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Preparation of Amidoximated Acrylonitrile-g-Waste Polypropylene Adsorbent by Radiation Grafting Method and Its Application on the Adsorption of Cr (VI) from Aqueous Medium

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Abstract

In this study, a new amidoximated adsorbent based on waste polypropylene (PP) fabric was prepared for the adsorption of aqueous Cr (VI) metal ions. Pre-irradiation technique was employed for grafting of acrylonitrile (AN) on PP fabric. The grafting reaction was carried out at 80°C in a water bath for 4 hours utilizing sulfuric acid (2% of AN) as additive and the percentage of grafting obtained was 150% using 60% AN concentration and 30 kGy radiation dose. The amidoximated adsorbent was produced by treating acrylonitrile (AN) grafted PP (AN-g-PP) with $\text{NH}_2\text{OH}\cdot\text{HCl}$ and characterized by FTIR, SEM, TGA and DMA. The removal of Cr (VI) was examined under several conditions such as contact time, pH, temperature, initial Cr (VI) concentration. The equilibrium adsorption data were fitted to both Langmuir and Freundlich isotherm models. The maximum adsorption capacity of the adsorbent was found to be 232.56 mg/g calculated from Langmuir equation. Kinetic studies have exhibited that the highest removal was achieved after 40 hours that was 126.82 mg/g at pH 1.5 and Cr (VI) concentration 120 ppm. The kinetic data follow the pseudo-first order model having a good agreement between the experimental and calculated adsorption capacity. The thermodynamic data showed that the sorption process was endothermic and spontaneous taking place by increasing the randomness of the system. Furthermore, study of desorption of Cr (VI) from the adsorbent surface and reuse of the adsorbent indicate that the adsorbent can be applied effectively for the efficient removal of Cr (VI) ions from aqueous solution.

Keywords: Adsorption, Pre-irradiation, Grafting, Isotherm, Adsorption capacity, Desorption.

Introduction

All over the world, environment pollution due to the discharge of hazardous metals into the water streams has become one of the most extreme problems because these pollutants are deleterious to ecosystem and human being [1]. Chromium is one of the poisonous elements existing two different oxidation states in the aquatic system; trivalent chromium [Cr (III)], and hexavalent chromium [Cr (VI)] which are considerably different in toxicity,

first form is the important trace element for the metabolism in mammals and less toxic while the second form is carcinogenic and significantly toxic due to its higher solubility and mobility in water [2,3]. The poisonous Cr (VI) is discharged into the environment from leather tanning, paint and pigments, electroplating, steel fabrication, cement, dyeing, fertilizer, photography, textile and canning industry [4]. It is not only carcinogenic but also genotoxic and hemotoxic [5]. The cause of the toxicological behavior of Cr (VI) is its oxidizing ability and formation of free radicals when it is reduced to Cr (III) taking place inside the cell [6]. It is therefore very essential to completely eliminate traces of Cr (VI) present in the various industrial effluents before releasing into the aquatic environment.

For this purpose, the physiochemical methods have been utilized. They are solvent extraction, ion- exchange, chemical precipitation, sulphide precipitation, cementation, electro-dialysis, evaporation, electrochemical reduction, reverse osmosis and adsorption [7]. However, these methods have some demerits and the most recommended technique for the removal of precarious metals is the adsorption method due to its high efficiency, inexpensiveness, availability, simplicity of operation [8,9]. Many researchers have been used different types of adsorbents including biomaterials [10], activated carbon [11] and nanomaterials [12,13].

Recently, the use of graft polymer as adsorbent for the removal of heavy metals have been drawn remarkable attention to the scientists of this field [14 –17]. Grafting is a polymerization reaction in which various functional monomers are attached covalently to the main polymer chain. The advantage of grafting is to the injection of different functional monomers possessed by graft polymer to the parent polymer remaining the unchanged the mechanical property of the main polymer [18, 19]. The different graft polymerization methods include plasma treatment, UV light, ionizing radiation, decomposition of chemical initiators and radiation- induced grafting. Among the aforementioned methods, radiation- induced grafting is advantageous to all other methods because of its simplicity of operation, no need of local heating, free radical process, mosaic grafting etc.[20].

Non-oven polypropylene is commonly employed as packaging stuff and utilized in various industries for multiple purposes [21]. Now a day, polypropylene (PP) fabric is one of the visible plastic wastes in our daily life. PP fabric bags are discarded to here and there informally and thus, our environment is polluted day by day. So, it is very urgent to find out a recycling process of the bags. For feasible recycling process, it is very indispensable to set up an effective implementation of recovered PP fabrics. It can be used in the elimination of heavy metals from industrial effluents. Grafted polypropylene fibers have been used by different researchers for the removal of precarious metals from aqueous solution [22-24].

The main objective of the present study is to prepare and investigate the adsorption capacity of a new adsorbent based on waste polypropylene nonwoven fabric through radiation grafting technique. The specific objectives of this study are (1) preparation of acrylonitrile (AN) grafted PP fabrics (AN-g-PP), (2) Amidoximation of AN-g-PP using $\text{NH}_2\text{OH} \cdot \text{HCl}$, (3) Application of the adsorbent for the removal of Cr (VI) from aqueous solution, (4) fitting the adsorption data to several kinetic and isotherm models, (5) studying the effect of temperature and pH on the adsorption process and (6) investigation desorption of the metal ions from the adsorbent surface and its reuse.

Materials and methods

Waste Polypropylene fabrics bags were collected from the local market (Bolivodro bazar, Ashulia, Savar, Dhaka) and cut into small size before washing with acetone and drying in oven at 60°C until constant weight was obtained. The salt used for the adsorption study was $\text{K}_2\text{Cr}_2\text{O}_7$ (Techno, pharmchem, India). Monomer, Acrylonitrile (AN) and hydroxyl amine hydrochloride were purchased from Sigma Aldrich, USA. Acetone, 1, 5-diphenylcarbazine, sulphuric acid and sodium carbonate were supplied by Merck, Germany.

Characterization of the adsorbent

FTIR spectrometer (AA-6800, Shimadzu, Japan) in the wavelength range $700\text{-}4000\text{ cm}^{-1}$ having resolution 4 cm^{-1} was utilized to analysis functional groups attached to the adsorbent after grafting. Mechanical property of the adsorbent was checked by DMA (dynamic mechanical analyzer), Triton technology TTDMA, UK heating the sample at the rate 4°C in the temperature range $25\text{ to }200^\circ\text{C}$ and retaining oscillating frequency of 1 Hz. Scanning electron microscope (SEM) of model JEOL 6400 was performed at an acceleration voltage of 10 kV to explore the surface morphology of the adsorbent. UV-Visible spectrophotometer (AA-6800, Shimadzu, Japan) was applied to estimate the concentration concentration of Cr (VI) in solution. To study the thermal stability of the adsorbent, TGA was employed at the heating rate $10^\circ\text{C}/\text{min}$ ranging temperature from 25°C to 600°C . The source of radiation was Co-60 gamma ray which is a Co-60 Batch Type Panormic Irradiator from BRIT, India which activity was 68.63 kCi with dose rate 13.7 kGy h^{-1} .

Grafting of AN onto the PP fabrics

Gamma radiation from Co-60 source was utilized to irradiate the PP fabric at 30 kGy radiation dose at room temperature. After irradiation, the fabrics were kept in a freeze at dry-ice temperature until use. Sixty percent AN and sulphuric acid (2 % of AN) in methanol were stirred well to obtain the monomer solution. Argon gas was passed through the solution in order to remove dissolved oxygen. Then, the de-oxygenated monomer solution was transferred into a glass bottle carrying the irradiated PP fabrics. To avert the incorporation of air oxygen the bottle was locked firmly using a cork and kept in a water bath heated at 80°C for 6 hours for grafting of AN onto the PP

fabrics. After the reaction, the grafted fabrics were cleaned by methanol firstly and then using distilled water once and once again to wipe off the unreacted monomer and homo-polymer of AN. The amount of grafting was estimated using the equation

$$\% \text{ grafting} = (W_g - W_o / W_o) \times 100 \quad (1)$$

Where, W_o and W_g are the dry weight of the PP fabrics and grafted PP fabrics respectively.

Amidoximation of nitrile group of AN-g-PP fabrics

An aqueous solution was prepared by dissolving 80 g of hydroxyl amine hydrochloride in 1 liter distilled and sodium carbonate was added to neutralize the solution. The AN-g-PP was plunked into the solution which was then placed into a water bath warmed up at 80°C. After 4 hours, the PP adsorbent was washed by methanol and then with distilled water until the residual salts were separated. Finally, the amidoximated fabrics were desiccated in air. The transformation of nitrile group of AN-g-PP fabric to amidoxime group was determined by the equation (2):

$$C_n = [(W_{am} - W_g) / W_g] \times (M_{AN} / M_{HA}) \times 100 \quad (2)$$

Where W_{am} and W_g are the weight of the amioximated and AN grafted fabrics respectively. M_{HA} denotes the molecular mass of the hydroxyl amine hydrochloride and M_{AN} represents the molecular mass of the AN.

Adsorption of hexavalent Chromium by the amidoximated adsorbent

The adsorbent obtained from the amidoximation of AN-g-PP was immersed in an aqueous solution of $K_2Cr_2O_7$ of certain volume and concentration at ambient conditions. The removal of Cr (VI) was investigated applying various states of contact time, temperature, pH and initial concentration of the metal ion. Particular concentration of HCl and NaOH was employed to customize the pH of the solutions. A UV Spectro-Photometer was used to estimate the concentration of Cr (VI) in the aqueous solutions before and after sorption by the amidoximated AN-g-PP adsorbent; For this a complexing agent, 1, 5 di phenyl carbazide was mixed with aqueous Cr (VI) solution in acidic condition which develops a red-violet color solution and measured at 540 nm wavelength [25]. All the experiments were conducted triplicate and average value was taken. The sorption capacity of the adsorbent was calculated by the equation (3):

$$Q = V (C_o - C_1) / W \quad (3)$$

Where, Q is the adsorption capacity in mg/g of the adsorbent, V is the volume of the solution in liter, C₀ and C₁ is the concentration of the metal ion in aqueous solution before and after immersing of the adsorbent respectively and W is the mass of the amidoximated adsorbent in gram.

Desorption of the hexavalent ion

Desorption studies of Cr (VI) ions from the surface of amidoximated AN-g-PP was carried out by soaking the adsorbent in a 2M solution of NaOH for 24 hours and the concentration of the metal ion concentration in desorbed solution was measured using UV-Visible method. The percentage of desorption was estimated using the equation (4).

$$\text{Desorption \%} = (\text{Cr (VI) desorbed in mg} / \text{Cr (VI) adsorbed in mg}) \times 100 \quad (4)$$

Results and discussion

Grafting of AN onto the PP fabrics

Pre-irradiation method was applied for the grafting of AN onto the PP fabric. The advantage of this technique is that it is not required to irradiate the monomer solution i.e. only polymer backbone are irradiated so that free radicals are formed on the backbone and production of homo-polymer of monomer becomes relatively low. Grafting reaction was taken place between irradiated (30 kGy radiation dose) polymer substrate and the monomer solution (60 % AN) in methanol. Concentrated H₂SO₄ (2% of AN) was added to reaction mixture as an additive. The amount of grafting in percentage was 150%.

Conversion of nitrile group into amidoxime

pH of the NH₂OH.HCl aqueous solution (80 g/L) was adjusted to 7.0 by the addition of Na₂CO₃ salt [26]. After the treatment of AN-g-PP with this solution for 4 hours at 80°C in a water bath, the percentage of conversion of nitrile group into amidoxime became 75%. The probable reaction mechanism for the grafting of AN on to PP and amidoximation of the AN grafted fabric could be given by **Fig. 1**.

FTIR analysis

The **Fig. 2** represents the FTIR spectra of the non-woven PP fabric, AN-g-PP and amidoximated AN-g-PP. The backbone and the side chain of the PP fabric consist of a number of methylene (–CH₂–) and methyl (–CH₃) groups respectively. In FTIR spectra of PP fabric, the absorption bands at 2914 and 2953 cm⁻¹ are assigned to the symmetric stretching vibrations of the methylene (CH₂) and methyl (CH₃) groups respectively. The peaks at 2872 and 2835 cm⁻¹ correspond to their (CH₃, CH₂) asymmetric stretching and the bending vibrations of these groups are appeared at 1374 and 1452 cm⁻¹. These absorption peaks of the aforementioned groups are also noticeable in the spectra of acrylonitrile grafted PP and amidoximated AN-g-PP. A sharp peak at 2243 cm⁻¹ corresponding to

the nitrile group confirms the grafting of AN on to the PP backbone. The IR spectra of amidoximated AN-g-PP obtained from the conversion of AN into amidoxime group, exhibits some peaks at 1647, 1267 and 912 cm^{-1} which are attributed to the $-\text{C}=\text{N}-$, $\text{N}-\text{H}$ and $\text{N}-\text{O}$ groups respectively [27]. It is observed that the peak at 2243 cm^{-1} corresponding to nitrile group is reduced remarkably and the peak ascribing to the $-\text{C}=\text{N}-$ (1647 cm^{-1}) increases that is the clear indication of transformation of nitrile group into amidoxime group [28].

Scanning Electron Microscopy

Scanning electron microscopy was done to inspect the surface morphology of PP fabric, AN-g-PP and amidoximated AN-g-PP and shown by the **Fig. 3**. It is noticeable that the physical appearance of the SEM images of the PP, AN-g-PP and amidoximated AN-g-PP is not similar. Broadening of the chain diameter and appearance of grafted object in the SEM images of the AN-g-PP is observed compared to that of original PP. This provides further physical evidence of grafting of AN on to the waste PP fabric. Again clear change of the SEM image of amidoximated AN-g-PP compared to AN-g-PP indicates the amidoximation of acrylonitrile grafted polypropylene fabric.

Analysis of thermal stability

Thermo-gravimetric analysis (TGA) of the original PP fabric, AN-g-PP fabric and amidoximated AN-g-PP was performed to examine their thermal hardness. The results displaying in **Fig. 4** revealed that the thermal stability of the pristine PP was up to 227° C. Then, its weight loss kicks off and left 6.58% residues over 600°C. The weight loss appearing in the initial stage is due to moisture sucked up from the air. The AN-g-PP stands thermally persistence up to 230° C and then starts weight loss because of the degradation of its grafted chain and base polymer. It yields 28.64% residue upon heating over 600° C. The amidoximation of the AN-g-PP fabric results in the reduction of its thermal strength as it weight loss initiates at very low temperature due to complex decomposition of the grafted, amidoximated and original PP chain. It generates 2.78% residue over 600° C. The stability of PP fabrics at high temperature indicates that the PP based adsorbent can be applied in the adsorption of heavy metals like Cr (VI).

Dynamic Mechanical Analyzer (DMA)

Dynamic mechanical analysis of waste PP fabric, AN-g-PP and amidoximated AN-g-PP are shown in the **Fig. 5**. As observed, the modulus of AN-g-PP is smaller than that of original PP fabric and after amidoximation of the AN-g-PP, its exhibits a significant increase. The initial modulus loss was attributed to the moisture present in the samples. The storage modulus of PP fabric and AN-g-PP shows a gradual decrease with the increase of

temperature and become zero at around 155°C. On the other hand modulus of amidoximated AN-g-PP increases initially and after going through a certain maximum value its decreases continuously and reaches to zero at 173° C. The glass transition region for original PP fabric begins at around 40° C. The glass transition states of AN-g-PP and amidoxime AN-g-PP initiates at around 47° C and 88° C respectively.

Effect of initial Cr (VI) concentration on adsorption capacity

Fig. 6 explains the change of adsorption capacity with the initial Cr (VI) concentration (129 ppm, 223 ppm, 309 ppm and 373 ppm). The Q_e value increases gradually when the concentration of metal ion raises which could be demonstrated by considering the chelating sites present on the adsorbent surface. With the augmentation of metal concentration, the rate of occupation of chelating sites by the Cr (VI) molecule increases which favors the adsorption process. However, at certain strength of metal ion, the adsorption sites will be saturated and then adsorption will be reached at a plateau value. Similar trend was observed in previous study [26].

Study of adsorption isotherms

For the elucidation of equilibrium adsorption, the adsorption data were fitted to Langmuir and Freundlich isotherms [29]. The linear forms of the isotherms are given by the equations (5) and (7).

Langmuir:

$$C_e/Q_e = C_e/Q_0 + 1/Q_0b \quad (5)$$

$$R_L = 1/(1+Q_0b) \quad (6)$$

Freundlich:

$$\log Q_e = \log K_F + (1/n) \log C_e \quad (7)$$

Where, C_e , Q_e and Q_0 are the initial Cr (VI) concentration (mg/L), equilibrium and monolayer adsorption capacity (mg/g) respectively. b indicates the affinity of the binding sites and adsorption energy. The equilibrium parameter, R_L describes the favorability of an adsorption process such as for favorable adsorption process, $0 < R_L < 1$; For linear adsorption, $R_L = 1$; $R_L > 1$ and 0 represent unfavorable and irreversible adsorption respectively [30]. The value of Q_0 and b can be obtained from plot C_e/Q_e vs C_e as shown in **Fig. 7a** and listed in **Table 1**. The Q_0 value was found to be 232.56 mg/g. The R_L value calculated from the **equation 6** was obtained 0.29 which lie between 0 and 1 indicating favorable Cr (VI) adsorption by the amidoximated AN-g-PP fabric. The correlation coefficient, R^2 for Langmuir adsorption was 0.9623.

Equation 7 exhibits the linear representation of Freundlich isotherm. The magnitude of heterogeneity factor n and Freundlich constant K_F can be estimated from the slope and the intercept of the plot $\log Q_e$ against $\log C_e$. For favorable adsorption, n is greater than one [30]. In this study, the n value obtained was 2.80. Thus the adsorption of Cr (VI) onto the amidoximated AN-g-PP is a favorable process. The regression coefficient, R^2 for Freundlich isotherm was 0.9320.

Considering all the isotherm parameters it can be concluded that the experimental sorption data follows Langmuir as well as Freundlich isotherm models.

Effect of contact time on the removal of Cr (VI) ions

To investigate the effect of the amidoximated AN-g-PP was placed in aqueous solution of Cr (VI) at pH 1.5 and initial metal concentration 120 ppm.

The change of concentration was monitored at regular interval showing in the **Fig. 8**. As observed, initially sorption of Cr (VI) was very fast showing 58% of adsorption in first 5.5 hour and eventually comes to the plateau after 40 hours with highest adsorption of 126.82 mg/g. Similar trend was observed in previous study [26].

Kinetic study

The kinetic data of Cr (VI) adsorption were fitted to several kinetic models including first order kinetic model, second order kinetic model, intra-particle diffusion model and Elovich model [31]. The linearized forms of the models are shown by the following equations:

First order kinetic model:

$$\log (Q_e - Q_t) = \log Q_e - (k_1/2.303) t \quad (8)$$

Second order kinetic model:

$$t/Q_t = 1/(k_2 Q_e^2) + t/Q_e \quad (9)$$

Intra-particle diffusion model:

$$Q_t = k_1 \sqrt{t} + I \quad (10)$$

Elovich model:

$$Q_t = \alpha + \beta \ln t \quad (11)$$

Where, Q_e and Q_t are the adsorption capacity at equilibrium and at time t respectively in mg/g of the adsorbent. k_1 (1/h), k_2 (g/h. mg) and k_i (mg/g.h)^{1/2} represent rate constant of the first order, second order, intra-particle diffusion respectively. In Elovich kinetic model, α indicates initial adsorption rate constant and β describes desorption rate constant.

The kinetic parameters for the adsorption of Cr (VI) are given in **Table 2**. **Fig. 9b** interprets the second order kinetic model. The experimental Q_e value (126.82 mg/g) and the calculated Q_e value (238.10) obtained from second order kinetic model were not in agreement with each other and also the correlation coefficient value, R^2 is low. In case of intra-particle diffusion model, the magnitude of R^2 was high but the line obtained from plotting Q_t against \sqrt{t} (**Fig. 9c**) did not pass through the origin and thus intra-particle diffusion was not the rate limiting step for the Cr (VI) removal using amidoximated AN-g-PP.

As seen from first order kinetic model demonstrated by **Fig. 9a**, the value of R^2 was very high (> 0.99) compared to second order and Elovich kinetic model (**Fig. 9d**). Also there was excellent consensus between the experimental (126.82 mg/g) and calculated (127.06 mg/g) equilibrium adsorption capacity. Therefore, the adsorption of Cr (VI) onto the amidoximated AN-g-PP adsorbent follows the mechanism of the pseudo first order kinetic model.

Effect of pH

The adsorption capacity of an adsorbent largely depends on pH of the medium. The change of pH affects the ionization of acidic and basic groups of the adsorbent due to their protonation and de-protonation, hence surface structure of the adsorbent could be modified. Also Cr (VI) remains in different forms when solution pH changes. The **Fig. 10** represents the effect of pH on the adsorption of Cr (VI) ions onto the amidoximated AN-g-PP adsorbent. It is noticed that with the decrease of pH of the solution, the elimination of the metal ions increases gradually and maximum sorption obtained was 126.82 mg/g at pH 1.5. Similar trend of Cr (VI) adsorption was found by Nazia Rahman et al. [26]. The dissimilarity of the removal of Cr (VI) by the aforementioned adsorbent can be explained by the fact that at different pH, the adsorbent is attracted by the different species of the metal ion, such as at acidic pH, these forms are H_2CrO_4 , $HCrO_4^-$, CrO_4^{2-} , $Cr_2O_7^{2-}$. In addition, at low pH, the amino groups ($-NH_2$) that exist on the surface of the amidoximated adsorbent become protonated and form positively charged, $-NH_3^+$ that attract the species of the metal ions which are negatively charged because of the coulombic forces. Conversely, at high pH value the $-NH_2$ groups are de-protonated by the formation of negatively charged $-NH_2...OH^-$. The repulsive force operating between $-NH_2...OH^-$ and negatively charged Cr (VI) ions is responsible for the reduction of adsorption of the metal ions.

Thermodynamic study

The adsorption of Cr (VI) using amidoximated AN-g-PP was studied at different temperature as shown in **Fig.11**.

The Van't Hoff equation for free energy change is as follows:

$$\Delta G^\circ = -2.303 RT \log k_d \quad (12)$$

$$K_d = Q_e/C_e = (\Delta S^\circ/2.303R) - (\Delta H^\circ/2.303 RT) \quad (13)$$

Where, ΔG° is the standard free energy change in KJ/mol, ΔS° and ΔH° represent the standard entropy change in KJ/mol and the standard enthalpy change in kJ/mol/K respectively. K_d is a constant at a certain temperature, the molar gas constant is R in J/mol/K and T indicates the kelvin temperature in K. The value of ΔS° and ΔH° could be calculated from the intercept and slope of the **Fig. 12** and different thermodynamic parameters are given in the **Table 3**.

As observed from the **Table 3**, the adsorption of Cr (VI) was spontaneous and thermodynamically reasonable as the value of ΔG° was negative at different temperature. At higher temperature, the sorption efficiency increases as shown in **Fig. 11**. Similar Cr (VI) adsorption change with temperature was observed by Nazia Rahman et al. [32]. The positive value of ΔH° (26.40 J/mol/K) indicates the adsorption process was endothermic. The removal of Cr (VI) utilizing the aforementioned adsorbent went on by the increase of disorder and degree of freedom at the solid-liquid interface due to the positive value of ΔS° (0.087 kJ/mol) [33].

Desorption study

The adsorbed Cr (VI) ions were desorbed from the amidoxime adsorbent surface. The adsorbent was reused for further Cr(VI) adsorption. The desorption process were performed by treating the adsorbent with 2M NaOH solution for 24 hours. The desorption ratio obtained was 80%. Reuse of adsorbent for three successive cycles showed consistency of adsorption capacity.

The adsorbent is promising for the removal of Cr (VI) as compared to the other adsorbent listed in **Table 4**

Conclusion

Radiation induced grafting method was applied for the preparation of the AN-g-PP from the reaction between waste PP and 60% AN at 80° C for 4 hours. At 30 kGy radiation dose the graft yield was 150% using H₂SO₄ as additive. To obtain amidoximated adsorbent, the AN-g-PP was allowed to react with hydroxyl amine hydrochloride. The adsorbent was inspected using SEM, TGA, FTIR and DMA and applied for the removal of Cr

(VI) from aqueous solution. Kinetic data were better fitted to the pseudo- first order model maintaining a good consensus of experimental and theoretical adsorption capacity and equilibrium adsorption data were explained using both Langmuir and Freundlich isotherm model. The removal process was endothermic and spontaneous as seen from the thermodynamic investigation. The result of desorption and reuse of the amidoximated adsorbent was also satisfactory. Thus, it can be decided that the adsorbent is suitable for the removal Cr (VI) from aquatic environment because of its high removal capacity, low cost and wide availability.

Declarations

Competing interests

The authors declare that they have no competing interests

Availability of data and materials

All data generated or analyzed during this study are included in this published article

Code Availability

Not Applicable

Authors' contributions

Md. Nabul Sardar and Nazia Rahman analyzed and interpreted the metal adsorption data. Md. Nabul Sardar and Shahnaz Sultana performed the experimental part of adsorbent preparation. Md. Nabul Sardar, Nazia Rahman and Nirmal Chandra Dafader was major contributors in writing the manuscript.

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

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Table 1 parameters of different adsorption isotherms

Langmuir		Cr (VI)
Q_0 (mg/g)		232.56
R_L		0.29
R^2		0.9623
Freundlich		
K_F (mg/g)		23.22
n (L/mg)		2.80
R^2		0.9320

Table 2 Kinetic parameters for the adsorption of Cr (VI) onto the amidoximated AN-g-PP adsorbent

Pseudo first-order	Cr (VI)
k_1 (1/h)	0.138
Q_e (mg/g)	127.06
R^2	0.9967
Pseudo second-order	
k_2 (g/h. mg)	0.0003
Q_e	238.10
R^2	0.9323
Intra-particle diffusion	
k_i (mg/g. h)	38.076
C	-22.582
R^2	0.9973
Elovich model	
α	13.541
β	28.921
R^2	0.9849

Table 3 thermodynamic parameters for the sorption of Cr (VI)

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/K)	R^2
278	- 23.71	26.40	0.087	0.9980
298	- 25.45			
333	- 28.50			

Table 4 Comparison of maximum adsorbent capacity of various adsorbents

Adsorbent	Adsorption capacity (mg/g)
Amidoximated AN grafted waste PP (present study)	232.56
Amidoximated-PE [26]	200
Activated carbon derived from acrylonitrile-divinyl benzene Co- polymer [34]	101.20
Amine functionalized nanofibers [28]	137
Polypyrrole/Fe ₃ O ₄ magnetic nanocomposite [35]	243.9
Surface modified tannery waste [36]	217

Figure captions

Fig. 1: Probable reaction mechanism for grafting of AN on to the waste PP fabric and amidoximation of the grafted fabric

Fig. 2: FTIR spectra of waste PP fabric, AN-g-PP and amidoximated AN-g-PP adsorbent

Fig. 3: SEM images of (a) PP fabric, (b) AN-g-PP and (c) amidoximated AN-g-PP

Fig. 4: TGA thermograms of waste PP fabric, AN-g-PP and amidoximated AN-g-PP

Fig. 5: Storage modulus of waste PP fabric, AN-g-PP and amidoximated PP

Fig. 6: Effect of concentration on the removal of Cr (VI) from aqueous media using amidoximated AN-g-PP adsorbent at pH 1.5

Fig. 7: Adsorption isotherm plots (a) Langmuir and (b) Freundlich

Fig. 8: Effect of contact time on the removal of Cr (VI) (Concentration = 120 mg/L and pH =1.5)

Fig. 9: kinetic study plots (a) pseudo first-order, (b) pseudo second-order, (c) intra-particle diffusion model and (d) Elovich model

Fig. 10: Influence of pH on the adsorption Cr (VI) having concentration of 120 mg/L

Fig. 11: Change of adsorption of Cr (VI) with increasing of temperature (time: 6 hours, concentration: 120 (mg/L)

Fig. 12: $\log(Q_e/C_e)$ vs $1/T$ plot for Cr (VI) adsorption

Figures

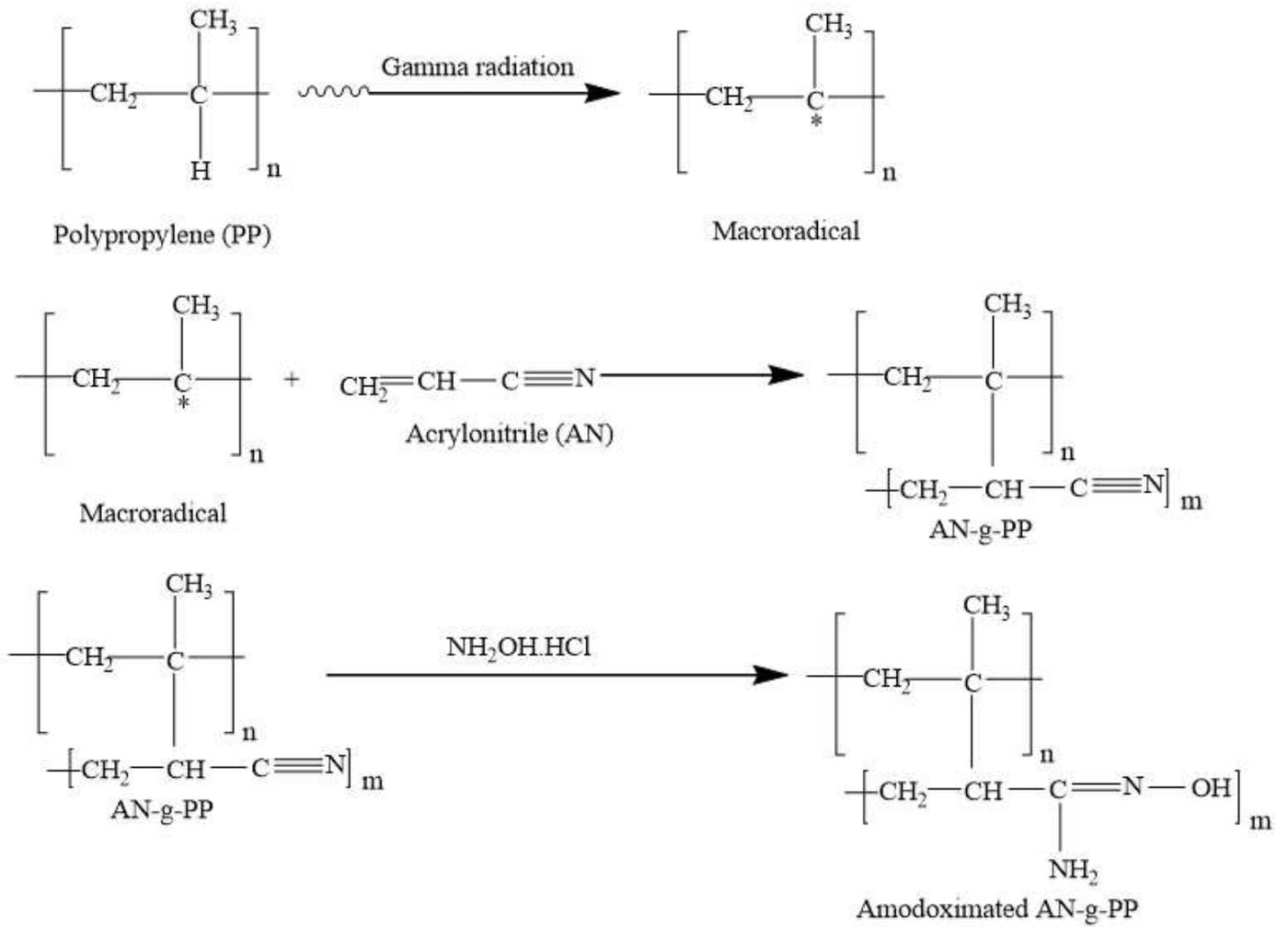


Figure 1

Probable reaction mechanism for grafting of AN on to the waste PP fabric and amidoximation of the grafted fabric

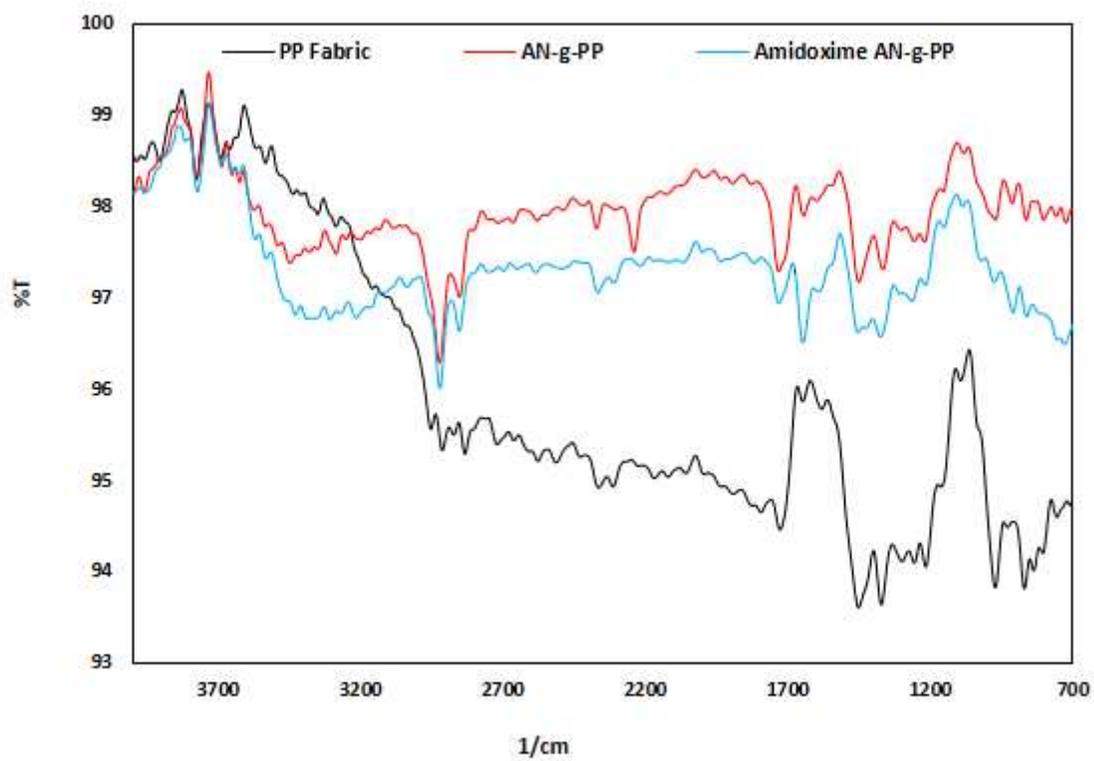
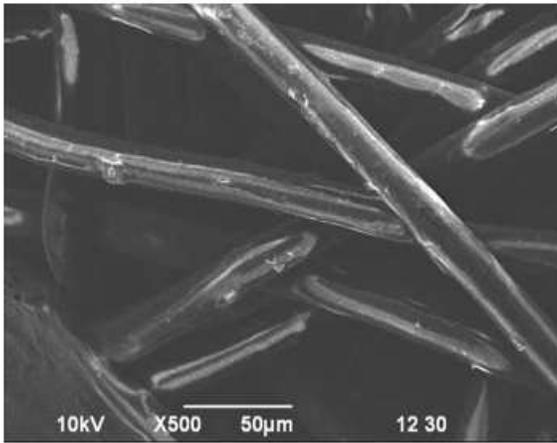
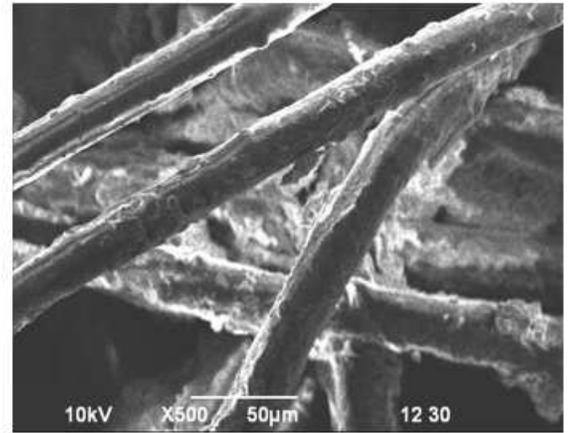


Figure 2

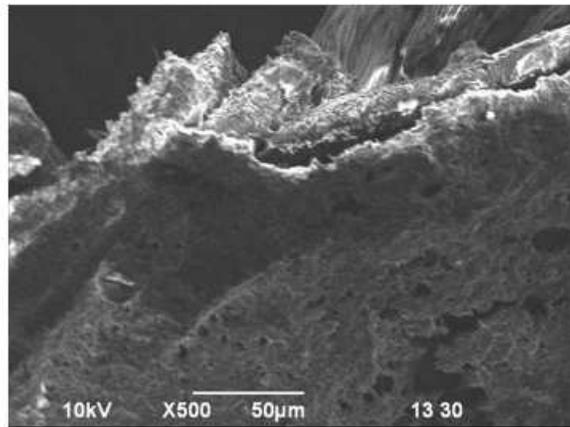
FTIR spectra of waste PP fabric, AN-g-PP and amidoximated AN-g-PP adsorbent



(a)



(b)



(c)

Figure 3

SEM images of (a) PP fabric, (b) AN-g-PP and (c) amidoximated AN-g-PP

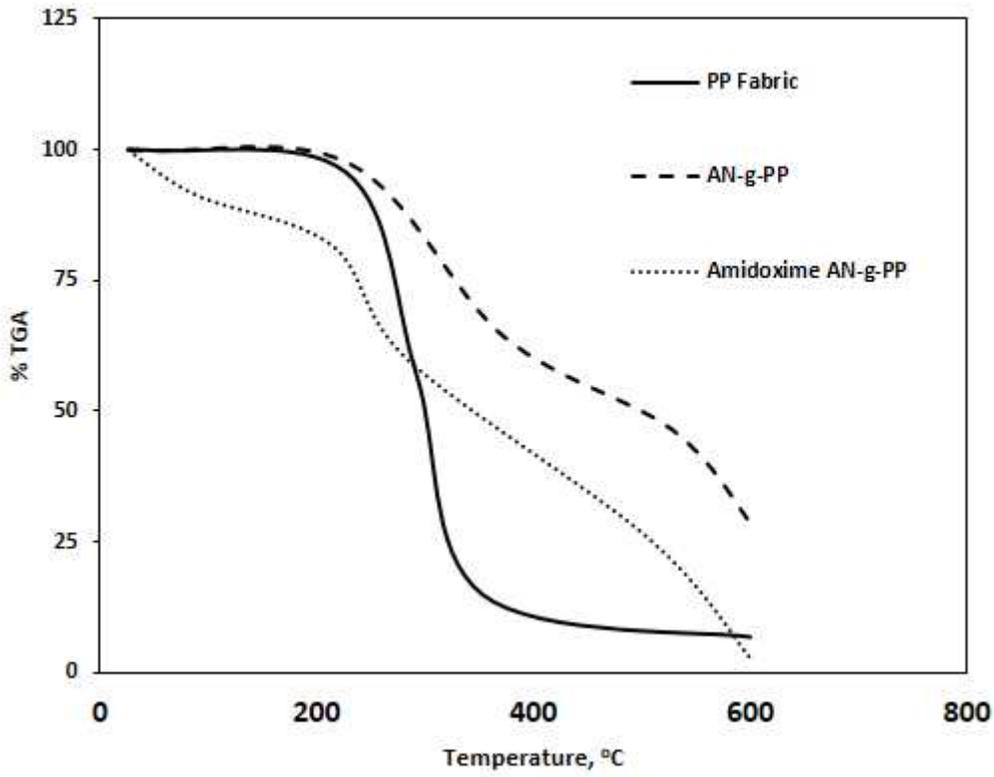


Figure 4

TGA thermograms of waste PP fabric, AN-g-PP and amidoximated AN-g-PP

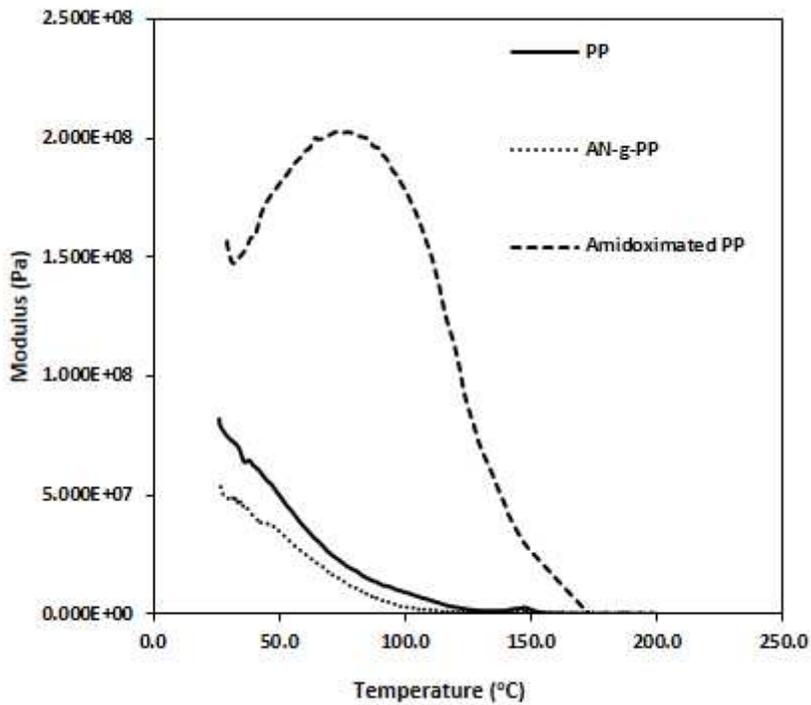


Figure 5

Storage modulus of waste PP fabric, AN-g-PP and amidoximated PP

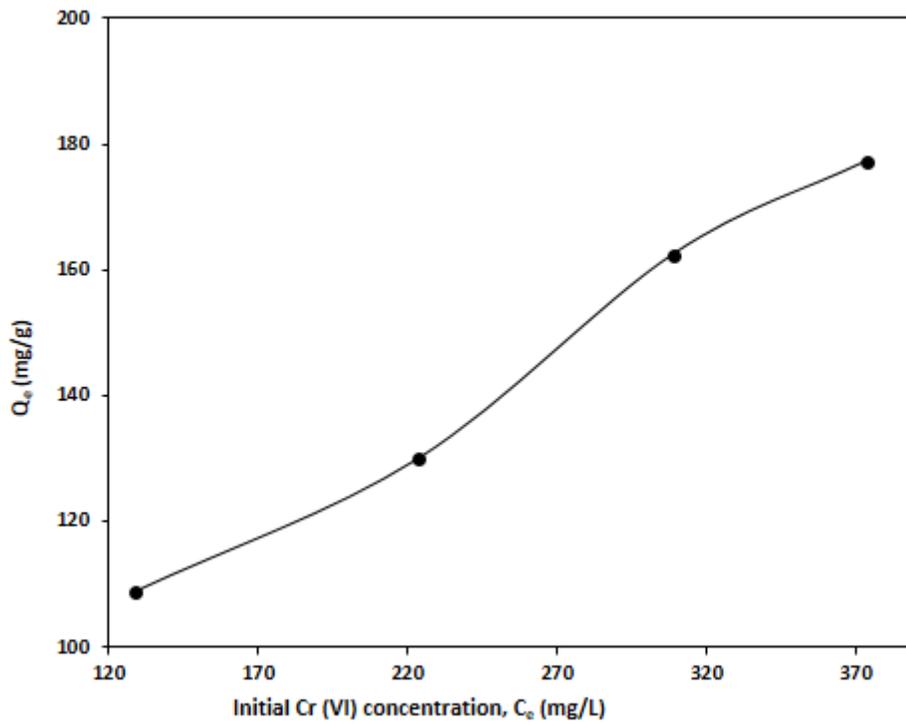
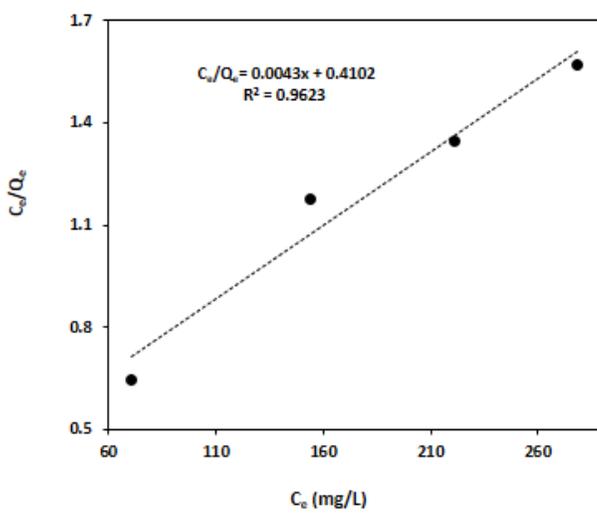
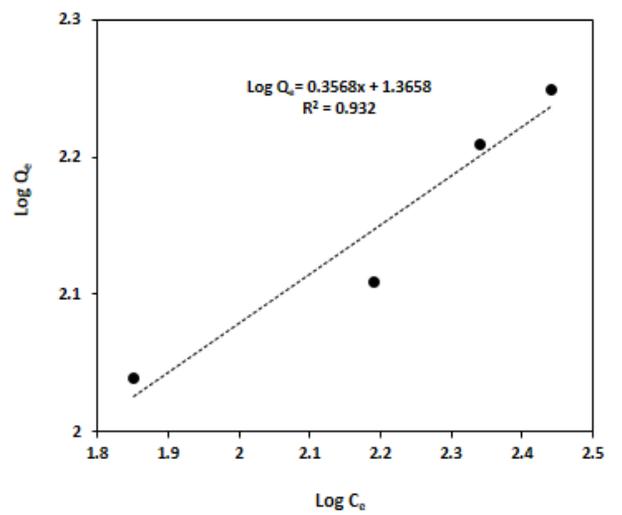


Figure 6

Effect of concentration on the removal of Cr (VI) from aqueous media using amidoximated AN-g-PP adsorbent at pH 1.5



(a)



(b)

Figure 7

Adsorption isotherm plots (a) Langmuir and (b) Freundlich

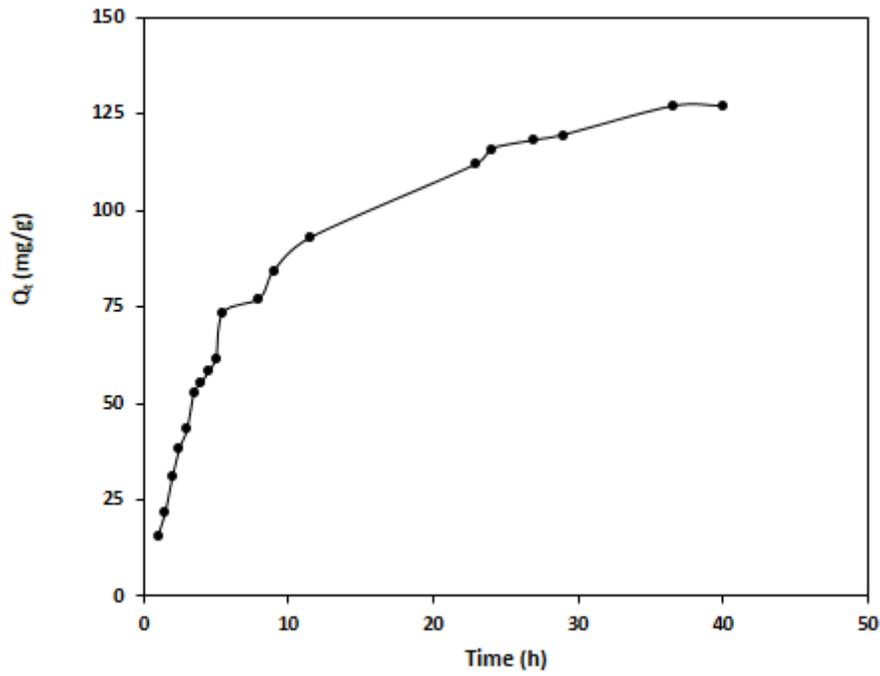


Figure 8

Effect of contact time on the removal of Cr (VI) (Concentration = 120 mg/L and pH =1.5)

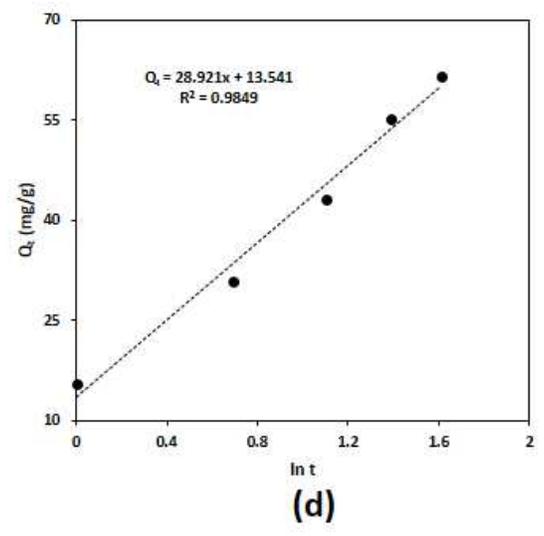
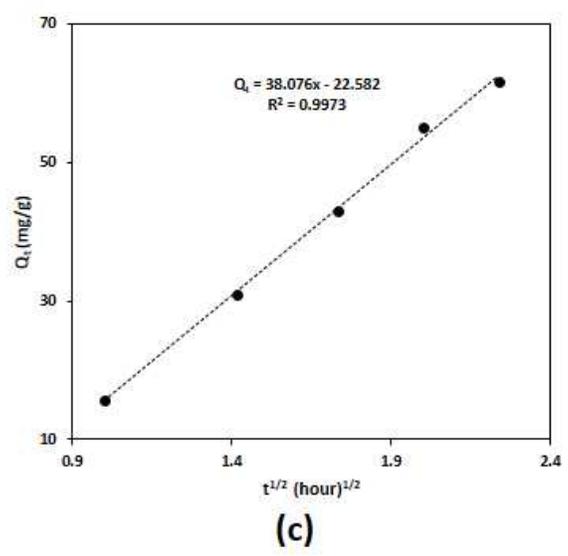
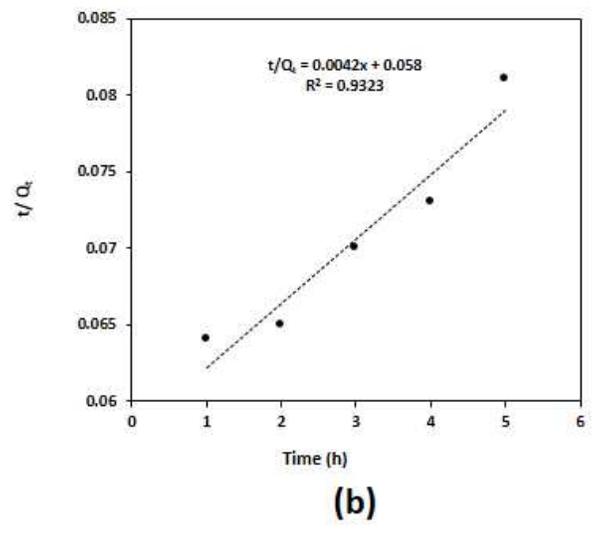
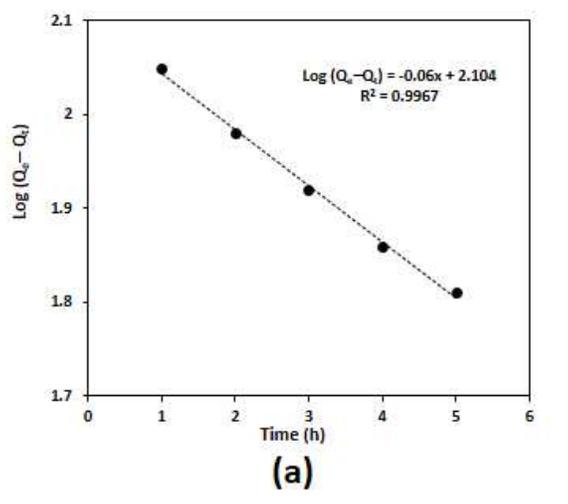


Figure 9

kinetic study plots (a) pseudo first-order, (b) pseudo second-order, (c) intra-particle diffusion model and (d) Elovich model

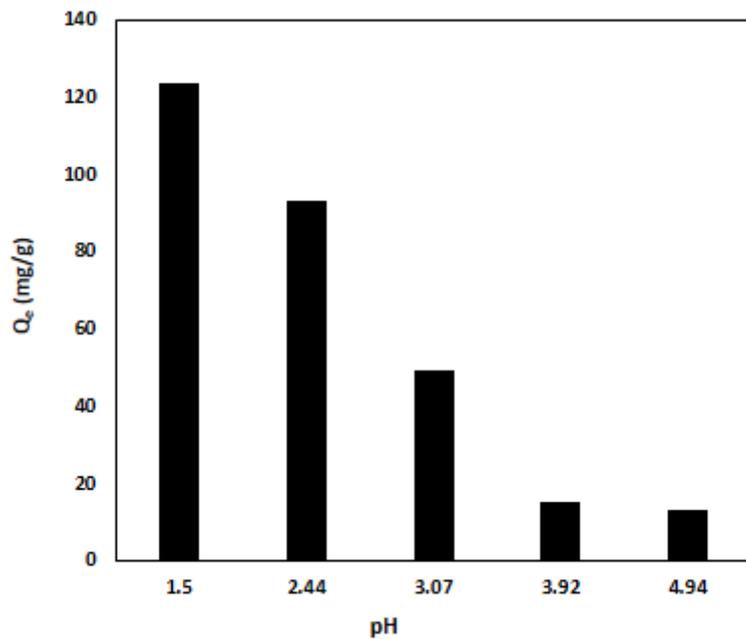


Figure 10

Influence of pH on the adsorption Cr (VI) having concentration of 120 mg/L

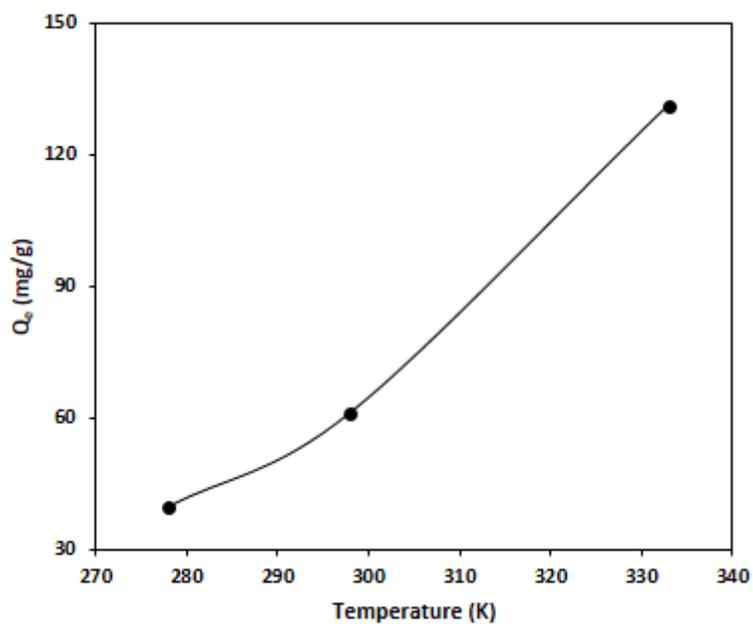


Figure 11

Change of adsorption of Cr (VI) with increasing of temperature (time: 6 hours, concentration: 120 (mg/L))

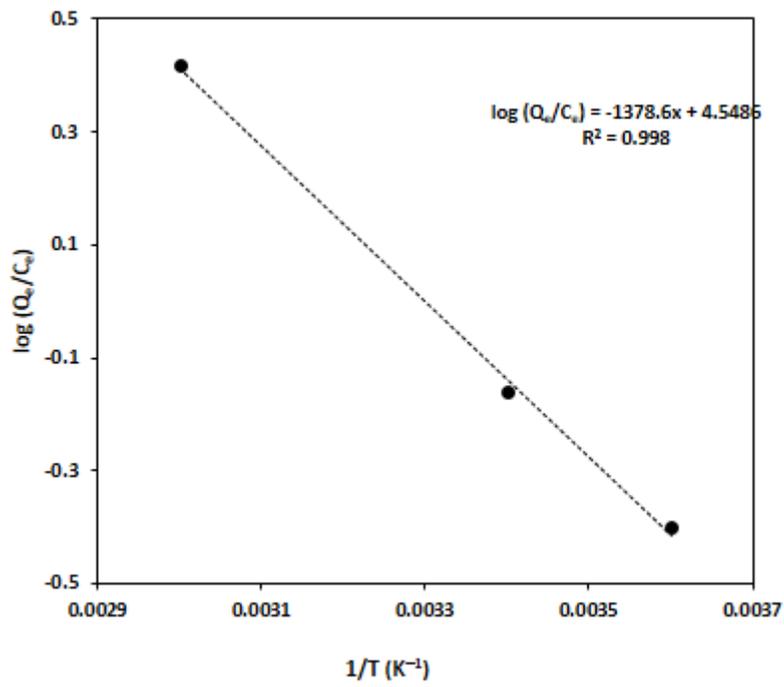


Figure 12

$\log(Q_e/C_e)$ vs $1/T$ plot for Cr (VI) adsorption