries in Bangladesh also generates effluents containing large amount of Chromium.90% of the tanneries in Bangladesh use chrome tanning method. However, in the course of the chrome tanning method, 40% unemployed chromium salts are commonly discharged in the final effluents initiating a serious hazard to the environment. Various interpretations showed that average amount of chromium produced in the effluent of chrome tanning process varies between 2000 to 5000 mg L^{-1}. Composite effluents generated from a tannery can comprise 100-250 mg L^{-1} of chromium. Most of these effluents are discharged into the nearby water bodies without proper pre-treatment which leads to severe environment pollution. At present most of the tannery uses chromium (III) salts as a tanning agent which does not possess as much threat as chromium (VI) at low concentration. But recent studies revealed that under certain legand conditions, Cr (III) can be toxic at higher concentration [5]. Lead is also found in leather waste water. High level of Lead exposure can cause anemia, weakness, and damage of kidney and brain. Very high Lead exposure can be deadly. Low level of lead exposure may harm different biochemical procedures and psychological activities [6].

Recent technologies applied for heavy metal removal are chemical precipitation, complex-formation, oxidation-reduction, evaporation, electro-deposition and the liquid-liquid surface extraction, membrane separation, reverse osmosis, and adsorption. Most of these techniques are expensive and also unsuccessful when the concentration of heavy metal cation is low. Adsorption is considered as the most effective, cheap, convenient and widely used method for the removal of hazardous heavy metals from wastewater [7-8]. A good number of researches have been conducted on the elimination of toxic metals or dyes using adsorption process [9-15].

Recently, elimination of heavy metal from aqueous solution using graft polymers has become a new approach [16-26]. High value of adsorption capacity of the adsorbent and ability to reuse reduces the probability of secondary pollution. Graft polymer is formed by covalent bonding of monomers with appropriate functionality onto the parent polymer chain. The achievement of graft polymerization is that it allows combination of various functions of the grafted monomer to the parent polymer without affecting the mechanical properties of the parent polymer [27-28]. Radiation-induced grafting is more suitable than other methods for example plasma treatment, oxidation of polymers, decomposition of chemical initiators etc., due to the high penetration ability of ionization radiation into the polymer matrix that induces quick and regular formation of radicals [29].

The trunk polymer utilized to prepare metal adsorbent in present study is non-woven polyethylene. Numerous researches have reported elimination of toxic heavy metal ions by monomer grafted polyethylene (PE) [30-34]. In present study the preparation of a new adsorbent based on non-woven PE fabric were attempted by radiation grafting

technique using binary monomersacrylic acid (AAc) and sodium styrene sulfonate (SSS). The prepared adsorbent is also investigated for adsorption of Pb(II) and Cr(III) from synthetic aqueous solution. The grafted fabric was analyzed by Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and Thermo-gravimetric Analysis (TGA). Adsorption capacity of the adsorbent for Cr(III) and Pb(II) was investigated under different environments by changing the contact time, pH and initial metal ion concentration. The kinetics and isotherm of Pb(II) and Cr(III) adsorption were investigated using established models.

2.   MATERIALS AND METHOD

2.1. Reagents and materials

The trunk polymer used for making grafted adsorbent was non-woven polyethylene (PE) fabric collected from Kurashiki Textile Manufacturing Co. Ltd. Acrylic acid and sodium styrene sulfonate procured from Sigma Aldrich (USA) were utilized as monomers to graft onto PE. NaOH, NaCl, and HCl were supplied by Merck, Germany. $Pb(NO_3)_2$ and $Cr(NO_3)_3.9H_2O$ (Merck, Germany) were used in the adsorption experiments.

2.2. Preparation of the adsorbent

The non-woven PE films were subjected to gamma ray irradiation at 50 kGy radiation dose at an ambient temperature. The Cobalt-60 gamma source utilized was a Panoramic Irradiator of 90 kCi Batch Type supplied by BRIT, India. The irradiator activity was 50 kCi and the dose rate used was 13 kGy h^{-1}. The irradiated PE films were stored at dry-ice condition until next use. The monomer solution consisted of 30 % AAc, 10 % SSS and 4 % NaCl in distilled H$_2$O were bubbled with argon gas to eliminate dissolved oxygen. The de-aerated monomer solution was poured into glass bottle containing irradiated PE films. After the glass bottle was fulfilled with monomer solution, it was securely closed with a lid to escape invasion of oxygen from the air into the monomer solution. Subsequently the grafting reaction was conducted in a water bath at temperature 80°C for 4 h. After that, the grafted PE fabric was washed properly to remove remaining monomer and homopolymer. The degree of grafting was determined by the following formula:

$$\text{Degree of grafting } (\%) = \frac{W_1 - W_0}{W_0} \times 100$$

(1)

Where, W_1 is the dry weight of the grafted PE film and W_0 is the dry weight of the pristine PE film.

The grafted PE films were treated with 1M NaOH at room temperature for 20 minutes. The NaOH treatment is done to ionize the functional groups of the grafted film to improve the metal adsorption.

2.3. Metal ion adsorption by the adsorbent form synthetic wastewater

0.1 g of the adsorbent was dipped in the 50 mL aqueous solutions of Lead (II), and Chromium (III)

separately at 25°C. The adsorption studies were repeated at various times of contact, pH and initial metal ion concentrations. HCl and NaOH solutions were used to adjust the pH of the solutions. Atomic Absorption Spectroscopy were utilized to detect metal ion concentration in the solutions before and after dipping of adsorbent. Using the following formula adsorption capacity of the adsorbent was calculated,

$$Q_0 = \frac{C_1 - C_2}{W} \times V \qquad (2)$$

Here,

Q_o = Adsorption capacity of the adsorbent (mg g^{-1})

W= Mass of dry adsorbent (g)

V= Volume of Metal ion solution (L)

C_1 = Initial concentration of metal ions (mg L^{-1})

C_2 = Final concentration of metal ions after adsorption (mg L^{-1})

2.4. Desorption of metals ions and reuse of adsorbent

Pb(II) and Cr(III) were desorbed from the adsorbent by treatment with 2 M HCl and 2M NaOH respectively for 24 hours. The formula used to calculate desorption percentage is given below:

$$\text{Percentage of desorption} = \frac{\text{Desorbed ions (mg)}}{\text{Adsorbed ions (mg)}} \times 100 \qquad (3)$$

After desorption of the metal ions, the adsorbent was reused for metal ion adsorption.

2.5. Adsorption of Cr from real wastewater

Two types of waste water were collected from savar tannery industrial estate. The preliminary properties of the waste waters were as follows: (1) Waste water before treatment (raw waste water): Colour: Deep blue, Odour: Pungent, pH: 7.76, EC: 8.98 mS cm^{-1} (2) Waste water after treatment by conventional (precipitation) method: Color: Light yellow, Odor: No bad odor, pH: 8.2, EC: 1. mS cm^{-1}. The waste waters were digested and then used for adsorption of Cr by the prepared adsorbent. Initial Cr concentration of waste water before treatment (raw waste water) was 1200 mg L^{-1} and initial Cr concentration of waste water after treatment by conventional method was 4 mg L^{-1}.

3. RESULTS AND DISCUSSION

3.1. Preparation and characterization of adsorbent

We have grafted acrylic acid (AAc) and sodium styrene sulfonate (SSS) onto non-woven polyethylene fabric by pre-irradiation method using gamma rays from Co-60 source at room temperature (25°C). At first the non-woven PE polymer backbone was subjected to gamma irradiation to form primary free radicals. Then, the monomer solution was added to the irradiated polymer for grafting. In the reaction graft growing chain and termination reaction was occurred. Finally the graft copolymer was produced. In pre-irradiation technique, monomer is not irradiated directly and formation of homo polymer is relatively lower than simultaneous irradiation technique. A simplified mechanism of grafting is shown in Fig 1. 30 % AAc, 10 % SSS and 4 % NaCl in water was selected as the optimum composition of monomer solution for grafting. The radiation dose applied was 50 kGy. The graft yield achieved under this condition was 270 %. The grafted fabric was analyzed using Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and Thermo-gravimetric Analysis (TGA).

3.1.1. FTIR analysis of prepared adsorbent

The IR spectra of PE fabric and grafted PE fabric is shown in Fig 2. The distinctive features of the IR spectra of PE films are due to its C-H stretching and bending vibration. Strong peaks for C-H asymmetric and symmetric stretching were detected at 2910 and 2845 cm^{-1} respectively with weak C-H bending vibration at 1463 cm^{-1}. In grafted PE film, absorption band at 2917, 2848 and 1456 cm^{-1} corresponds to C-H asymmetric and symmetric stretching and C-H bending vibration. A strong absorption band is found at 1738cm^{-1} that denotes C=O group of acrylic acid. Peak at 1565 and 1370 cm^{-1} results from COO$^-$ and CH group of sodium acrylate [35]. Peaks at 1212 and 1010 cm^{-1} could be assigned to the SO$_3$-group antisymmetric and symmetric vibrational adsorption peaks, respectively [36]. Strong absorption bands of C=O (carboxylic acid) and S=O (sulfonate) group indicates the grafting AAc and SSS on in PE film respectively. The presence of peak for COO$^-$ group of sodium acrylate indicates the modification of acid group that increases the metal adsorption.

Irradiation at 50 kGy

[-CH$_2$-CH$_2$-]n $\longrightarrow$ [-CH$_2$-ĊH-]n

Non-woven PE fabric   **Radiated non-woven PE fabric**

[-CH$_2$-ĊH-]n   +   H$_2$C=CH-R $\longrightarrow$ [-CH$_2$-ĊH-]n

Monomer |

[-CH$_2$-CH-]m
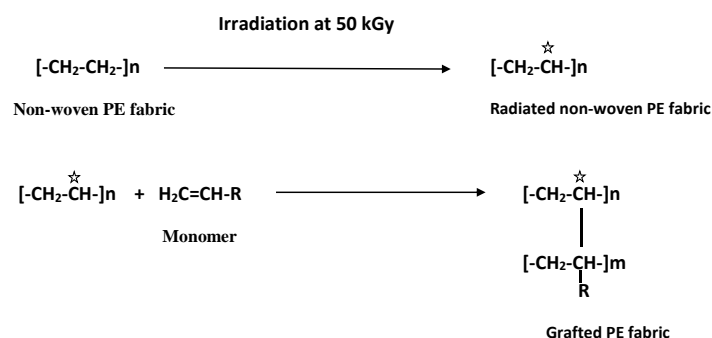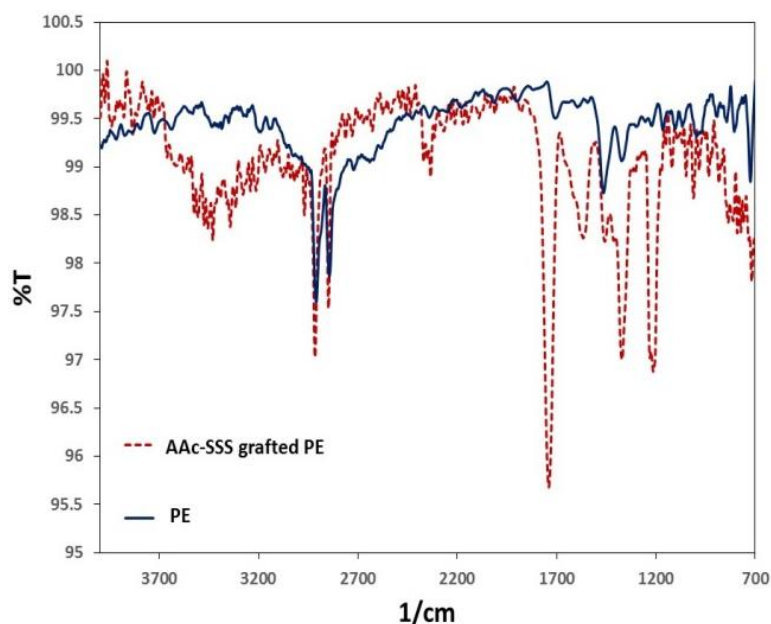R

Grafted PE fabric

Fig 1. Simplified grafting mechanism

Fig 2. FTIR spectra of PE and grafted Aac-SSS grafted PE

3.1.2. SEM analysis of the adsorbent

Scanning Electron microscopy of nonwoven PE, AAc and SSS grafted PE were analyzed by SEM to relate the physical characteristic of nonwoven PE, AAc and SSS grafted PE. The SEM images of non-woven PE are shown in Fig 3(a), (c) and the SEM image of AAc-SSS grafted PE are shown in Fig 3 (b) and (d). The SEM images of the nonwoven PE fabrics depict transformation of the physical appearance after grafting with AAc and SSS. It seems that a layer of grafted chains covered the surface of PE. The coverage of the surface of polymer with grafted chain is observed in previous study [37]. The grafted surface looks more closely netted due to the grafted chains that represent physical indications of the grafting.

3.1.3. TGA analysis of the adsorbent

The thermo-gravimetric analysis (TGA) thermo-grams for PE fabric and AAc/SSS-PE adsorbent are shown in Fig 4. The weight loss of grafted PE is higher than original PE upto 400°C and after 400°C the weight loss of grafted PE is lower than original PE. The original PE film shows thermal stability up to 200°C and above 200°C it starts to decompose. It shows a three decomposition steps, i.e., 200°C– 255°C, 255°C–499°C and above 499°C. There are six weight loss steps in the TGA curve for AAc/SSS-PE fabric adsorbent. The first weight loss appearing in the temperature range 26°C–129°C is easily understood to be due to the loss of moisture absorbed from air. The weight loss stages at 129°C–222°C, 222°C–376°C, 376-427°C, 427-481°C and above 481°C originated from degradation of grafted chain and degradation of PE.

3.2. Metal ions adsorption by the prepared grafted adsorbent using synthetic wastewater

### 3.2.1. Variation of metal ion adsorption with change of pH

pH is a key factor to influence the adsorption of metal ions on an adsorbent. The configuration of functional groups present on surface of the adsorbent alters with pH change and this factor affects the adsorption capacity. Fig 5 shows the variation of adsorption capacity of Cr(III) and Pb(II) with the pH variant. pH 6.2 and 5 were optimum for Pb(II), and Cr(III) respectively. Fig 5(b) shows acceleration of the adsorption capacity with the rise of pH from 3 to 5. When the pH is low, large amount of hydrogen ions occupy the surface of the adsorbent and it resists the progression of positively charged metal ions to the functional groups on the adsorbent surface. Again when the pH raised (higher than 5 for Cr(III) and higher than 6.2 for Pb(II))precipitates of hydroxides of Pb(II) and Cr(III) were produced and as a result the adsorption capacity decreased.

3.2.2. Change of adsorption capacity of the adsorbent with variation of metal ion concentration

Fig 6 shows how the initial concentration of metal ion affects the adsorption capacity of the adsorbent. The figure presents that with the acceleration of initial concentration of metal ions the adsorption capability raises and it reaches the equilibrium value at a high concentration of metal ions. The main cause behind this result is that the reaction sites on the surface of the adsorbent becomes saturated at the certain higher concentration. When the reaction sites are occupied there remains no sites accessible for additional adsorption of metal ions.
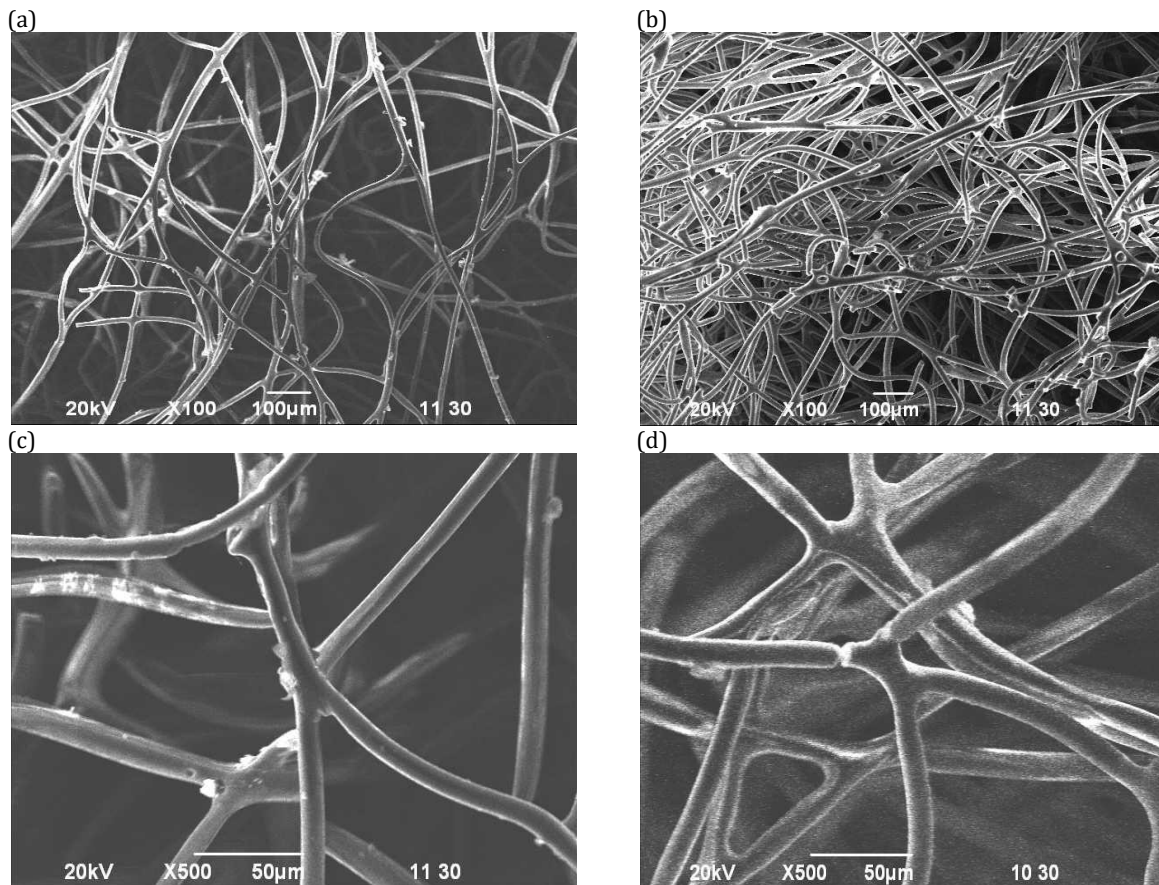
Fig 3. SEM image of non woven PE (a) before grafting (magnification X100) (b) after grafting (magnification X100) (c) before grafting (magnification X500) (d) after grafting (magnification X500)
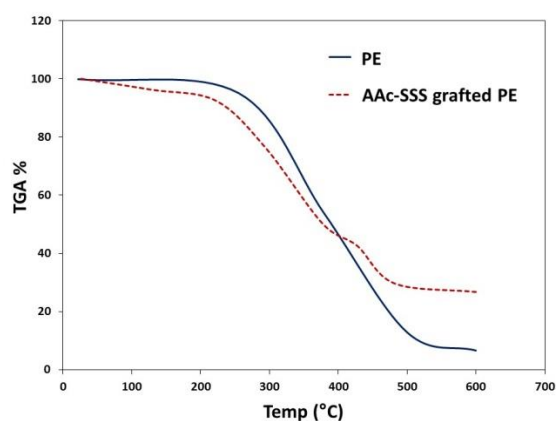
Fig 4. TGA thermogram of non woven PE fabrics and grafted PE fabrics

For realize metal ion adsorption, Langmuir isotherm model were utilized. The equation is as follows:

$$\frac{C_e}{Q_e} = \frac{\frac{C_e}{Q_0+1}}{Q_{ob}} \qquad (4)$$

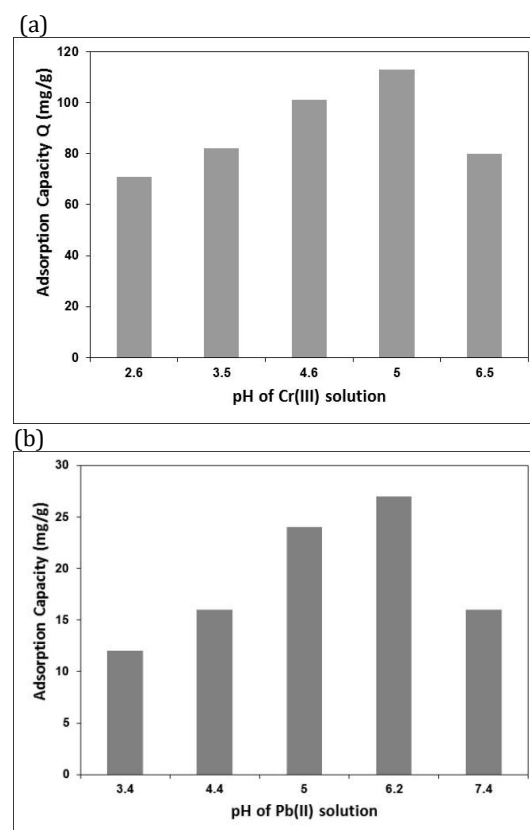Here,

C_e = Concentration at equilibrium (mg L^{-1})

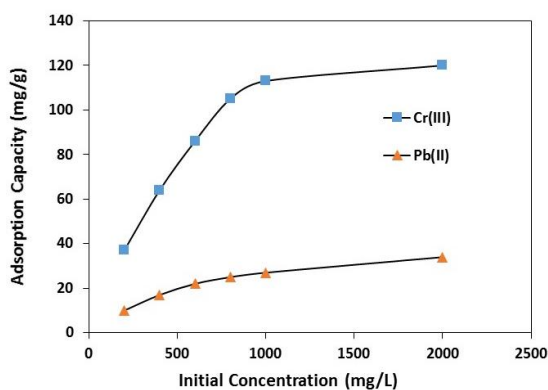Q_o= Monolayer saturation adsorption capacity(mg g^{-1})

Q_e= Capacity of adsorption at equilibrium

b = Langmuir adsorption constant (L mg^{-1}).

**Fig. 5.** Adsorption variation of (a) Chromium (III) and (b) Lead(II) due to pH change

Fig 6. Adsorption capability variation with starting concentration of metal ions

Fig 7 and 8 represents two diagrams obtained by plotting Ce/Qe against Ce with the data presentedin Fig 6. The linearity of Ce/Qe vs Ce plot demonstrated that the Langmuir adsorption isotherm is obeyed by the adsorption process. Using Langmuir equation, adsorption capacity of monolayer saturation for the Cr(III) and Pb(II) adsorption by the prepared adsorbent was measured as166.66and 45.25(mg g^{-1}) respectively.
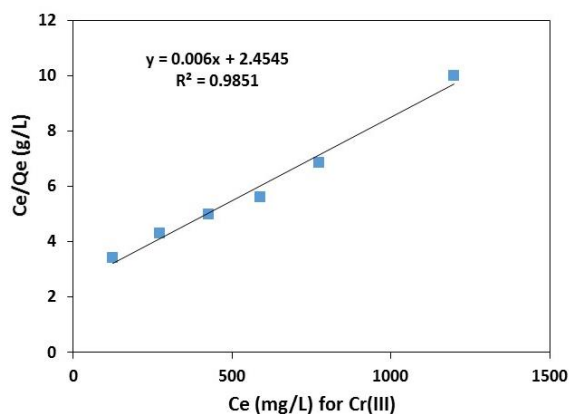

Fig 7. Chromium(IIi) adsorption Isotherm (Langmuir) plot
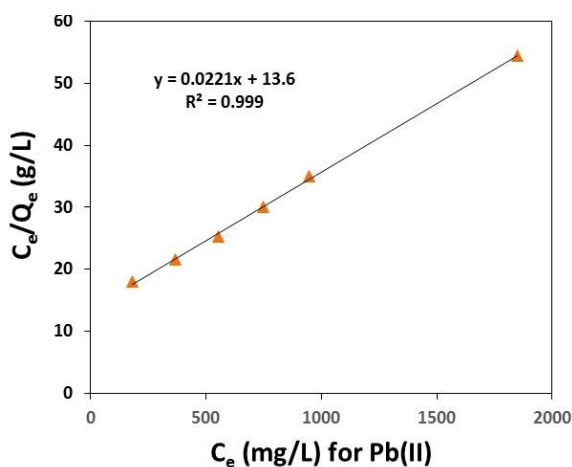
Fig 8. Lead(II) adsorption Isotherm (Langmuir) plot

3.2.3. Change of adsorption capability with contact time

The change of adsorption of Pb (II) and Cr(III) by the adsorbent with change of contact time were studied (Fig 9). 1000 ppm Cr(III) solution with pH 5 and 1000 ppm Pb(II) with pH 6.2 were used in this study. From Fig 4 it can be understood that at the beginning the adsorption rate of Pb(II) and Cr(III) is very fast, then gradually it slows down to reach the equilibrium. After 48 hours the equilibrium adsorption of 113.27 mg g^{-1} and 27 mg g^{-1} was achieved for Cr(II) and Pb(II) metal ions respectively.
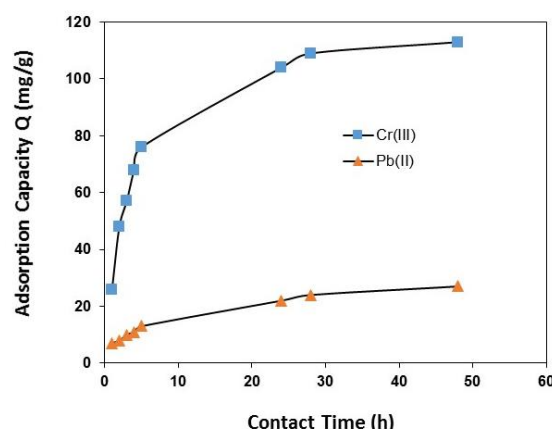
Fig. 9. Capacity of adsorption of against standing time

Cr(III) and Pb(II) adsorption were analyzed using pseudo 1st and pseudo 2nd order kinetic model. The pseudo 1st and pseudo 2nd order models [38-39] are described by the following equations

$$logQ_e - Q_t = logQ_e - \frac{k_1}{2.303}t \qquad (5)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$
(6)

Here,

Q_t= Adsorption capacity at any time (mg g^{-1})

Q_e= Adsorption capacity at equilibrium (mg g^{-1})

k_1 = 1st order rate constant (1 h^{-1})

k_2 = 2nd order rate constant (g h^{-1} mg^{-1})

From the graph of log (Q_e - Q_t) vs. t, pseudo 1st order rate constant have been determined (Fig 10). The values of k_1, Q_e, R^2 (correlation coefficient) for both Pb(II) and Cr(III) were presented in Table 1. Results show that the experimental Q_e value and Q_e value measured from the 1st order kinetic model are different from each other. Again from the graph of t/Q_t against t, pseudo 2nd order rate constants have been determined (Fig 11). The values of k_2, Q_e, R^2 are presented in Table 1. Results show that the experimental Q_e value and the Q_e value measured from the 2nd order kinetic model matches with each other. Therefore, the pseudo 2nd order kinetic model is the best model to interpret Pb(II) and Cr(III) adsorption. As the adsorption follows pseudo 2nd order model the adsorption process might have controlled by the intra-particle diffusion [40].

Moreover it suggests that chelating interaction plays the lead role in the metal adsorption [41].
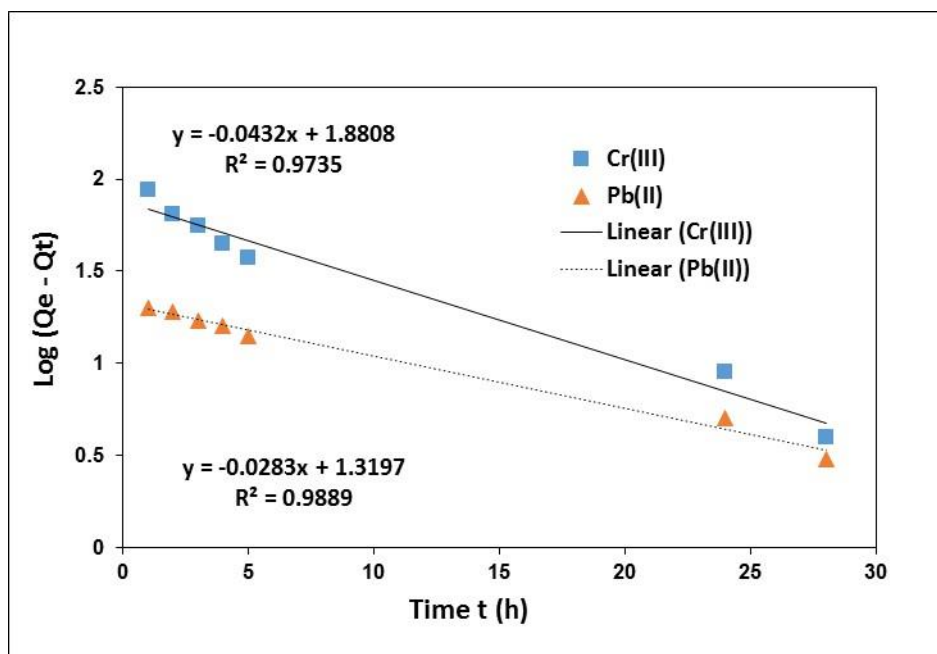

Fig. 10. Pseudo 1st order graph for Lead(II) and Chromium(III) adsorption
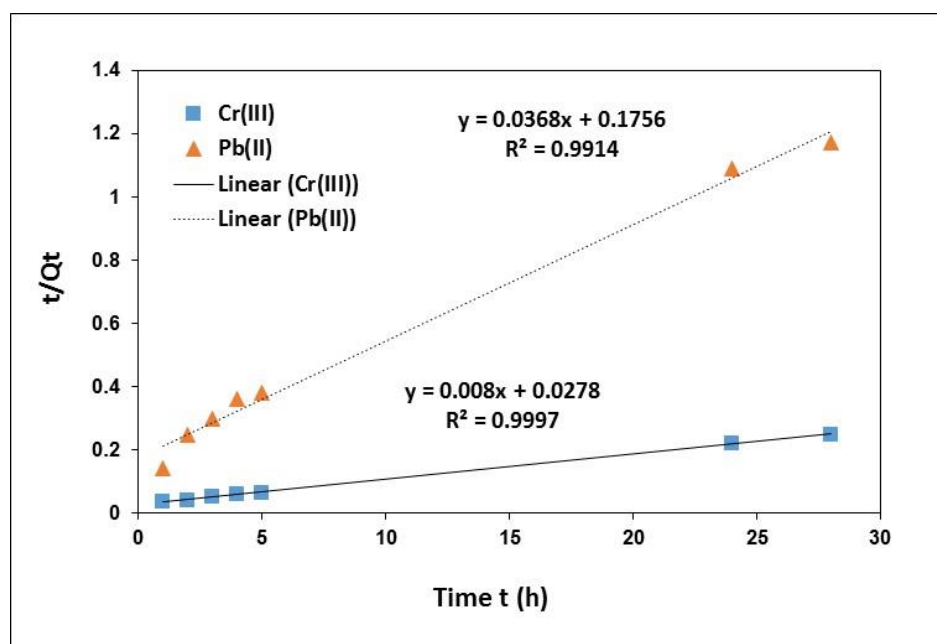
Fig. 11. Pseudo 2nd order graph for Lead(II) and Chromium(III) adsorption

The adsorbent we fabricated exhibited superior metal ion adsorption capacity than other existing adsorbents. Table 2 demonstrates a comparison between present adsorbent with others.

3.2.4.   *Reuse and desorption*

When the adsorption process revealed successful result, the desorption of Pb(II) and Cr(III) was attempted using 2M HCl and 2M NaOH solution respectively. It took 24 hours to reach desorption equilibrium. The percentage of desorption reached 99 for Pb(II) but 70 % for Cr(III). The Pb(II) and Cr(III) adsorption were tried up to five successive cycles but the successive use of the adsorbent indicated that the sorption capacity not changed noticeably. In addition up to five successive cycles the adsorbent remains usable although there is some degradation of the polymer. The results suggest that the adsorbent can be renewed and used persistently preserving identical efficiency.

Table 1. Determination of rate constants for metal ions adsorption by the grafted adsorbent

Ions of Metal	Qe (experimental) (mg g-1)	Pseudo (1st-order)			Pseudo (2nd-order)		
		Qe (theor.) (mg g-1)	k1 (h-1)	R²	Qe (theor.) (mg g-1)	k₂(h g-1 mg-1)	R²
Chromium(III)	113	76	0.09	0.97	125.62	0.0023	0.99
Lead(II)	27	21	0.07	0.99	27.19	0.0078	0.99

Table 2. Lead(II) and Chromium (III) uptake capacity of adsorbent compared with other adsorbents

Adsorbent	Uptake Capability of Pb(II) (mg g-1)	Uptake Capability of Cr(III) (mg g-1)
AAc-SSS grafted PE (current study)	45	166
Rice husk [42]	11.62	-
Silica Ceramic[43]	2.7	-
Activated carbon from Phoenix dactylifera. L [44]	9.91	-
Activated carbon from Eichhornia[45]	16.61	-
Lignin [46]	-	17.97
Coal [47]	-	2.5-2.6
Chitosan flakes [48]	-	138
Passion-fruit shell biomass [49]	-	27.93

3.3. Adsorption of Cr from real wastewater

Two types of waste water were collected from savar tannery industrial estate: (1) Waste water before treatment (raw waste water) and (2) Waste water after treatment by conventional (precipitation) method. The waste waters were digested and then used for adsorption of Cr by the prepared adsorbent. Initial Cr concentration of waste water before treatment (raw waste water) was 1200 mg L^{-1} and using this water Cr adsorption capacity of the adsorbent was found to be 65 mg g^{-1} at pH 2.5. Initial Cr concentration of waste water after treatment by conventional (precipitation) method was 4 mg L^{-1} and using this water Cr adsorption capacity of the adsorbent was found to be 0.4 mg g^{-1}. The success of present work will encourage us to conduct a study on a real waste water that may be more practical than synthetic one.

4. CONCLUSION

In present study AAc-SSS grafted PE adsorbent were fabricated effectively by the pre-irradiation technique. The adsorbent was investigated by FTIR, TGA and SEM. The prepared adsorbent was investigated to adsorb Pb(II) and Cr(III) ions from aqueous solution. Metal ion adsorption took 48 hours to attain the equilibrium value. pH 6.2 and 5 was observed best for Pb (II) and Cr(III) adsorption respectively. The prospect of the adsorbent for Cr(III) and Pb(II)

adsorption was presented by the maximum adsorption capacity of 113 and 27 (mg g^{-1}) respectively. Investigation of kinetic data depicted better correlation with the pseudo 2nd order kinetics. Again inspection of adsorption isotherm revealed fitting with Langmuir isotherm model. Desorption of metal ions and recycling of the adsorbent were also conducted with success. Furthermore the adsorbent showed promising result in Cr(III) adsorption from real waste water.

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