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Fabrication of a Novel and Efficient Radiation Grafted Functionalized Polymer Adsorbent and Investigation of its Applicability in the Adsorptive Removal of Cr (VI) Ion from Aqueous Solution

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Abstract

The grafting of glycidyl methacrylate (GMA) onto non-woven polyethylene (PE) fabric was accomplished using a radiation-initiated grafting technique. The grafted textiles were allowed to react using triethylamine to create functioning amine groups. Upon bond formation yield, the impact of grafting intensity has been examined. Utilizing the appropriate technologies, such as FTIR, TGA, and SEM, the adsorbents were rigorously examined. There was evidence of GMA grafting and diamines according to FTIR, TGA, and Tem analyses. For the purpose of adsorbing clearance of Cr (VI) ions from aqueous solution, amino cluster GMA-g-non-woven PE films was drenched in HCl to promote anionic metal adsorption. Adsorption capacity was investigated through varying the adsorption parameters. Contact time changed from 1 to 26 h, pH changed from 1.2 to 6, temperature changed from 30 to 75ºC and initial metal ion concentration changed from 200 to 1000 mg/L. The optimal circumstance that can lead highest adsorption of Cr (VI) by the adsorbent was established to be contact time 24 hours and initial metal concentration 600 mg/L, pH 1.2 and temperature 75ºC. Langmuir and Freundlich isotherm model were used for the analysis of Cr (VI) adsorption process by the adsorbent to understand and explain the adsorption mechanism. The equilibrium experimental data of Cr (VI) adsorption exhibited better matching with Langmuir isotherm model proposing the formation of monolayer saturation on the adsorbent surface. The highest adsorption capacity derived from Langmuir isotherm model was 50.76 mg/g. The adsorption kinetics was inspected by means of pseudo-first order and pseudo-second-order models with the aid of a pseudo-second-order equation, the adsorption equilibrium of Cr (VI) ion could've been effectively constructed. The satisfactory outcome of investigation of desorption of Cr (VI) and reuse of the adsorbent film proposed the prospect of recycling of the polymer adsorbent in case of practical application.

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Keywords: Polyethylene, Glycidyl methacrylate, Radiation grafting, Chromium adsorption, Adsorption isotherm, Adsorption kinetics.

INTRODUCTION

Nowadays, heavy metals become a global anxiety as it has possessed a great threat to all forms of living life. The improper disposal of toxic heavy metal containing waste effluents from industries like tannery, pharmaceuticals, steel plants, battery industries, thermal power plant causes severe environmental pollution. Heavy metals can easily endure in air, water, soil and can be stored in plant and animal tissue through food chain. Heavy metals can create serious health issues to mankind like nerve disease, skin disease, birth defects, cancer and damages of kidney, lungs, brain on exposure to high threshold concentration [1–2]. One of the major contributor of heavy metal pollution is tannery industry. Tannery waste water comprises heavy metals as for example chromium (Cr), cadmium (Cd), cobalt (Co), lead (Pb), nickel (Ni), selenium (Se) and arsenic (As). Particularly, in tanning process chrome tanning agents are used, which actually contributed to the chromium pollution. Hexavalent chromium ion is more soluble and highly toxic than trivalent chromium ion [3–6]. There are some traditional methods for the removal of heavy metal ions from industrial waste water effluents such as precipitation, ion exchange, neutralization, membrane filtration, flotation and electrolytic method [7–9]. But these mentioned methods are not always eco-friendly and cost effective. Even these methods can be linked with difficulties like low removal rate and inadequacy of regeneration and reuse. So the researchers were always keen to find out an alternative way and they focused on adsorption technology. The researchers studied cost effective adsorbents like sawdust [10], sporopollenin [11], chitosan [12], peat [13], cellulose [14], clay material and they observed better efficiency on the removal of heavy metal ions in contrast to the conventional methods. One of the new advancement in the field of heavy metal removal from waste water is the use of functionalized grafted polymer fiber as adsorbent [15–23]. The mechanical property of the polymer fiber is maintained during grafting procedure, which resulted in the comparatively larger external surface area and higher adsorption kinetics [24]. There are diverse approaches for initiating graft co-polymerization as for example exposing ionizing radiation/ultraviolet light/plasma treatment or use of chemical initiator or oxidation of polymers. Among them, the radiation induced grafting technique is much more effective due to its high penetration into the polymer matrix and rapid formation of homogeneous radical sites for initiating grafting [25].

In the current study, non-woven polyethylene was carefully selected as the foundation polymer to create an effective Cr (VI) adsorbent. Many researchers have examined the prospect of adsorption of toxic heavy metal ions by various functional monomer grafted polyethylene (PE) [26–30]. Present study emphases on the preparation of an efficient novel adsorbent from non-woven PE fabric through pre-irradiation technique utilizing monomer glycidyl methacrylate (GMA) followed by amination. The prepared amine functionalized GMA-g-non woven PE films were examined extensively for the adsorptive removal of Cr (VI) ions from aqueous solution. To the best of our knowledge no previous study reported the radiation induced grafting of GMA on non-woven PE fabric and no previous study reported the adsorption of hexavalent chromium (VI) by GMA-g-PE fabrics. FTIR, TGA, and SEM were used in the current investigation to examine the produced adsorbent. Kinetics and isotherm of Cr (VI) adsorption were studied. The adsorbent was regenerated and reused.

EXPERIMENTAL

Materials and Reagents

As base polymer, non-woven polyethylene (PE) fabric provided by Kurashiki MFG Co. was utilized in this work. Glycidyl methacrylate (GMA) and Tween 20 (Polyoxymethylene sorbitan monolaurate) were bought from Sigma Aldrich Co. (USA). Triethylamine obtained from Fluka Chemika was used for introducing amine group to the epoxy ring of GMA (glycidyl methacrylate). Merck, Germany was the supplier of Sodium Hydroxide and Hydrochloric acid. Potassium dichromate (Sigma Aldrich Company) was used for the adsorption study.

Instrument and Apparatus

The free radical site creation on non-woven polyethylene film was induced by the Co-60 gamma-irradiator at Institute of Food and Radiation Biology (IFRB) of Atomic Energy Research

Establishment (AERE), Savar, Dhaka. The non-woven PE films, GMA-g-PE films, Amine functionalized GMA-g-PE films, chromium adsorbed fabrics were successfully analyzed by applying advanced technique such as FTIR (ATR) spectrophotometer (IR Prestige 21 supplied by Shimadzu Corporation, Kyoto, Japan) to understand the bonding between the different groups of polymer and monomer. The wavelength range used was 700–4000 cm^{-1}. The surface morphology of the fabrics were examined by using a scanning electron microscope (SEM), Model JSM-6490LA, JEOL. The accelerating voltage used was 20 kV. For investigation of thermal properties a Perkin-Elmer TGA 7-thermal analyzer were used.

Preparation of Adsorbent

Non-woven PE films were weighted before irradiation with the Co-60 gamma radiation source. 30 kGy radiation dose were exposed at an ambient temperature. The irradiated PE films were put in dry-ice condition for storage up to subsequent usage. The monomer solution's composition was 5 percent glycidyl methacrylate and 0.5 percent Tween 20 in 94.5 percent distilled water. In this instance, Tween 20 was used to create an emulsion. For a hours, a magnetic stirrer was being used to combine the emulsion solution. To remove oxygen in the water, argon gas was pumped through the produced emulsion solution in a gas passing jar for roughly an hour. After being exposed to radiation, the non-woven PE textiles were transported to a test tube, and then 70–75 ml of the de-aerated emulsion solution were poured into the tube. To reduce the possibility of introducing any oxygen from the air, the tube was filled with polymeric solution then it was securely shut using a cover. After that, it took the grafting reactions between the monomer and the PE fabric required 4 hours of heating in a water bath at 80°C. The grafted non-woven PE fabric that was eventually obtained was thoroughly cleaned distilled water to flush out any unreacted different ways depending on or monomers. After washing, the fabrics were dried in an oven and weighted. The equation written as follows was used to calculate the degree of grafting:

$$W_g = \frac{W_a - W_b}{W_b} \times 100 \quad (1)$$

Where,

W_a = Weight of the Non-woven PE film after grafting (g)

W_b = Weight of the Non-woven PE film before grafting (g)

W_g = Degree of grafting of the Non-woven PE film (%)

To introduce the amine group into the GMA grafted non-woven polyethylene fabric, a solution was prepared by the addition of 50% triethylamine and 50% water. The grafted films were immersed into the beaker containing the solution. Then the solution along with the grafted films immersed in it, was heated at 80ºC for 6 hours with constant stirring. Thus the amination reaction was carried out [31]. Amination occurs with the ring opening reaction of epoxy group of GMA. Then the aminated GMA-g- non woven PE films were cleaned well through washing with distilled water. After washing, they were dried in an oven and the amination yield for each of the films was calculated. In order to calculate the value amination yield the subsequent equation was applied:

$$\text{Amination yield } (\%) = \frac{M_a - M_g}{101.19} \div \frac{M_g - M_0}{142.15} \quad (2)$$

Where,

M_o = Measured weight of the Non-woven PE film (g)

M_g = Measured weight of the GMA grafted Non-woven PE fabric (g)

M_a = Measured weight of the aminated fabric (g)

Here, 101.19 and 142.15 denotes the molecular weight value of triethylamine and glycidylmethacrylate respectively. Preparation scheme of the adsorbent is shown in Figure 1.

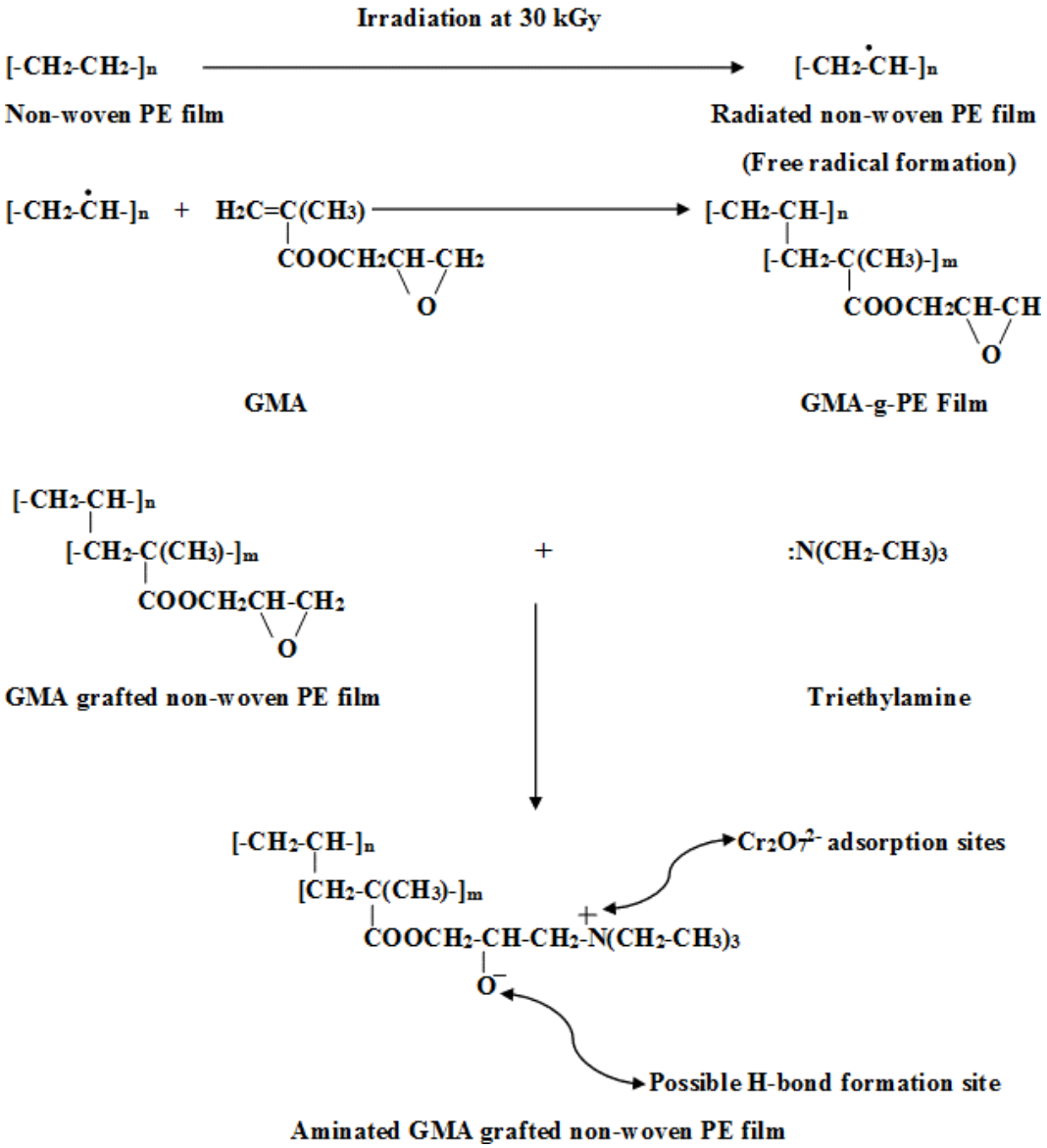

Figure 1. Preparation scheme of the adsorbent.

Determination of Chromium Adsorption

The potassium dichromate was used as source of hexavalent chromium ions. Next, the ability of the absorbents to adoptively remove chromium (VI) ions from simulated aqueous solutions was investigated. To enhance the adsorption capacity of the aminated GMA-g-non woven PE film, the films were immersed in 1 M solution of HCl acid for several minutes. The adsorption process was investigated under different environments through changing first the contact time, then pH, then initial metal ion concentration and lastly temperature. The Cr (VI) ion concentrations of the solution before the immersion of the adsorbent and after completion of the adsorption process were analyzed by the help of UV-Visible Spectrophotometer. Adsorption capacity of the adsorbent (Aminated GMA-g-non woven PE film) was determined by the following formula:

$$\text{Adsorption capacity} = \frac{(C_1 - C_2)V}{W} \text{ mg/g} \quad (3)$$

Here,

C_1 = Initial concentration of the Cr (VI) ion solution (ppm)

C_2 = Concentration of Cr (VI) ion solution after adsorption (ppm)

V = Volume used for adsorption (L)

W = Weight of the adsorbent (g)

Desorption of Chromium Ions

The regeneration of the adsorbent fabrics was carried out by the desorption of Cr (VI) ions through treatment with 1 M aqueous solution of NaOH. Adsorbed film was placed in a beaker containing NaOH solution for 24 hours. The amount of the Cr (VI) ions desorbed was analyzed by the help of UV-Visible Spectrophotometer and the percentage of desorption was calculated by the following equation:

$$\text{Desorption percentage} = \frac{\text{Ions Desorbed (mg)}}{\text{Ions Adsorbed (mg)}} \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Gamma radiation initiated grafting of monomer glycidyl methacrylate (GMA) were experimented on base polymer non-woven PE fabrics. To the best of our knowledge there is no previous study reporting the radiation initiated grafting of the monomer GMA onto non woven PE fabric. GMA carries a reactive epoxy group which was functionalized by triethylamine. Amination yield differs at different grafting percentages. Figure 2 shows that initially amination yield increases with the increase of grafting percentages and after a certain percentage of grafting, amination yield tends to decrease. This is due to a fact that the availability of epoxy group is suppressed when the grafting is densely packed. A maximum amination yield was obtained at 200 percentage of grafting.

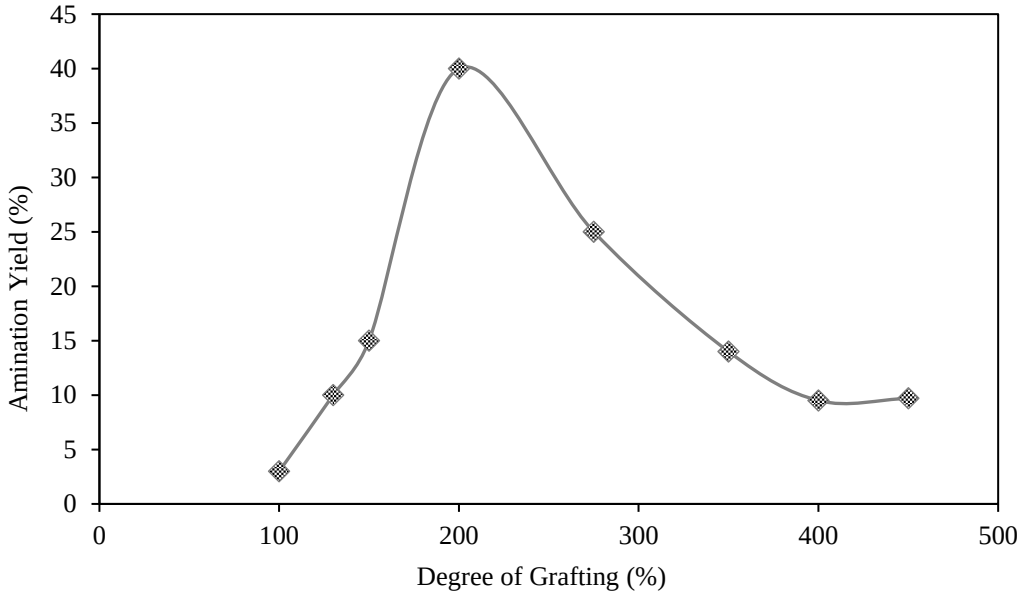

Figure 2. Effect of degree of grafting on amination yield.

In this study the application of amine functionalized GMA-g-PE fabrics for the adsorptive removal of hexavalent chromium (VI) ions from aqueous solution were extensively investigated. To the best of our knowledge there is no previous study describing the adsorptive removal of hexavalent chromium (VI) using GMA-g-PE fabrics as reusable adsorbent. Investigation of the application probability of the newly prepared adsorbent (amine functionalized GMA-g-PE fabrics) is the main goal of this research. Aminated GMA-g-PE films were treated with 1 M HCl to enhance the adsorption capacity of the films. Figure 3 demonstrates the outcome revealed by the treatment of aminated GMA-g-non woven PE film with HCl. It is clear from the figure that HCl treated aminated GMA-g-non woven PE film has better adsorption capacity than the HCl non-treated aminated GMA-g-non woven PE film.

Aminated GMA-g-PE film contains protonated amino group and a possible H-bond formation site. Cr (VI) ions exist as $Cr_2O_7^{2-}$ ion in aqueous solution. Protonated amino group pulls the $Cr_2O_7^{2-}$ ions from the aqueous solution and thus the adsorption of Cr (VI) ions is occurred. If the aminated GMA-g-non woven PE film was treated with HCl solution then the positive H^+ ion would bind with the H-bond formation sites and consequently the positivity of protonated amino group will increase. As the protonated amino group is responsible for the adsorption of Cr (VI) ion from the solution, the greater positivity of protonated amino group will enhance the adsorption amount. That is why, the HCl treated aminated GMA-g-non woven PE film shows greater adsorption capacity than the HCl non-treated aminated GMA-g-non woven PE film.

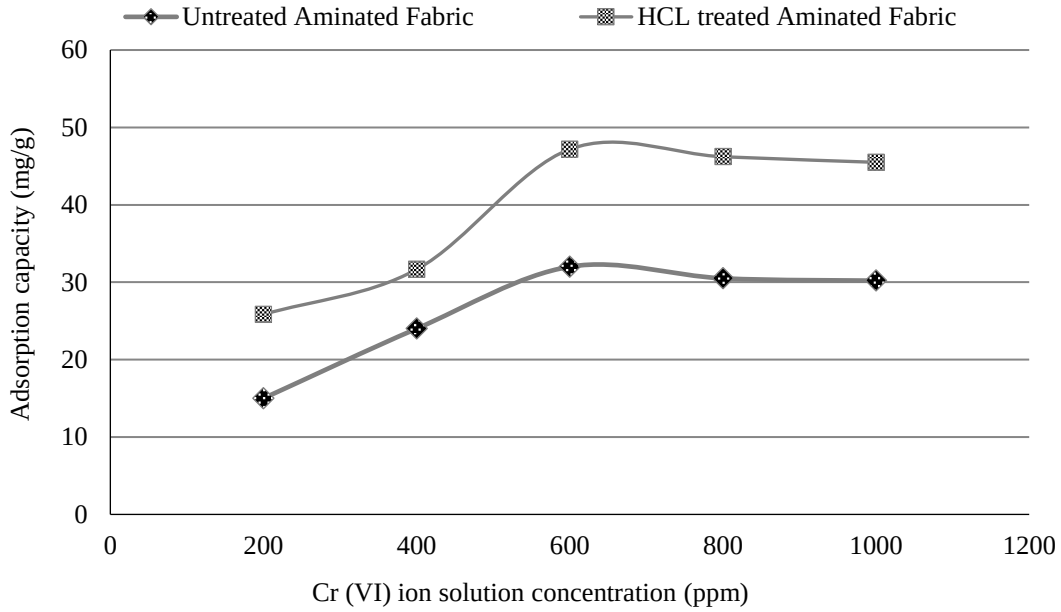

Figure 3. Effect of HCl treatment on adsorption capacity (pH 4.5, contact time 24 hours and at room temperature).

Figure 4 shows the IR spectra of PE, GMA-g-PE, Aminated GMA-g-PE and Cr (VI) ion adsorbed film. The specific properties of the IR spectrum of PE fabric are its C–H stretching vibrations (as in Figure 4, peaks at 2910 and 2845 cm^{-1} denotes C–H asymmetric and symmetric stretching vibrations respectively) and C–H deformation vibrations (as in Figure 4, C–H bending, wagging and rocking deformation of CH_2 group are detected at 1479, 1369 and 721 cm^{-1} respectively).

The FTIR spectrum of GMA grafted PE provides evidences for the grafting of GMA. The peak at 1716 cm^{-1} corresponds to the stretching vibration absorption peak of C=O in GMA, the peaks at 1273 cm^{-1} and 1147 cm^{-1} correspond to the symmetric and asymmetric vibration of C-O in GMA and the characteristic absorption peaks of epoxy chain appear at 856 cm^{-1} and 912 cm^{-1}. The FTIR spectrum of functionalized PE fabric provides evidence for the amination of GMA grafted non-woven PE film. Because, the characteristic absorption peaks of epoxy chain at 912 cm^{-1} and 856 cm^{-1} are disappeared after the ring opening reaction between the epoxy group and triethylamine. The characteristic band in amines is due to its N-H bond stretching and here it is appeared at 3302 cm^{-1}. In FTIR spectrum of Cr (VI) adsorbed fabric, appearance of peak around 890 cm^{-1} is indicative of Cr-O stretch.

Non-woven PE film, GMA-g-PE fabric, amine functionalized GMA-g-PE fabric and Cr (VI) ion adsorbed fabric were characterized by SEM to compare the physical appearance of each of them. The SEM images of the ungrafted, grafted, functionalized and Cr (VI) loaded PE fabrics are shown in Figure 5.

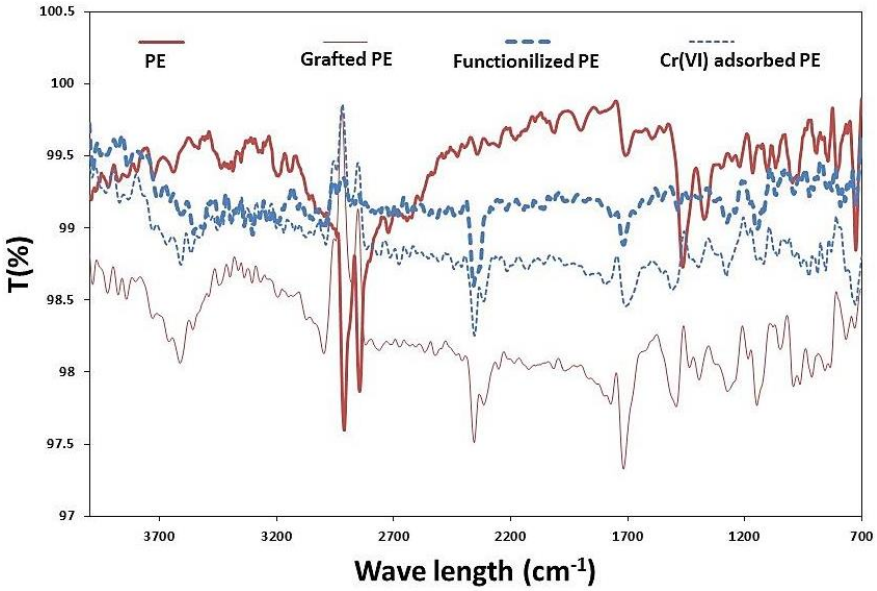

Figure 4. IR spectra of PE, GMA-g-PE, Aminated GMA-g-PE and Cr (VI) adsorbed film.

Comparison of Figure 5(b) with 5(a) clearly depicts the appearance of new grafted chains crosslinked and closely packed on the surface of the GMA grafted PE fabric that offer additional physical evidences for the grafting. Figure 5(c) shows some changes in physical appearance as the amine groups are introduced in between the grafted chains due to the epoxy ring opening reaction between GMA and triethylamine and it provides an evidence for the formation of amine functionalized GMA grafted non-woven PE film. The Figure 5(d) shows that the grafted chains are fully covered by the Cr (VI) ions adsorbed.

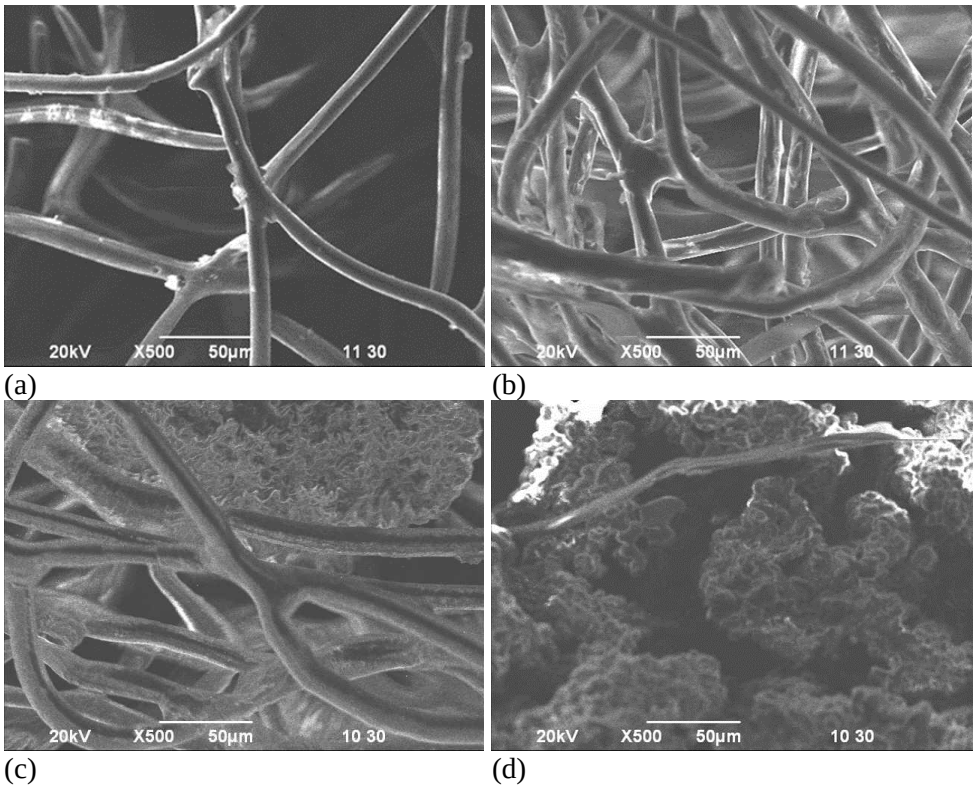

Figure 5. SEM image of (a) non-woven PE fabric, (b) GMA grafted non-woven PE fabric, (c) Functionalized GMA grafted non-woven PE, (d) Cr (VI) adsorbed PE fabric.

The results of thermo-gravimetric analysis (TGA) of the ungrafted, grafted, functionalized and Cr (VI) loaded non-woven PE fabrics are presented in Figure 6. Non-woven PE film retains thermal stability up to 200°C, increase of temperature above 200°C initiates decomposition. It demonstrates three degradation stages, i.e., 200°C–255°C, 255°C–499°C and above 499°C. GMA grafted non-woven PE film preserves thermal stability up to 180ºC and increase of temperature above above 180ºC initiates decomposition. It shows a four decomposition state, i.e. 180–184ºC, 184–277ºC, 277–358ºC and above 358ºC. There are five weight loss steps in the TGA curve for Aminated GMA grafted non-woven PE film. The weight loss stages are at 18–79ºC, 79–223ºC, 223–304ºC, 304–375ºC and 375–499ºC. There are five degradation stages in the TGA thermo-gram of Cr (VI) loaded fabric. The weight loss stages are at 25–89ºC, 89–241ºC, 241–344ºC, 344–439ºC and 439–499ºC. It can be concluded that the thermal stability of the fabric decreases after grafting and amination but still the thermal stability is satisfactory as an adsorbent.

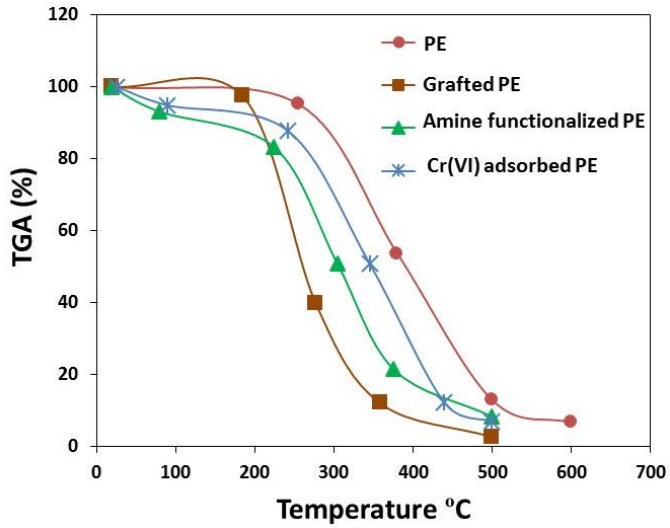

Figure 6. TGA thermo-gram of PE, GMA-g-PE, Aminated GMA-g-PE and Cr (VI) adsorbed film.

It is quite evident that the contact time of adsorbent has an impact on the adsorption amount. Figure 7 shows the relationship between the contact time of adsorbent and the adsorption amount at solution pH and at room temperature. Figure 7 depicts that the adsorption amount of Cr (VI) experiences upward trend with the increase of contact time. Here the adsorption equilibrium reaches after 24 hours and the adsorption capacity at that point was recorded 49.13 mg/g. The result obtained from the experiments were used to study the kinetics of Cr (VI) ion adsorption. The rate of kinetics of Aminated GMA-g-non woven PE film has been analyzed using pseudo-first-order model and pseudo-second-order model.

The following is the pseudo-first-order rate formula Lagergren proposed in 1898 [32]:

$$dQ\ t = dt = k\ 1\ (Q\ e\text{-}Q\ t) \quad (5)$$

Here, Qe signifies the level of desorption at equilibrium (mg/g), Qt the The first order rate constant is k1, and the quantity of adsorption at any given time before equilibrium is reached is (mg/g). Log (Q e-Q t) = log Q e-k 1/2.303 t is the result of converting the above equation through integration while taking into account the limiting conditions

$$t = 0 \text{ to } t = t \text{ and } Q = 0 \text{ to } Q = Q. \quad (6)$$

This is a representation of the frequently employed pseudo-first-order kinetic equation. Figure 8 depicts the curve of log (Qe-Qt) against t, from which pseudo-first-order rate constants can be derived. First-order-kinetics parameters for the adsorption of Cr (VI) ion obtained from Figure 8 are presented in Table 1. The value of correlation coefficient obtained for this equation is 0.95.

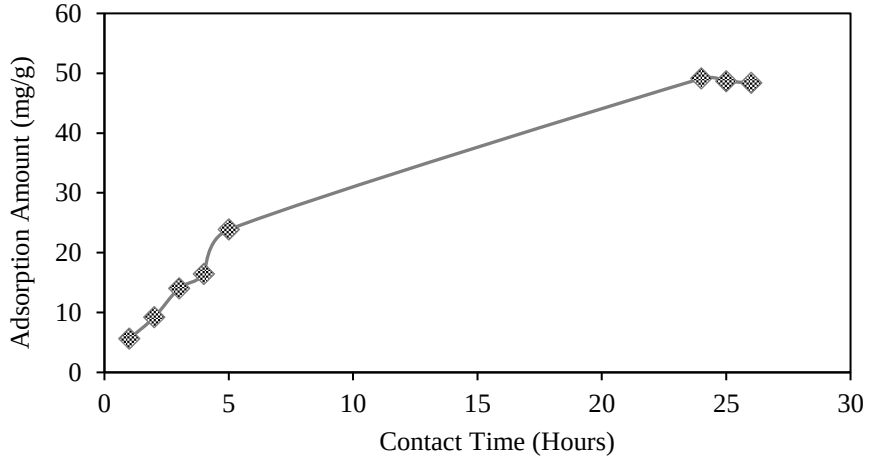

Figure 7. Effect of contact time on adsorption amount (initial metal concentration 600 ppm, pH 4.5 and at room temperature).

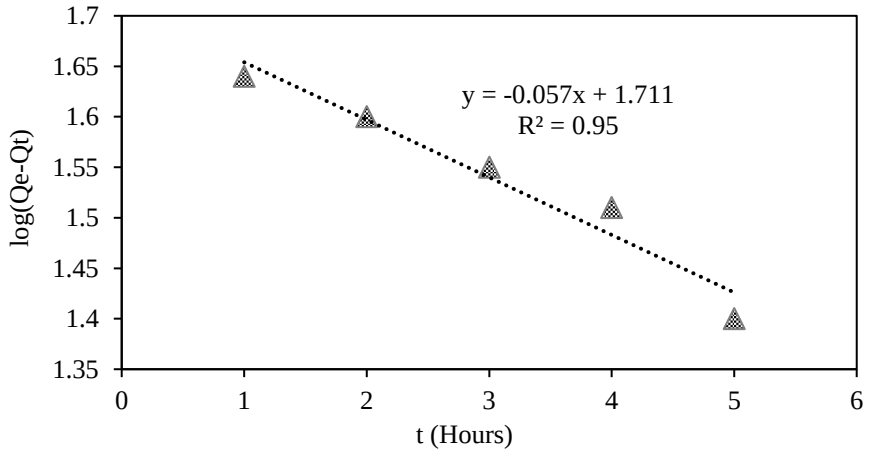

Figure 8. Pseudo-first-order curve for the adsorption of Cr (VI) ions at room temperature.

Table 1. The pseudo-first-order and pseudo-second-order kinetic parameters for Cr (VI) ion adsorption.

	Pseudo-first-order rate constant			**Pseudo-second-order rate constant**		
Q_e (experimental) mg/g	Q_e (theoretical) mg/g	k_1 (h^{-1})	R^2	Q_e (theoretical) mg/g	k_2 $gh^{-1}mg^{-1}$	R^2
49.13	51.40	0.131	0.9500	72.99	0.001095	0.9894

Ho and Mckay revised the Lagergen equation to get the differential equation as follows [33]:

$$\frac{dQ_t}{dt} = k_1(Q_e - Q)^2 \quad (7)$$

Conversion of the mentioned equation through integration considering the limiting conditions t = 0 to t = t and Q = 0 to Q = Q gives:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (8)$$

This represents is the pseudo-second-order kinetic equation most widely used. Here also Q_t and Q_e are the adsorption quantity at any time (mg/g) and equilibrium respectively. k_2 (gm/h/mg) stands for the rate constant of second-order adsorption. Figure 9 represents the plot of t/Q_t vs. t. It is possible to get value of k_2 and Q_e from the slope and intercept of the curve. Pseudo-second-order kinetics parameters that were determined from Figure 9 are presented in Table 1. The value of correlation coefficient (R^2) obtained for this model is 0.9894.

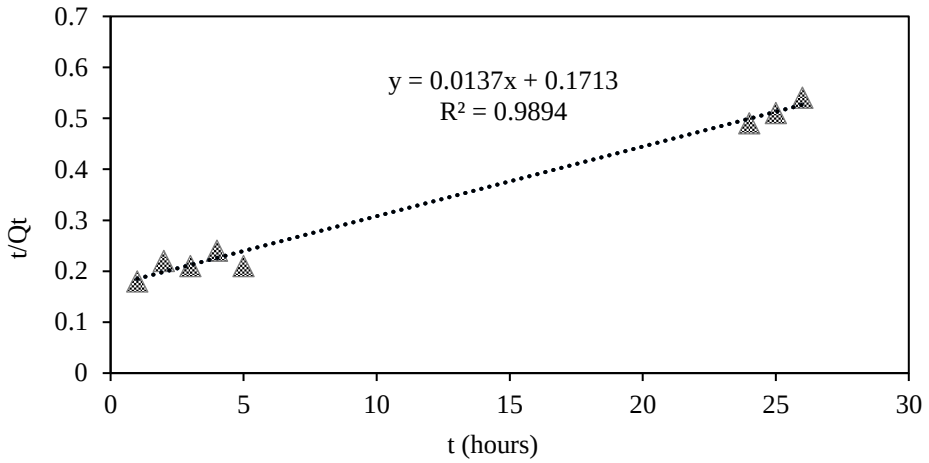

Figure 9. Pseudo-second-order kinetic plots for the adsorption of Cr (VI) ions at room temperature.

From the above experimental data, it can be observed that the correlation coefficient value (R^2) of pseudo-second-order model is greater than pseudo-first-order model. So, it is understandable that the pseudo-second-order equation is appropriate for interpretation of Cr (VI) adsorption kinetics by the aminated GMA-g-non woven PE fabric. It proposes that the intra-particle diffusion course may be the rate determining stage of the Cr (VI) adsorption. It also suggests that the ion exchange sites play a key role for adsorption and the possibility of chemical adsorption phenomenon of the adsorbent.

The pH of the metal solution directly controls the adsorption of metal ions from the solution. The experimental outcomes of the consequences of the changing pH on the quantity of adsorption of the Cr (VI) ions are shown in Figure 10. It was found that the adsorption amount increased significantly with the decrease of pH from 4.5 to 1.2 and the adsorption decreases with the increase of pH from 4.5 to 6.0. The maximum adsorption capacity was recorded 49.74 mg/g at pH 1.2 after 6 hours experimental time. The lower pH contributes high amount of H^+ ion to the solution. Functionalization of GMA-g-non woven PE film with triethylamine leaves H-bond formation sites and protonated amino group. Protonated amino group is the reason behind the affinity of the adsorbent to adsorp Cr (VI) ions from the solution. At lower pH, the H^+ ion binds with the H-bond formation sites and consequently the positivity of the protonated amino group increases. As the protonated amino group is responsible for Cr (VI) ion adsorption, the greater positivity of protonated amino group will enhance the adsorption amount. That is why, the adsorption amount of Cr (VI) ion increases at lower pH value of the solution.

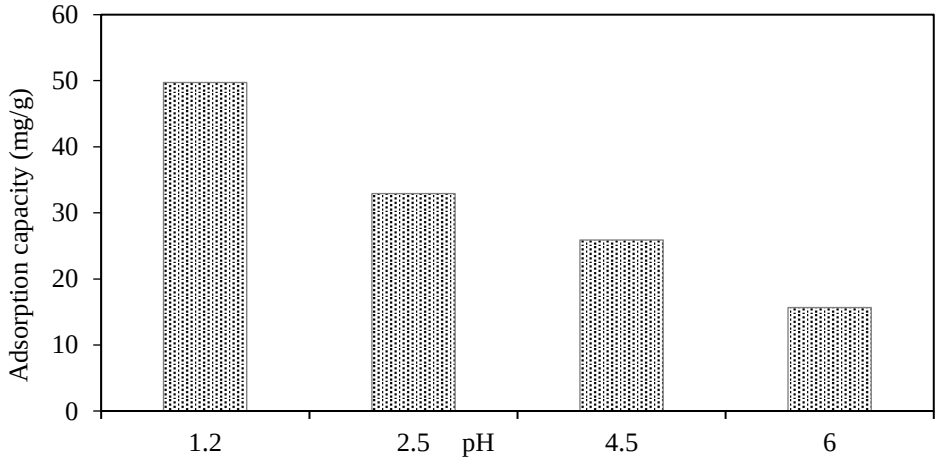

Figure 10. Effect of pH on adsorption amount (initial metal concentration 600 ppm, contact time 6 hours and at room temperature).

Figure 11 shows the relationship between the initial metal ion concentration and the adsorption amount at constant pH and room temperature. It is conclusive from the figure that the adsorption quantity of Cr (VI) ions show increasing trend with rising initial metal ion concentration and touched a plateau value at certain greater concentration. This is due to the fact that the ion exchange positions of the adsorbent turned into occupied state after the increase of metal ion concentration beyond certain value. A maximum adsorption capacity (47.34 mg/g) was obtained at 600 ppm concentration of Cr (VI) ion solution.

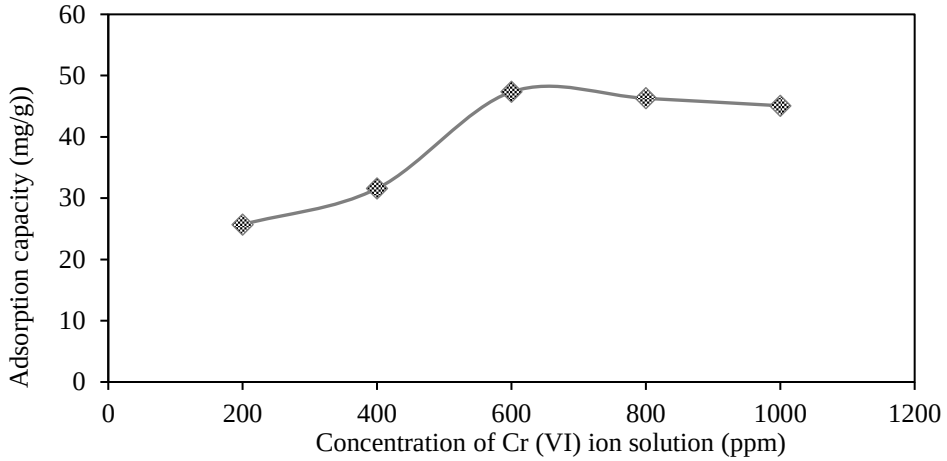

Figure 11. Effect of initial metal ion concentration on adsorption (pH 4.5, contact time 24 hours and at room temperature)**.**

The interaction of Chromium (VI) ion with aminated GMA-g-PE adsorbent was investigated by adsorption isotherm. The data of the equilibrium studies for adsorption of Cr (VI) onto aminated GMA-g-PE film may follow the following Langmuir model [34]:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \quad (9)$$

Where, C_e is the equilibrium concentration (mg/l). Q_m represents the maximum adsorption capacity (mg/g), Q_e represents equilibrium adsorption quantity and b represents the Langmuir adsorption constant (L/mg). When the curve of C_e/Q_e aqainst C_e provide a straight line having a slope of $(1/Q_m)$ and an intercept of $(1/Q_m b)$ it is said that adsorption follows Langmuir model. The determined values of Q_m and b are reported in Table 2. In order to do additional analysis on the basis of separation factor R_L, the following equation is used

$$R_L = \frac{1}{1+b(C_0)} \quad (10)$$

Table 2. Langmuir isotherm model constant and correlation coefficients for the adsorption of Cr (VI) ions at room temperature.

Isotherm constants	Value for Cr (VI) ion
Q_m(mg/g)	50.761
b (L/mg)	0.016
R^2	0.9808
R_L	0.238-0.058

Where b stands for the Langmur adsorption constant (L/mg) and C_0 stands for the initial Cr (VI) concentration (mg/L). The value of R_L varies from 0 to 1 for satisfactory adsorption. The experimental isotherm data has been matched with Langmuir isotherm model which can be seen in Figure 12. The standard value of correlation coefficient (R^2 = 0.9808) directs a good compatibility with the model and establishes the formation of monolayer of Cr (VI) ions onto the surface of aminated GMA-g-PE film.

The dimensionless equilibrium parameter R_L ranges from 0.238 to 0.058 which lie between 0 and 1 ($0<R_L<1$). Matching of experimental data with Langmuir model proposes that a monolayer saturation adsorption of ions on the adsorbent is appropriate to describe the Cr (VI) adsorption on aminated GMA-g-non woven PE film. This also recommends that the adsorption was primarily chemical adsorption and the adsorption sites are similar to the metal ions.

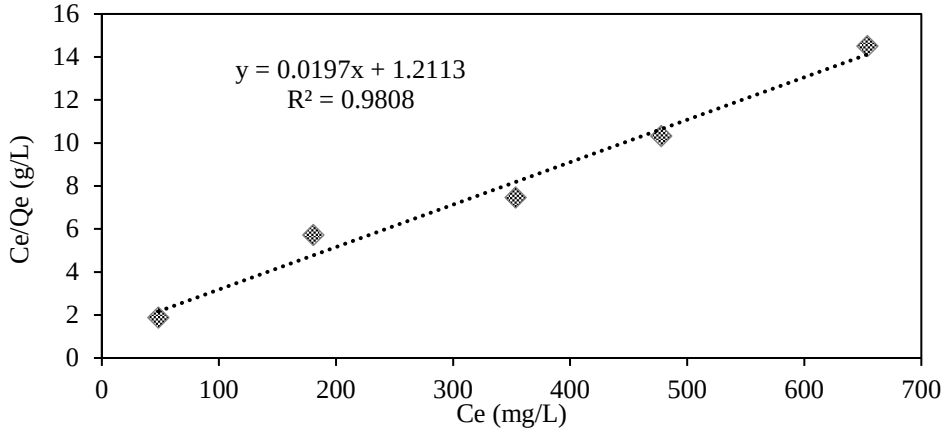

Figure 12. Langmuir isotherm plot for Cr (VI) adsorption at room temperature.

The Freundlich model can be useful for explaining multilayer sorption process. This model is expressed as [35]:

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e \quad (11)$$

Where C_e represents the equilibrium concentration of ions (mg/L), Q_e represents the equilibrium adsorption capacity (mg/g), K_F stands for the sorption constant and n denotes an empirical parameter. The plot of log Q_e vs. log C_e shown in Figure 13 was drawn from the experimental data. The K_F, n and correlation coefficient R^2 values are presented in Table 3. Thus a plot of log Q_e vs. log C_e should be a straight line with a slope 1/n and an intercept of log K_F. This model is designed for the multilayer adsorption of the ions on the surface of an adsorbent. In this instance, the adsorption process is said to be advantageous if the solution to the equation for n is greater than unity.In the present study the value of n = 4.011 is greater than 1, indicating that the adsorption process is favorable. In particular, the achieved regression value (R^2) revealed to be higher for Langmuir isotherm compared to Freundlich. So, this comparison suggests that the adsorption follows highly the Langmuir model. The highest adsorption capacity attained by the present adsorbent is related with the maximum adsorption quantity achievable by other adsorbents as shown in Table 4.

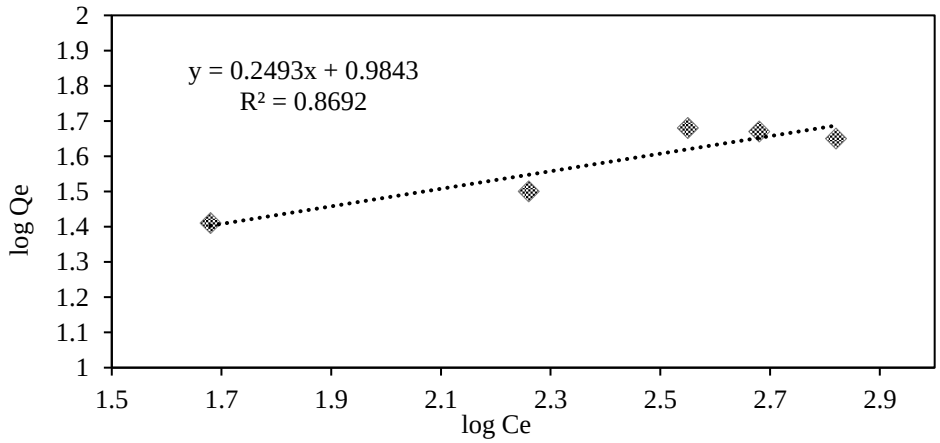

Figure 13. Freundlich isotherm plot for Cr (VI) adsorption at room temperature.

Table 3. Freundlich isotherm model constants and correlation coefficients for the adsorption of Cr (VI) ions at room temperature.

Isotherm constants	Value for Cr (VI) ion
K_F	9.644
n	4.011
R^2	0.8692

Table 4. The adsorption capacity of amine functionalized GMA-g-PE adsorbent compared with other adsorbents.

Adsorbent	Adsorption capacity (mg/g)
Amine functionalized GMA-g-PE film (present study)	49
Palm trunk charcoal [36]	24.7
Ethylenediamine-modified cross linked magnetic chitosan resin [37]	39.7
Modified red pine sawdust [38]	22.6
n-butylacrylate grafted chitosan [39]	17.14
Grafted bamboo charcoal [40]	17.93
Chitosan-Cl-poly (alginiacid) hydrogel [41]	26.49

It was revealed by the experimental results that the adsorption amount of Cr (VI) can be increased by the increase of temperature. At room temperature, the amount of adsorption was 25.77 mg/g and the maximum adsorption amount was recorded 43.08 mg/g at 75ºC temperature (contact time 6 hours).

An crucial requirement for cost reduction, effective industrial use, and environmental preservation is the adsorbent's capacity for regeneration. In the present study, the adsorbent was regenerated effectively. Desorption of Cr (VI) was done by treating the adsorbent with 1 M NaOH for 24 hour at room temperature. The adsorbent was reused three times with no significant loss of activity.

CONCLUSION

Amine functionalized adsorbent was prepared through radiation induced grafting of glycidyl methacrylate on polyethylene fabric followed by chemical modification and has been investigated for the adsorption of chromium (VI) ions from aqueous solution. The adsorbent was successfully characterized through FTIR, SEM and TGA technology. The study showed that the aminated GMA-g-PE adsorbent was efficient towards adsorption of Cr (VI) ions. Results of adsorption study revealed that the adsorption amount of Cr (VI) by the adsorbent follows upward trend until reached the adsorption equilibrium after 24 h. Pseudo-second-order kinetic model was applicable for the kinetics study of the adsorbent. At lower pH, the adsorption amount was higher than the adsorption amount at higher pH. The maximum adsorption amount was obtained at pH 1.2. The adsorption process agrees well with the Langmuir isotherm model and it also indicated that the adsorption of Cr (VI) by the prepared adsorbent might have proceeded through chemisorption process. Adsorption was favorable at higher temperature than room temperature and the maximum adsorption amount was recorded at 75°C. Desorption and reuse of the films were also successful. The results of present investigation indicate that the newly prepared adsorbent (amine functionalized GMA-g-PE fabrics) has good Cr (VI) adsorption capacity (50.76 mg/g) and it has good prospect for anionic heavy metal removal from industrial waste water.

Declarations

Competing Interests

The authors are pleased to announce that they have no competing interests

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Abbreviations: PE-Polyethylene, GMA-Glycidyl methacrylate.

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