

Multivariate Optimization of Removing of Cobalt(II) with an Efficient Aminated-GMA Polypropylene Adsorbent by Induced-Grafted Polymerization under Simultaneous Gamma-Ray Irradiation

Fatemeh Maleki

Shahid Beheshti University

Mobina Gholami

Shahid Beheshti University

Rezvan Torkaman

Nuclear Science and Technology Research Institute

Meisam Torab-Mostaedi

Nuclear Science and Technology Research Institute

Mehdi Asadollahzadeh (✉ masadollahzadeh@aeoi.org.ir)

Nuclear Science and Technology Research Institute

Research Article

Keywords: Adsorption Procedure, Glycidyl Methacrylate, Radiation Grafting, Amino Groups, Gamma-Ray

Posted Date: June 30th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-668224/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

**Multivariate Optimization of Removing of Cobalt(II) with an Efficient Aminated-GMA
Polypropylene Adsorbent by Induced-Grafted Polymerization under Simultaneous
Gamma-Ray Irradiation**

**Fatemeh Maleki^a, Mobina Gholami^a, Rezvan Torkaman^b, Meisam Torab-Mostaedi^b,
Mehdi Asadollahzadeh^{b*}**

^a Nuclear Engineering Department, Shahid Beheshti University, Tehran, Iran

^b Nuclear Fuel Cycle Research School, Nuclear Science and Technology Research Institute,
P.O. Box: 11365-8486, Tehran, Iran

*Corresponding author: Mehdi Asadollahzadeh (masadollahzadeh@aeoi.org.ir; mehdiasadollahzadeh@iust.ac.ir; mehdiasadollahzadeh@yahoo.com)
Tel: +982188221117; Fax:+982188221116

Abstract

Nowadays, radiation grafting polymer adsorbents have been widely developed due to their advantages, such as low operating cost, high efficiency. In this research, glycidyl methacrylate monomers by simultaneous irradiation of gamma-ray with a dose of 20 kGy were grafted on polypropylene polymer fibers. The grafted polymer was then modified using different amino groups and tested for adsorption of cobalt ions in an aqueous solution. Finally, modified polymer adsorbent with the high efficiency for cobalt ions adsorption was synthesized and tested for further investigation. Different modes of cobalt ions adsorption were tested in other adsorption conditions, including adsorption contact time, pH, different amounts of adsorbent mass, and different concentrations of cobalt ions solution. The adsorbent structure was characterized with FT-IR, and SEM techniques and illustrated having an efficient grafting percentage and adsorption capability for cobalt removing by batch experiments. The optimum conditions were obtained by a central composite design as follows: adsorbent mass =0.07 g, initial concentration=40 mg/L, time=182 min, and pH =4.5 with ethylenediamine as a modified monomer and high amination percentage. The features such as inexpensive adsorbent, easy to prepare, high efficiency, and stability allow the radiated-induced grafted adsorbent to constitute one of promising materials for heavy metals remediation.

Keywords:

Adsorption Procedure, Glycidyl Methacrylate, Radiation Grafting, Amino Groups, Gamma-Ray

1. Introduction

Today, the removal of heavy metals from wastewater due to their environmental importance and eliminating pollution from industrial facilities is a priority for researchers ^{1,2}. On the other hand, heavy metals are not degradable and can accumulate in the body of living organisms and cause abnormalities and diseases ^{3,4}. Also, due to limited resources related to heavy metals such as cobalt and their application in industry and technology, the recovery of heavy metals from wastewater has been considered in various procedures ^{5,6}. Different physical, chemical, and biological mechanisms have been developed to remove heavy metal ions from effluents, as shown in Fig.1 ⁷⁻¹⁴.

Fig.1

Among the various methods, the adsorption method is a suitable method for removing heavy metals from effluents. Depending on the type of bond between adsorbent and sorption materials, adsorption is divided into physical and chemical adsorption ¹⁵. In physical adsorption, the molecules in the fluid are adsorbed by the presence of London and van der Waals forces or electrostatic and Coulomb forces on the adsorbent. In chemical adsorption, the pressure exerted between molecules is much stronger than the intermolecular forces in physical adsorption, such as covalent bonding. Although the rate of chemical adsorption is much faster than physical adsorption, many adsorption processes performed in the industry are in the form of physical adsorption ¹⁶⁻²⁰.

Cross-linked and modified polymer adsorbents are most interested in retrieving heavy metals from solution for the following reasons ²¹: Polymeric adsorbents have a high adsorption capacity, and selectivity to remove the target material increases with specific ligands. Functional groups are added to polymer chains to increase adsorption capacity. As a result, the polymer is durable and flexible. Various forms of polymeric adsorbents are prepared in large quantities. Radiation-grafted polymerization is an effective method that leads to new

adsorbents with high adsorption capacity by creating grafted branches in polymer bases and then applying them ²². Radiation-grafted polymerization is performed in two main ways, including simultaneous irradiation and pre-irradiation methods. In the simultaneous mode, the parent polymer is irradiated while immersed in a monomeric solution. A side effect of homopolymerization may be initiated in this method, which can be controlled by applying a lower radiation dose rate or adding inhibitors. In a pre-irradiation way, the primary polymer is irradiated in a vacuum or inert medium to produce radicals. After irradiation, it is placed in a monomeric solution under controlled conditions ²³. On the other hand, the parent polymer may be irradiated in air containing peroxide or hydroperoxy groups in a process called peroxidation or hydroperoxidation. Bonding is initiated by the decomposition of peroxides to radicals at high temperatures in the presence of a monomer. In the pre-irradiation method, the formation of homopolymer is much less. The selection criteria for radiation-grafted polymerization methods depend on the availability of radiation sources, the monomer reaction, and the sensitivity of the main polymer body to radiation ^{22, 24, 25}.

In a study by Omichi and co-workers, the coated polypropylene fabric as a substrate was used for the adsorption of cobalt ions. The fabric was irradiated with gamma-ray in the range of 5-20 kGy. The mixture containing 5 wt% GMA and 0.5 wt% Tween20 was used as a monomeric structure. The adsorption capacity of cobalt ion (50 ppm in initial solution) was obtained above 80% after 6h at 25 °C²⁶. Hegazy and co-workers have studied the low-density polyethylene films with monomeric solution consisted of acrylic acid and 2-vinyl pyridine for the adsorption preparation. The maximum adsorption from aqueous solution (zinc and cobalt ions~200 ppm) was obtained equal to 147 mg/g for zinc ions and 116 mg/g for cobalt ions ²⁷. In another study, the PE/PP NWF polymer was irradiated by electron irradiation at a dose of 30 kGy under a nitrogen atmosphere. After, the irradiated polymer was then placed in a monomeric mixture containing glycidyl methacrylate (GMA) and modified by amine groups. The adsorption

experiments showed an adsorption rate equal to 50 mg/g²⁸. The nonwoven fabric PP/PE as an adsorbent was used to adsorb metals such as Cu (II), Ni(II), Co (II) with acrylamide as a monomer. The gamma radiation at a dose of 20-30 kGy was applied in the experiments²⁹. Nasaf and co-workers have investigated the application of PE films to remove heavy metal ions such as Pb(II), Cu(II), Co(II), and Ni(II). The films were placed in styrene and divinylbenzene and filled with nitrogen gas. It was then irradiated. In the modification stage, it was then placed in a mixture of chlorosulfonic acid and dichloromethane. The adsorption efficiency was obtained higher than 60% for Cu(II), Co(II), and Ni(II)³⁰.

The adsorption of different metals by the adsorbent is subject to several conditions, the infinity of which is not practically possible. Various software, such as Design Expert, which with statistical and mathematical models, has made it possible to study different adsorption conditions and different adsorption synthesis conditions³¹⁻³³.

Response surface methodology (RSM), or the same as the response surface method, is known as one of the methods of experimental modeling and experimental design. One of the goals of RSM is to improve the process by finding optimal inputs, fixing problems and weaknesses of the process.

The response level method is used as a statistical technique to optimize the output variable. In each experiment, input parameters are changed to check for changes in output, and parameters that do not have a significant impact on the investigation. The experiments will then be defined. In the next step, the results obtained from the software are statistically examined, and finally, the optimal value is calculated for each parameter in this experiment. One of the advantages of using the response level method, in addition to reducing the number of experiments, is the possibility of providing a mathematical relationship between independent and dependent variables.

In this study, the response surface method was used to evaluate the removal of heavy metal from an aqueous solution to optimize the test conditions and find the maximum effect. This method designs the test matrix by criteria for the number of variables and the maximum and minimum limits set for each variable. This method is preferable to bulky methods such as full factorial because it reduces the number of tests ³⁴.

A limited number of investigations are devoted to the adsorption of cobalt ions using polymeric adsorbent with Radiation-grafted polymerization. The present study illustrated synthesizing a new polymer adsorbent by direct irradiation under gamma-ray and glycidyl methacrylate monomer. The effect of different amines on the modification of the adsorbent structure and the adsorption investigations with the central composite design approach were first discussed to elucidate the impact of main parameters on the adsorption efficiency.

2. Experimental

2.1. Materials

Glycidyl methacrylate ($C_7H_{10}O_3$, $\leq 97\%$, Sigma-Aldrich, USA), methanol (CH_3OH , Merck, Germany), Iminodiacetic acid ($C_4H_7NO_4$, $>99\%$, Merck, Germany), Ethylenediamine ($NH_2CH_2CH_2NH_2$, $>99\%$, Merck, Germany), Diethylamine ($(CH_3CH_2)_2NH$, $>99\%$, Merck, Germany), Ethanolamine ($HOCH_2CH_2NH_2$, $> 99\%$, Fluka, Switzerland), Triethylamine ($N(CH_2CH_3)_3$, $> 99\%$, Merck, Germany), cobalt chloride hexahydrate ($CoCl_2(H_2O)_6$, Merck, Germany) and ammonium ferrous sulfate ($Fe(SO_4)(NH_4)_2(SO_4).6H_2O$, Merck, Germany) were used in the adsorbent synthesis. In this study, polypropylene nonwoven fabrics were used as a substrate for adsorption preparation.

2.2. Procedure of Graft Polymerization

$A^{60}Co$ gamma source was used to graft the GMA monomers to nonwoven polypropylene polymer fibers. First, the nonwoven polypropylene fibers were cut into small pieces and washed with water and acetone, and dried in an oven at $50\text{ }^\circ C$. The cut sections of nonwoven

polypropylene fibers were immersed in a monomeric solution of GMA (25%V) with methanol: water (6:4) and phosphoric acid for 18 hours. Iron ammonium sulfate salt (1% Wt) was used to prevent the formation of homopolymer reactions. Then, the vial containing polypropylene substrate and the monomeric solution was filled with nitrogen gas and sealed. By simultaneous irradiation polymerization method, the prepared vial was irradiated under gamma radiation at a dose of 20 kGy. The grafted nonwoven fibers were washed with water and methanol free of any homopolymer and monomer that did not react. The grafted sample was then dried in an oven at 60 °C and weighed. The percentage increase in weight determined the grafted percentage; according to the following relationship:

$$\%Grafting \text{ Percentage} = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where W_o and W_g represent the initial weight and the grafted weight of the fabric, respectively.

2.3. Modification of Grafted Polymer with Amine Group

Modification of polymeric substrates grafted with GMA was performed separately with five different amines (iminodiacetic acid, ethylenediamine, diethylamine, ethanolamine, triethylamine). For modification with ethylenediamine, diethylamine, ethanolamine, and triethylamine, the grafted polymeric substrates were immersed in amine solution: water (60:40) for 5 hours in a water bath at 65 °C. To modify with iminodiacetic acid, the grafted polymer substrate was immersed in an aqueous solution of isopropyl alcohol and iminodiacetic acid (0.425 M) for 3 hours in water bath at 80 °C. Then, it was washed with HCl solution (1M) for 1 hour and dried in an oven at 60 °C³⁵. Finally, the modified samples with different amines were washed with water and dried in an oven at 60 °C for 24 hours and weighed. The percentage of amination is obtained according to the following relationship:

$$\%Amination \text{ Percentage} = \frac{(W_a - W_g) / \text{molecular weight of amine}}{(W_g - W_o) / \text{molecular weight of GMA}} \quad (2)$$

where W_a , W_o , and W_g represent the amine-modified weight, initial weight, and the grafted weight of the fabric, respectively.

2.4. Characteristic Analysis

The pH value of the aqueous solution containing from adsorption procedure was measured on a Metrohm691 pH meter with a combined electrode. The radiation Grafted polymeric adsorbent was evaluated by scanning electron microscope (model Hitachi Su3500) to observe fabric adsorbents' structural characteristics. The infrared spectra of the composite of fabric adsorbents were tested by FTIR spectroscopy (Bruker, victor22) in transmittance mode using KBr pellets. The measurements were obtained in the wavelength range from 400 cm^{-1} to 4000 cm^{-1} . The concentrations of metal-containing solutions were measured by spectrophotometer UV/Vis (DR 6000).

2.5. Experimental Design for Optimization of Parameters

Optimization of cobalt removal by four independent variables, including adsorbent mass, aqueous solution concentration, time, and pH, was performed with the standard CCD design, one of the classic designs of the response surface method. Table 1 defines the range of independent variables.

According to Design-Expert 7.0 software, thirty experiments were performed. Optimal values for the defined variables are obtained by solving the regression equation and analyzing the response level graphs.

Table 1

2.6. Adsorption Experiments

Cobalt adsorption tests were performed under the same conditions by pp-g-GMA adsorbent modified with different amines (iminodiacetic acid, ethylenediamine, diethylamine, ethanolamine, triethylamine). Finally, the selected modification was selected based on the maximum amount of adsorption. Then, for the chosen adsorbent, the adsorption of cobalt at

different temperature conditions and different concentrations of cobalt solution was investigated. Finally, to determine the optimal state of adsorption conditions, cobalt adsorption was performed using design expert software in different conditions of time, pH, adsorbent mass, and different concentrations of cobalt solution. After analysis in each run, the adsorption percentage is determined as follows:

$$\% \text{ Adsorption} = \frac{C_0 - C}{C_0} \times 100 \quad (3)$$

where C_0 and C are the initial and equilibrium concentrations, respectively, of cobalt ions in an aqueous solution (mg/L).

3. Results and Discussion

The radiation grafting method was used to bond GMA functional monomers to polypropylene nonwoven bedding. The type of amine is very effective in modifying the adsorbent on the adsorption rate of heavy metals. On the other hand, the variables of adsorption conditions such as adsorption contact time, pH, solution concentration, adsorbent mass, etc., are very effective on the adsorption rate. The effects of the mentioned variables are illustrated and analyzed in the following sections.

3.1. Effect of Modification with Different Amine Groups for Cobalt Adsorption

As explained in Section 2.3, nonwoven fibers grafted with GMA monomers were modified separately with various materials such as iminodiacetic acid, diethylamine, ethylenediamine, triethylamine, and ethanolamine. Each adsorbent was then tested for adsorption of cobalt under precisely the same conditions to select the final modification based on the maximum adsorption. The percentage of amination (DA) for adsorbents using different amines is shown in Fig.2. As can be seen, the percentage of amination (DA) for modification with ethylenediamine is higher than other amines. A new adsorbent with a grafted percentage of 139.45% and an absorption capacity of 25.34 mg/g of adsorbent was obtained with the radiation induced-grafted polymerization.

Fig.2

3.2. Characterization Results

Characterization and validation of the synthesized polymer adsorbent were performed by FT-IR and SEM tests.

3.2.1. Infrared Spectroscopy

Infrared spectroscopy is widely used in the identification and characterization of chemical compounds. It is a non-invasive and non-destructive method based on the absorption of electromagnetic radiation in the infrared range and the study of vibrational mutations of atomic molecules and ions. The response prompted FTIR distinction spectroscopy was utilized to choose vibrations relating to single compound gatherings associated with a particular response^{36, 37}. FT-IR analysis was performed to determine the type of grafts in the sample, for initial validation, and to determine the bonds in the material's structure. The infrared spectra analysis of PP-nonwoven fabric and PP-g-(GMA/EDA) appears in Fig.3. It is seen that the infrared absorption peaks of the PP-g-(GMA/EDA) (Fig. 3b) can be assigned as follows: The peak of 1251 cm^{-1} is related to factor P = O in phosphoric acid. Effective grafting and amination responses utilizing three different amines were affirmed by FTIR spectroscopy. In the wake of uniting, new assimilation groups showed up at $1,725$, $1,255$, 905 , and 845 cm^{-1} . The solid band at $1,725\text{ cm}^{-1}$ and the frail broadband at $1,255\text{ cm}^{-1}$ are ascribed to -C=O and C-O -extending of acrylate, separately³⁸.

The two little peaks at 905 and 845 cm^{-1} are characteristic bands of the epoxy ring³⁹⁻⁴¹. There was no huge change in the position and force of the carbonyl band of poly(GMA) at $1,725\text{ cm}^{-1}$ during the amination response with DEA. Then again, the trademark groups of the epoxy ring at 905 and 845 cm^{-1} nearly vanished during the amination responses. Also, another broadband, ascribed to the O-H stretch, showed up at $3,500\text{--}3,000\text{ cm}^{-1}$ due to the expansion of hydroxyl gathering to the construction. Aliphatic amines likewise showed a C-N extending vibration at

1,250–1,020 cm^{-1} . A few trademark pinnacles of the s-PP made this region profoundly swarmed, prompting the darkening of the C-N peak. These outcomes approved the viable amination of the united examples through opening the epoxy rings of the joined poly(GMA).

Fig.3

3.2.2. Scanning Electron Microscopy

The examining electron magnifying lens (SEM) utilizes an engaged light emission energy electron to create different signs at the outside of strong examples. The signs got from electron-test collaborations uncover data about the example, including outside morphology (surface), substance creation, and glasslike design, and direction of materials making up the example. In many applications, information is gathered over a chose space of the example's surface, and a 2-dimensional picture is created that shows spatial varieties in these properties ⁴². The morphology of the synthesized polymer adsorbents is shown in Figs. 4, and 5, for propylene nonwoven fabric, and ethylenediamine modified PP-g-GMA adsorbent. Comparing these two diagrams showed that the degree of grafting in the irradiated sample compared to the polymer base is clear. The increase in fiber diameter in the adsorbent structure indicates a high degree of grafting by irradiation and a mixture of monomers and the functional group.

Fig.4

Fig.5

3.3. Investigation of Adsorption at Different Temperatures and Concentration

Different industrial environments, wastewater, or marine environment each have different concentrations of heavy metals, and the appropriate adsorbent will be selected according to the concentration of the environment. Since adsorbents behave differently in the face of the concentration of solute (considering the mass transfer phenomena) and the initial concentration of the solution can be significantly effective in the results, this parameter for the concentration range of 20-100 ppm in different temperatures was tested and evaluated. The results are shown

in Figures 6-9. As can be seen from the results, in all the mentioned concentrations and temperature range of 25-80°C for 0.10 gr of adsorbent and 40 cc volume of cobalt solution, more than 95% adsorption percentage is obtained with the novel adsorbent synthesized with glycidyl methacrylate with gamma radiation and modified with ethylenediamine.

Fig.6

3.4. Response Surface Methodological Approach

RSM is a combination of mathematical and statistical methods used to optimize processes. RSM usually consists of three steps: 1) design and experiments, 2) modeling the response surface through regression, 3) optimization. The main purpose of RSM is to determine the optimum state or range to meet the test conditions. In the response level method, the independent parameters and the response are related as follows:

$$y=f(x_1, x_2, x_3, \dots, x_n) \pm e \quad (4)$$

In the above equation, f is the answer function, y is the answer, e is the test error, and x_1, x_2, x_3 , etc., are also independent variables. When we draw the answers, we get a level called the response level. Figure may be a first-order polynomial or a higher-order polynomial depending on the shape of the curve. By carefully studying the response level model, the parameters can be adjusted to give the best response.

3.4.1. Experimental Design and Fitting of the Quadratic Model

The answers obtained from each experiment according to the parameters given by the software are shown in Table 2. Using the response level method based on parameter prediction provides an empirical relationship between independent input variables and responses. This equation is as follows:

$$Y= -86.83144 + 0.23973*A - 0.83080*B + 51.88759*C + 1678.77186*D - 1.52743E-003*A*B - 6.09601E-003*A*C + 0.039493*A*D + 0.012510*B*C + 9.32966*B*D -$$

$$145.43870*C*D - 2.61787E-004*A^2 - 5.33316E-004*B^2 - 4.44941*C^2 - 8170.40423*D^2$$

(5)

The coefficients A(time), B(concentration), C(pH), D(mass) are the same as the independent input variables. The results of the quadratic model for the percentage of adsorption in the form of analysis of variance (ANOVA) are given in Table 3.

The value of R^2 and adjusted R^2 are close to one. This value indicates the correspondence between the predicted and observed values. It suggests that the regression model illustrates the relationship between the defined independent variables and the answers given. The value of Prob.> F in the model is less than 0.0001, and this indicates that the model is statistically acceptable.

The lack-of-fit term is significant as it is desired. The significant value of lack of fit (more than 0.05) showed that the quadratic model was valid for the present study. Examination of the outputs shows that the quadratic model is statistically acceptable for the responses.

Table 2

Table 3

3.4.2. Response Estimation for Maximum Removal of Cobalt

In this study, to increase the accuracy of experiments and improve the results of the experimental design method has been used. In designing an experiment, the goal is to identify and analyze the variables affecting the outputs with the least number of experiments. In the design of the experiment, changes are made to the process or system to evaluate their impact on the process response, and conclusions are drawn from them, and the results obtained are implemented. One of the experimental design methods is the response level method. In many processes, due to a large number of control variables and computational complexity, they cannot model mathematically correctly. In such cases, the use of experimental modeling methods is effective.

In the present study, by defining four independent variables in the experiment, about 30 experiments were performed. The parameters of aqueous solution concentration, time, adsorbent mass, and pH in removing cobalt from the aqueous solution were investigated using the central composite design (CCD) in the response surface methodology.

3.4.2.1. Effect of pH and Adsorption Time

To investigate the simultaneous effect of pH and adsorption time, the response surface methodology has been used. The results are presented in the form of three-dimensional lines and graphs. The defined range for pH is 1-7, and the limited range for adsorption time is 20-240 minutes. As shown in Fig.7, the adsorption of cobalt ions by the adsorbent increased with increasing pH to 5.5. It is because at low pH values due to the high positive charge density on the adsorbent surface, electrostatic repulsion occurs between the adsorbent surface and the cobalt ion. Optimal points for pH and adsorption time can be obtained by examining the saddle point of the graph.

The amount of solution pH plays an essential role in the process through the effect on the chemistry of the solution and the effect on the activity of the functional groups on the adsorbent surface⁴³⁻⁴⁵. In a certain range of pH, with increasing its amount, the amount of adsorption increases to a certain amount and then decreases. Thus, there is a favorable pH range for the adsorption of a metal ion from a given solution⁴⁶. The value of pH affects the adsorption phenomenon in two aspects: the solubility of the metal ion and the total charge on the adsorbent surface⁴⁷. Environmental acidity affects the ability of hydrogen ions to compete with metal cations to bind to active sites on the adsorbent surface. In a highly acidic environment (pH = 2), due to the high concentration and mobility of hydrogen ions and their easier adsorption than metal ions, the least amount of adsorption of metal cations occurs⁴⁷. Also, at higher pH, the dissolution rate of the metal complexes decreases to such an extent that sediment formation is possible that it may complicate the adsorption process. At higher pH values, fewer hydrogen

ions and more negatively charged ligands increase the adsorption of metal ions. In the adsorption process, highly acidic conditions are not favorable for any cation.

Fig.7

3.4.2.2. Effect of pH and Solution Concentration

Fig.8 showed the effect of concentration and pH parameters on the amount of cobalt ion adsorption under the conditions defined in design expert software. As shown in the diagrams, the maximum metal uptake occurs at concentrations between 20 and 30 mg/L, and pH between 4.5 and 5.5. At low concentrations, due to the low amount of cobalt ions in the solution, the adsorbent capacity to adsorb these ions is higher. The defined range for the concentration in Design Expert is between 20-100 mg/L.

As a rule, increasing the initial concentration of metal ions increases the adsorption capacity of the adsorbent by providing the driving force to overcome the mass transfer resistance between the solution and the solid phase. However, with increasing initial metal ion concentration, the adsorption efficiency of the metal ion by the adsorbent initially increases. It is because at low initial concentrations, the ratio of the initial moles of the metal ion to the available surface area of the adsorbent is low, so all ions are adsorbed, and adsorption is independent of the initial concentration. While at higher concentrations, the sites available for adsorption are less than the moles present in the solution and therefore the removal of metal ions is strongly dependent on the initial concentration. Also, due to the saturation of the active sites, more ions remain unadsorbed in the solution, which reduces the removal efficiency⁴⁷. From the point of view of mass transfer, the rate of adsorption due to higher concentrations increases because at higher values of initial concentration, the high concentration gradient between the soluble mass and the external surface of the adsorbent facilitates the transfer of foreign mass⁴⁸.

Fig.8

3.4.2.3. Effect of pH and Mass of Adsorbent

Using CCD analysis, the combined effect of adsorbent value and pH in three-dimensional and linear diagrams, respectively. The graph can be seen in Fig.9. As it is known, with increasing the amount of adsorbent, the absorption of cobalt ions also increases. The reason for this is that as the amount of adsorbent mass increases, the number of empty sites for adsorption of cobalt ions also increases, so the adsorption rate increases. According to the graphs, the maximum adsorption of cobalt ions occurs at pH between 4.5-5.5. Considering the combined effect of the pH parameter with other parameters, it can be seen that in this study, the optimal value of solution pH for all experiments is in the range of 4.5-5.5. The range defined in the software for the adsorbent mass was 0.04-0.1 mg. The amount of adsorbent actually provides the active sites for the adsorption of metal ions and determines the potential for the removal of metal ions at a given initial concentration. For a constant initial concentration and in most cases, less adsorbent results in greater adsorption capacity and vice versa lower removal efficiency. An increase in the amount of adsorbent increases the area of the adsorbent surface and consequently increases the number of active sites available. Under these conditions, the amount of adsorbate (removal efficiency) usually increases, but the amount of adsorbate per unit of adsorbent mass (adsorption capacity) decreases. The decrease in adsorption capacity is due to the fact that there is not enough adsorbed material to completely cover all exchangeable (empty) positions in the adsorbent, which is due to the simultaneous and complex effect of several factors.

Fig.9

3.4.2.4. Effect of Adsorption Time and Mass of Adsorbent

In this case, with increasing the amount of adsorbent and subsequently increasing the number of empty sites for metal ion adsorption, the adsorption rate increases. With growing time, more adsorption has occurred. As shown in Fig.10, the optimal contact time for the maximum absorption will be about 200 minutes. Determining the optimal contact time required to achieve

the highest rate of metal ion removal is one of the important factors in experiments. In general, the rate of adsorbate is rapid, but this rate decreases over time to reach equilibrium. At the beginning of the process, due to the larger available surface area, the removal rate is high. But over time, due to competition for less accessible active sites, the removal rate decreases.

Fig.10

3.4.2.5. Effect of Adsorption Time and Solution Concentration

As shown in the linear and three-dimensional diagrams (see Fig.11), with increasing time and at low concentrations, the adsorption rate has reached its maximum value, which seems reasonable for the reasons mentioned in the previous sections. The optimum values for the concentration and contact time parameters are about 20 mg/L and 200 minutes, respectively.

Fig.11

3.4.2.6. Effect Mass of Adsorbent and Solution Concentration

With increasing the amount of adsorbent, and increasing the empty sites of cobalt ion acceptor, and decreasing the concentration of the solution, the amount of adsorption reaches its maximum value (see Fig.12). The optimal amount of adsorbent in cobalt ion adsorption is about 0.1, and the optimal amount of cobalt solution concentration is about 20 mg/L.

Fig.12

3.5. Confirmation Experiment

To confirm the results of modeling using Design Expert software, several experiments with different adsorption conditions were performed, and their results were compared with the results obtained from modeling. The results predicted by the model and the experimental results, and the error rate are given in Table 4. As can be seen, there is a good correlation between the predicted results and the experimental results.

Table 4

3.6. Optimal Cobalt Adsorption Condition from the Model

One of the goals of RSM is to improve the process by finding optimal inputs, fixing problems and weaknesses of the process. The response level method is used as a statistical technique to optimize the output variable. In each experiment, input parameters are changed to check for changes in output, as well as parameters that do not have a significant impact on the experiment. The experiments will then be defined. In the next step, the results obtained from the software are statistically examined, and finally, the optimal value is calculated for each parameter in this experiment. The optimal conditions of the adsorption test by the adsorbent according to the software modeling are presented in Table 5. The obtained experimental results confirm the optimal absorption conditions by the software.

Table 5

4. Conclusion

Recently, due to the benefits of removing heavy metals from effluents, the synthesis of radiation grafting polymeric adsorbents has received much attention due to their advantages. In this study, GMA monomers were grafted to nonwoven polypropylene fabric to remove cobalt using gamma rays. Then, different amino groups (immunodic acetic acid, ethylenediamine, diethylamine, ethanolamine, triethylamine) were used to functionalize them. The adsorbents were analyzed with varying groups of amino to remove cobalt. Finally, the ethylenediamine amine group was selected for functionalization due to its high adsorption percentage. The polymer adsorbent was investigated under different adsorption conditions, including adsorption contact time, pH, adsorbent amount, and concentration of the cobalt-containing solution, using Design Expert software (response surface methodology). Finally, the optimal adsorption conditions were introduced and the results obtained from the model, and experimental results were analyzed. Experimental results well confirmed the predicted effects of the model. In optimum conditions (pH=4, mass= 0.07 g, t=182 min, and Co(II) concentration=40 mg/L), the removal efficiencies of cobalt ions were found as 93.49%. The

results showed that with GMA-radiation induced-grafted adsorbent and modified by ethylenediamine is a novel, inexpensive environmentally friendly and efficient adsorbent. Additionally, CCD method is an effective and powerful approach for the adsorbent optimization.

Reference

1. Bolisetty, S., Peydayesh, M. & Mezzenga, R. Sustainable technologies for water purification from heavy metals: review and analysis. *Chem. Soc. Rev.* **48**, 463-487 (2019).
2. Wang, N., Qiu, Y., Hu, K., Huang, C., Xiang, J., Li, H., Tang, J., Wang, J. & Xiao, T. One-step synthesis of cake-like biosorbents from plant biomass for the effective removal and recovery heavy metals: Effect of plant species and roles of xanthation. *Chemosphere*, **266**, 129129 (2021).
3. Sall, M. L., Diaw, A. K. D., Gningue-Sall, D., Efremova Aaron, S. & Aaron, J.J. Toxic heavy metals: impact on the environment and human health, and treatment with conducting organic polymers, a review. *Environ. Sci. Pollut. Res.* **27**, 29927-29942 (2020).
4. Rathi, B. S., Kumar, P. S. & Show, P.L. A review on effective removal of emerging contaminants from aquatic systems: Current trends and scope for further research. *J. Hazard. Mater.* **409**, 124413 (2021).
5. Fu, X., Beatty, D. N., Gaustad, G. G., Ceder, G., Roth, R., Kirchain, R. E., Bustamante, M., Babbitt, C. & Olivetti, E. A. Perspectives on cobalt supply through 2030 in the face of changing demand. *Environ. Sci. Technol.* **54**, 2985-2993 (2020).
6. Ma, Y., Tang, J., Wanaldi, R., Zhou, X., Wang, H., Zhou, C. & Yang, J. A promising selective recovery process of valuable metals from spent lithium ion batteries via reduction roasting and ammonia leaching. *J. Hazard. Mater.* **402**, 123491 (2021).

7. Narin, I. & Soylak, M. Enrichment and determinations of nickel (II), cadmium (II), copper (II), cobalt (II) and lead (II) ions in natural waters, table salts, tea and urine samples as pyrrolydine dithiocarbamate chelates by membrane filtration–flame atomic absorption spectrometry combination. *Analytica Chim. Acta* **493**, 205-212 (2003).
8. Eksteen, J., Oraby, E. & Nguyen, V. Leaching and ion exchange based recovery of nickel and cobalt from a low grade, serpentine-rich sulfide ore using an alkaline glycine lixiviant system. *Miner. Eng.* **145**, 106073 (2020).
9. Dhiman, S. & Gupta, B. Partition studies on cobalt and recycling of valuable metals from waste Li-ion batteries via solvent extraction and chemical precipitation. *J. Clean. Prod.* **225**, 820-832 (2019).
10. Charemtanyarak, L. Heavy metals removal by chemical coagulation and precipitation. *Water Sci. Technol.* **39**, 135-138 (1999).
11. Lupi, C., Pasquali, M., Dell’Era, A. Nickel and cobalt recycling from lithium-ion batteries by electrochemical processes. *Waste Manag.* **25**, 215-220 (2005).
12. Yazidi, A., Sellaoui, L., Badawi, M., Dotto, G. L., Bonilla-Petriciolet, A., Lamine, A. B. & Erto, A. Ternary adsorption of cobalt, nickel and methylene blue on a modified chitin: Phenomenological modeling and physical interpretation of the adsorption mechanism. *Inter. J. Biolog. Macromol.* **158**, 595-604 (2020).
13. Saleh, H. M., Moussa, H. R., El-Saied, F. A., Dawoud, M., El Said, A. N. & Wahed, R. S. A. Adsorption of cesium and cobalt onto dried *Myriophyllum spicatum* L. from radio-contaminated water: Experimental and theoretical study. *Prog. Nucl. Energy* **125**, 103393 (2020).
14. Zhang, M., Gu, P., Yan, S., Liu, Y. & Zhang, G. Effective removal of radioactive cobalt from aqueous solution by a layered metal sulfide adsorbent: Mechanism, adsorption performance, and practical application. *Sep. Purif. Technol.* **256**, 117775 (2021).

15. Xia, M., Chen, Z., Li, Y., Li, C., Ahmad, N. M., Cheema, W. A. & Zhu, S. Removal of Hg(II) in aqueous solutions through physical and chemical adsorption principles. *RSC Adv.* **9**, 20941-20953 (2019).
16. Brunauer, S. & Copeland, L. In *Physical adsorption of gases and vapors on solids*, Symposium on Properties of Surfaces, ASTM International (1963).
17. Ho, Y. & McKay, G. A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Safe Environ. Protect.* **76**, 332-340 (1998).
18. Barakat, M. New trends in removing heavy metals from industrial wastewater. *Arabian J. Chem.* **4**, 361-377 (2011).
19. Peters, R. W., Ku, Y. & Bhattacharyya, D. In *Evaluation of recent treatment techniques for removal of heavy metals from industrial wastewaters*, AIChE J. 165-203 (1985).
20. Linsen, B. G., Physical and chemical aspects of adsorbents and catalysts. *Phys. Bull.* **21**, 559 (1970).
21. Kim, J., Tsouris, C., Mayes, R. T., Oyola, Y., Saito, T., Janke, C. J., Dai, S., Schneider, E. & Sachde, D. Recovery of uranium from seawater: a review of current status and future research needs. *Sep. Sci. Technol.* **48**, 367-387 (2013).
22. Nasef, M. M. & Güven, O. Radiation-grafted copolymers for separation and purification purposes: Status, challenges and future directions. *Prog. Polym. Sci.* **37**, 1597-1656 (2012).
23. Vega-Hernández, M. Á., Cano-Díaz, G. S., Vivaldo-Lima, E., Rosas-Aburto, A., Hernández-Luna, M. G., Martínez, A., Palacios-Alquisira, J., Mohammadi, Y. & Penlidis, A. A Review on the Synthesis, Characterization, and Modeling of Polymer Grafting. *Processes* **9**, 375-469 (2021).
24. Tahir, M., Raza, A., Nasir, A. & Yasin, T. Radiation induced graft polymerization of glycidyl methacrylate onto sepiolite. *Rad. Phys. Chem.* **179**, 109259 (2021).

25. Ueki, Y. & Seko, N. Synthesis of Fibrous Metal Adsorbent with a Piperazinyl-Dithiocarbamate Group by Radiation-Induced Grafting and Its Performance. *ACS Omega* **5**, 2947-2956 (2020).
26. Omichi, M., Ueki, Y., Seko, N. & Maekawa, Y. Development of a Simplified Radiation-Induced Emulsion Graft Polymerization Method and Its Application to the Fabrication of a Heavy Metal Adsorbent. *Polymers* **11**, 1373-1384 (2019).
27. Hegazy, E.S. A., El-Rehim, H. A. A. & Shawky, H. A. Investigations and characterization of radiation grafted copolymers for possible practical use in waste water treatment. *Radiation Phys. Chem.* **57**, 85-95 (2000).
28. Othman, N. A. F., Selambakkannu, S., Abdullah, T. A. T., Hoshina, H., Sattayaporn, S. & Seko, N. Selectivity of copper by amine-based ion recognition polymer adsorbent with different aliphatic amines. *Polymers* **11**, 1994 (2019).
29. Ibrahim, S. M., El-Salmawi, K. M., & El-Naggar, A. A. Use of radiation grafting of polyethylene-coated polypropylene nonwoven fabric by acrylamide for the removal of heavy metal ions from wastewaters. *J. Appl. Polym. Sci.* **102**, 3240-3245 (2006).
30. Nasef, M., Saidi, H., Ujang, Z. & Dahlan, K. Z. M. Removal of metal ions from aqueous solutions using crosslinked polyethylene-GTMFJ-polystyrene sulfonic acid adsorbent prepared by radiation grafting. *J. Chilean Chem. Soc.* **55**, 421-427 (2010).
31. Yang, J., Ma, C., Tao, J., Li, J., Du, K., Wei, Z., Chen, C., Wang, Z., Zhao, C. & Ma, M. Optimization of polyvinylamine-modified nanocellulose for chlorpyrifos adsorption by central composite design. *Carbohydrate Polymers*, **245**, 116542 (2020).
32. Karoui, S., Arfi, R. B., Mougin, K., Ghorbal, A., Assadi, A. A. & Amrane, A. Synthesis of novel biocomposite powder for simultaneous removal of hazardous ciprofloxacin and methylene blue: Central composite design, kinetic and isotherm studies using Brouers-Sotolongo family models. *J. Hazard. Mater.* **378**, 121675 (2021).

33. Javadian, H., Ruiz, M. & MariaSastre, A. Response surface methodology based on central composite design for simultaneous adsorption of rare earth elements using nanoporous calcium alginate/carboxymethyl chitosan microbiocomposite powder containing Ni_{0.2}Zn_{0.2}Fe_{2.6}O₄ magnetic nanoparticles: Batch and column studies. *Intern. J. Biolog. Macromol.* **154**, 937-953 (2020).
34. Garg, U. K., Kaur, M., Garg, V. & Sud, D. Removal of nickel (II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach. *Bioresource Technol.* **99**, 1325-1331 (2008).
35. Kavaklı, P. A., Kavaklı, C. & Güven, O. Preparation and characterization of Fe (III)-loaded iminodiacetic acid modified GMA grafted nonwoven fabric adsorbent for anion adsorption. *Radiat. Phys. Chem.* **94**, 105-110 (2014).
36. Zhou, W., Apkarian, R., Wang, Z. L., Joy, D. Fundamentals of scanning electron microscopy (SEM). In *Scanning microscopy for nanotechnology*, Springer, pp 1-40 (2006).
37. Bower, N. W. Principles of instrumental analysis. In ACS Publications: New York (1992).
38. Choi, S. H., Lee, K. P. & Nho, Y. C. Adsorption of urokinase by polypropylene films with various amine groups. *J. Appl. Polym. Sci.* **80**, 2851-2858 (2001).
39. Bondar, Y., Kim, H. J., Yoon, S. H. & Lim, Y. J. Synthesis of cation-exchange adsorbent for anchoring metal ions by modification of poly (glycidyl methacrylate) chains grafted onto polypropylene fabric. *React. Funct. Poly.* **58**, 43-51 (2004).
40. Zhuang, L., Chen, S., Lin, R. & Xu, X. Preparation of a solid amine adsorbent based on polypropylene fiber and its performance for CO₂ capture. *J. Mater. Res* **28**, 2881-2889 (2013).
41. Nasef, M. M., Abbasi, A. & Ting, T. New CO₂ adsorbent containing aminated poly (glycidyl methacrylate) grafted onto irradiated PE-PP nonwoven sheet. *Rad. Phys. Chem.* **103**, 72-74 (2014).

42. Berthomieu, C. & Hienerwadel, R. Fourier transform infrared (FTIR) spectroscopy. *Photosynthesis Res.* **101**, 157-170 (2009).
43. Vijayaraghavan, K. & Yun, Y.S., Bacterial biosorbents and biosorption. *Biotechnol. Adv.* **26**, 266-291 (2008).
44. Sar, P., Kazy, S. K. & D'Souza, S. F. Radionuclide remediation using a bacterial biosorbent. *Inter. Biodeteriorat. Biodegradat.* **54**, 193-202 (2004).
45. Choi, J., Lee, J. Y. & Yang, J.S. Biosorption of heavy metals and uranium by starfish and *Pseudomonas putida*. *J. Hazard. Mater.* **161**, 157-162 (2009).
46. Ahmaruzzaman, M. Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Adv. Colloid Inter. Sci.* **166**, 36-59 (2011).
47. Kotrba, P., Mackova, M. & Urbánek, V. *Microbial biosorption of metals—general introduction*. Springer, New York (2011).
48. Dotto, G. L., Buriol, C. & Pinto, L. A. A. Diffusional mass transfer model for the adsorption of food dyes on chitosan films. *Chem. Eng. Res. Des.* **92**, 2324-2332 (2014).

Figure Captions:

Fig.1. Various physical, chemical, and biological mechanisms for removal heavy metal ions

Fig.2. Amination percentage of the modified adsorbent with different amines

Fig.3. (a) Infrared spectra analysis of PP-nonwoven fabric; (b) Infrared spectra analysis of amine group modified PP-g-(GMA-co- H_2PO_3)

Fig.4. Real, microscopic and SEM images of PP-nonwoven fabric

Fig.5. Real, microscopic and SEM images of amine group modified PP-g-(GMA-co-diethyleneamine)

Fig.6. Percentage of cobalt absorption at 25 ° C

Fig.7. (a) 3D plot and (b) contour plot showing effect of adsorption time and pH on percentage adsorption of cobalt (II) ions (gram of adsorbent=0.06 g; Co(II) ions in aqueous solution=60 ppm)

Fig.8. (a) 3D plot and (b) contour plot showing effect of solution concentration and pH on percentage adsorption of cobalt (II) ions (gram of adsorbent=0.06 g; time=130 min)

Fig.9. (a) 3D plot and (b) contour plot showing effect of adsorbent mass and pH on percentage adsorption of cobalt (II) ions (time=130 min; Co(II) ions in aqueous solution=60 ppm)

Fig.10. (a) 3D plot and (b) contour plot showing effect of adsorbent mass and adsorption time on percentage adsorption of cobalt (II) ions (pH=4; Co(II) ions in aqueous solution=60 ppm)

Fig.11. (a) 3D plot and (b) contour plot showing effect of concentration and adsorption time on percentage adsorption of cobalt (II) ions (pH=4; gram of adsorbent=0.06 g)

Fig.12. (a) 3D plot and (b) contour plot showing effect of concentration and adsorbent mass on percentage adsorption of cobalt (II) ions (pH=4; time=130 min)

Table Captions:

Table 1. Experimental range of independent variables

Table 2. The defined CCD layout for four independent variables

Table 3. Analysis of variance (ANOVA) for quadratic model for cobalt adsorption

Table 4. Comparison of cobalt adsorption results from modeling and experimental

Table 5. Optimal cobalt adsorption conditions from the model

Table 1. Experimental range of independent variables

Independent variable	Low Actual	High Actual	Mean
time (min)	20	240	130
concentration (ppm)	20	100	60
pH	1	7	4
mass of adsorbent (mg)	0.04	0.08	0.06

Table 2. The defined CCD layout for four independent variables

Trial no.	Time (min)	Concentration (ppm)	pH	Mass of adsorbent (mg)	Adsorption (%)
1	130	60	7	0.06	80.64
2	130	60	4	0.02	47.08
3	130	60	4	0.06	82.77
4	20	60	4	0.06	73.61
5	130	60	1	0.06	2.87
6	85	40	5.5	0.04	83.40
7	175	40	5.5	0.08	86.40
8	130	60	4	0.06	82.50
9	130	60	4	0.06	81.82
10	75	80	2.5	0.04	26.58
11	75	80	5.5	0.04	50.91
12	185	40	2.5	0.08	93.72
13	240	60	4	0.06	83.45
14	130	20	4	0.06	100
15	185	80	5.5	0.04	51.73
16	75	40	5.5	0.04	75.71
17	185	40	2.5	0.04	62.13
18	130	60	4	0.06	83.45
19	185	80	2.5	0.04	32.35
20	130	60	4	0.10	90.37
21	75	80	5.5	0.08	79.07
22	185	40	5.5	0.08	96.36
23	130	60	4	0.06	83.04
24	130	60	4	0.06	82.77
25	75	80	2.5	0.08	72.48
26	75	40	2.5	0.08	83.26
27	75	40	2.5	0.04	48.12
28	185	80	2.5	0.08	74.89
29	130	100	4	0.06	61.89
30	185	80	5.5	0.08	85.26

Table 3. Analysis of variance (ANOVA) for quadratic model for cobalt adsorption

Sources of variation	Sum of squares	DF	Mean square	F-value	Probability > F
Model	13500.83	14	964.34	15.30	<0.0001
Residual	945.29	15	63.02		
Lack of fit	943.79	10	94.38	315.15	<0.0001
Pure error	1.5	5	0.3		
Total	14446.12	29			

$R^2 = 0.9346$; DF= Degree of freedom

Table 4. Comparison of cobalt adsorption results from modeling and experimental

Adsorption conditions	Response of model (%)	Response of experimental (%)	Error (%)
Time= 70 Concentration= 21.06 pH= 4 mass of adsorption= 0.05	88.53	81.85	8.1
Time=120 Concentration= 66.69 pH=4 mass of adsorption= 0.06	78.95	79.51	0.7
Time=182 Concentration= 44.1 pH=4.5 mass of adsorption= 0.07	100	93.5	6.9
Time=90 Concentration= 64.46 pH=4 mass of adsorption= 0.05	70.05	69.81	0.3
Time=71 Concentration= 27.76 pH=3.5 mass of adsorption= 0.03	64.77	60.12	7.7
Time=150 Concentration= 89.91 pH=6 mass of adsorption= 0.08	75.81	81.33	6.7
Time=150 Concentration= 98.48 pH=2.5 mass of adsorption= 0.08	63.28	70.89	10.7

Table 5. Optimal cobalt adsorption conditions from the model

Parameters	Time (min)	Concentration (ppm)	pH	mass of adsorption (gr)	Response (%)
Suggested solution	182	40	4.5	0.07	100
Actual results obtained after confirmation experiments	182	40	4.5	0.07	93.49

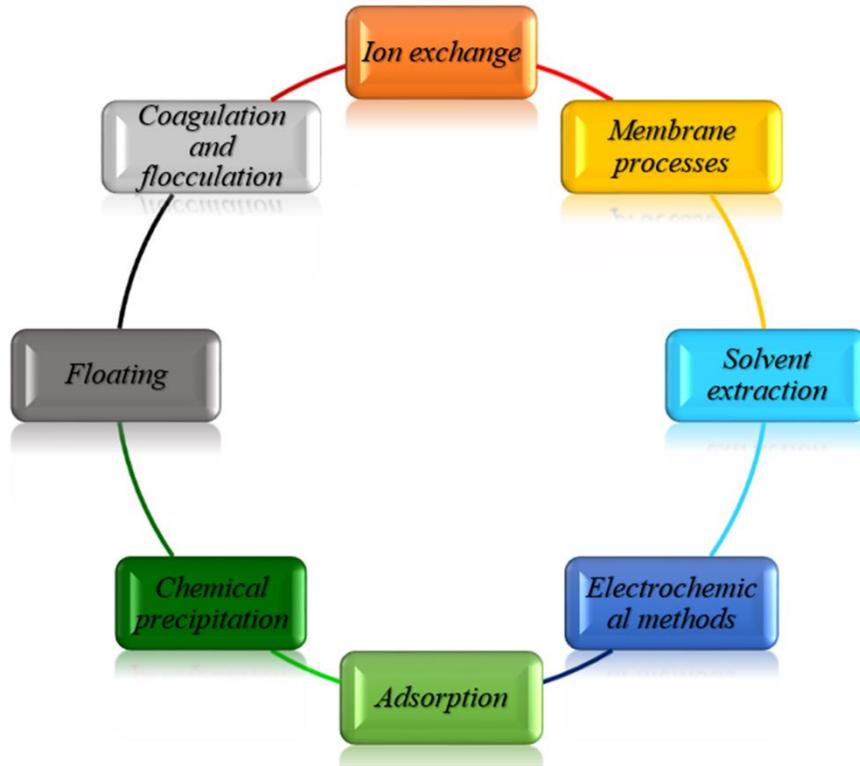


Fig.1. Various physical, chemical, and biological mechanisms for removal heavy metal ions

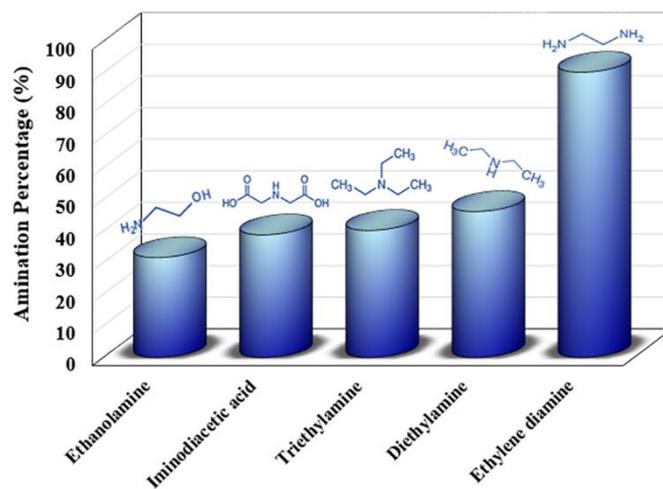


Fig.2. Amination percentage of the modified adsorbent with different amines

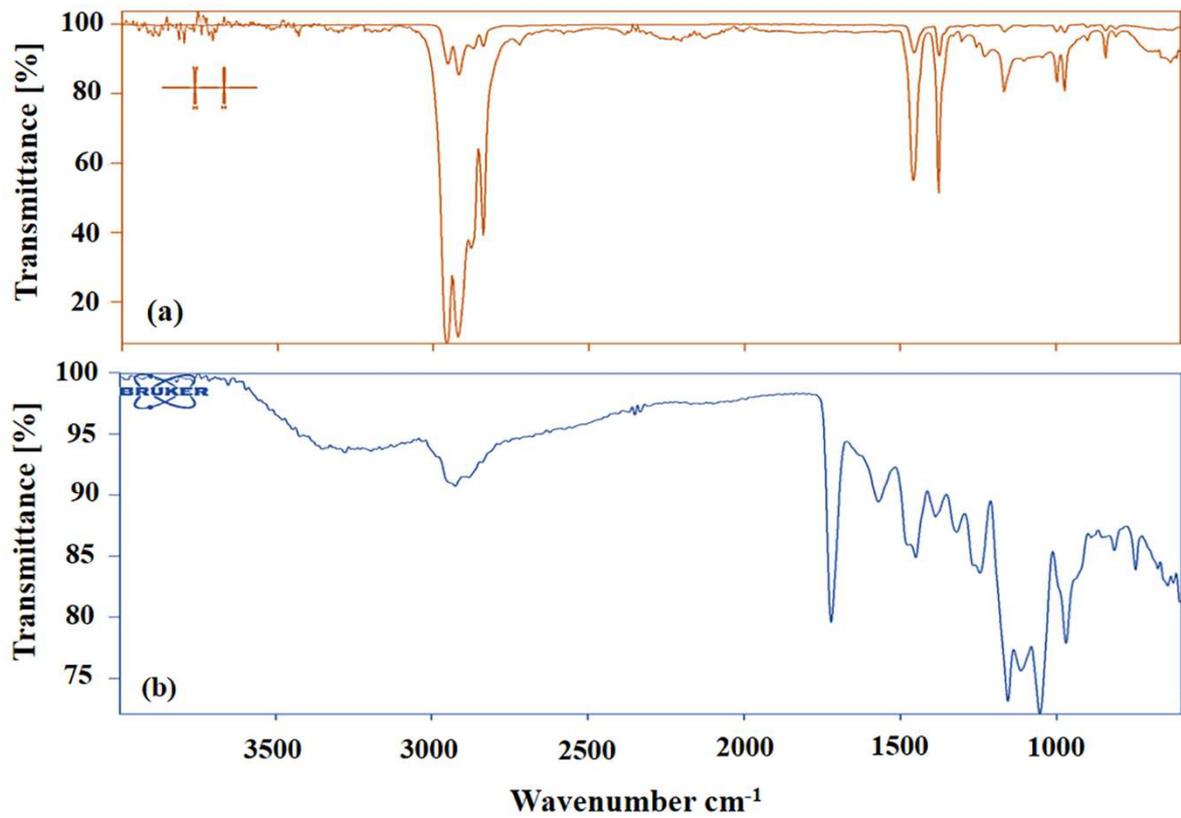


Fig.3. (a) Infrared spectra analysis of PP-nonwoven fabric; (b) Infrared spectra analysis of amine group modified PP-g-(GMA-co- H₂PO₃)

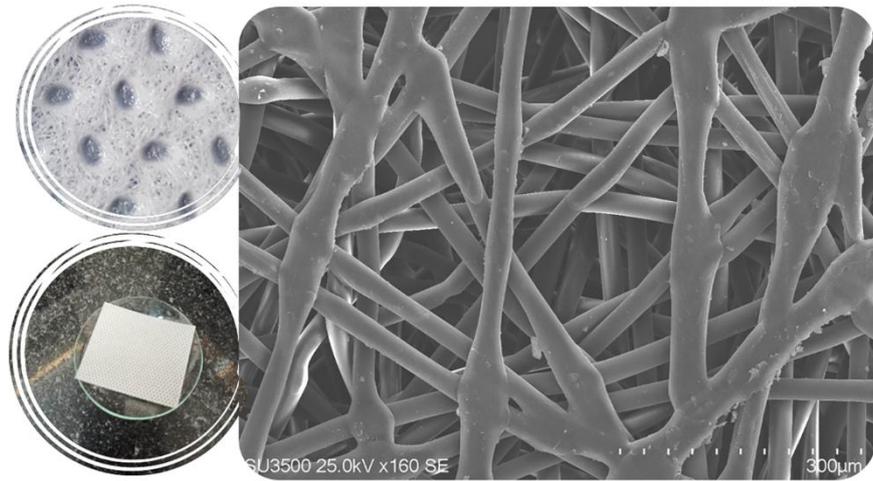


Fig.4. Real, microscopic and SEM images of PP-nonwoven fabric



Fig.5. Real, microscopic and SEM images of amine group modified PP-g-(GMA-co-H₂PO₃)

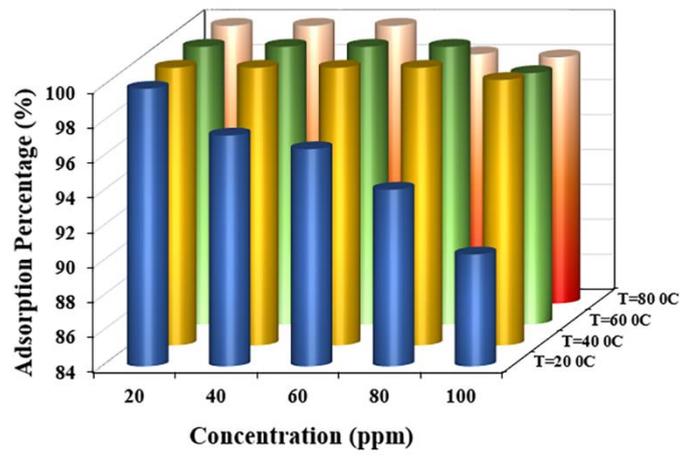


Fig.6. Percentage of cobalt absorption at 25 ° C

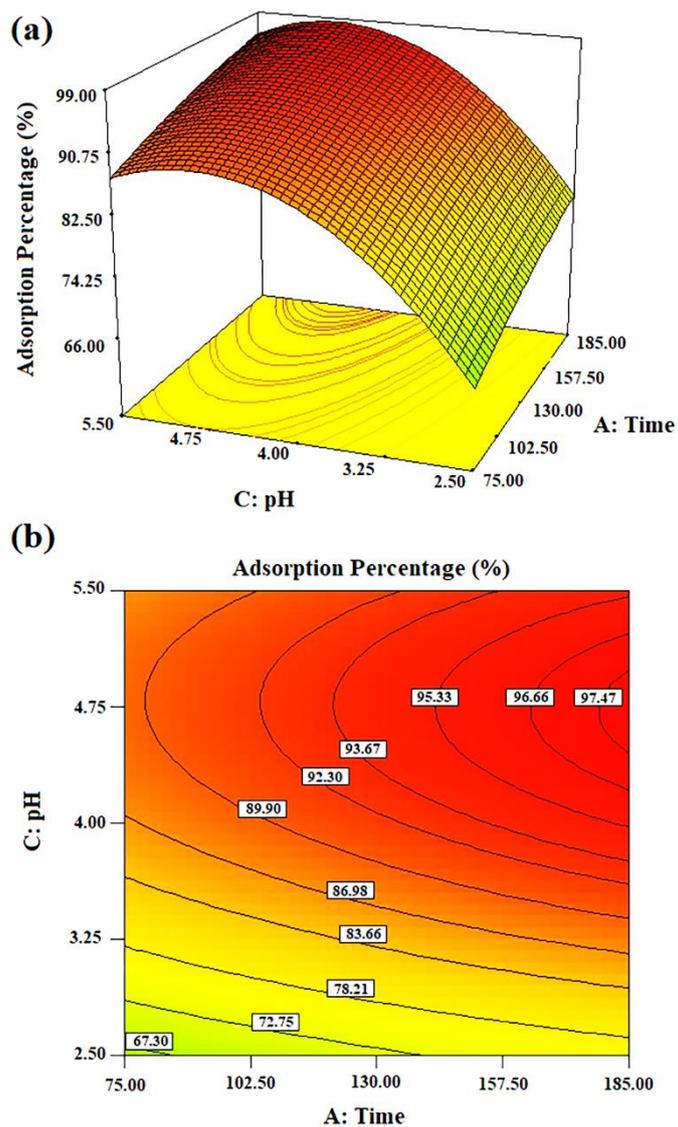


Fig.7. (a) 3D plot and (b) contour plot showing effect of adsorption time and pH on percentage adsorption of cobalt (II) ions (gram of adsorbent=0.06 g; Co(II) ions in aqueous solution=60 ppm)

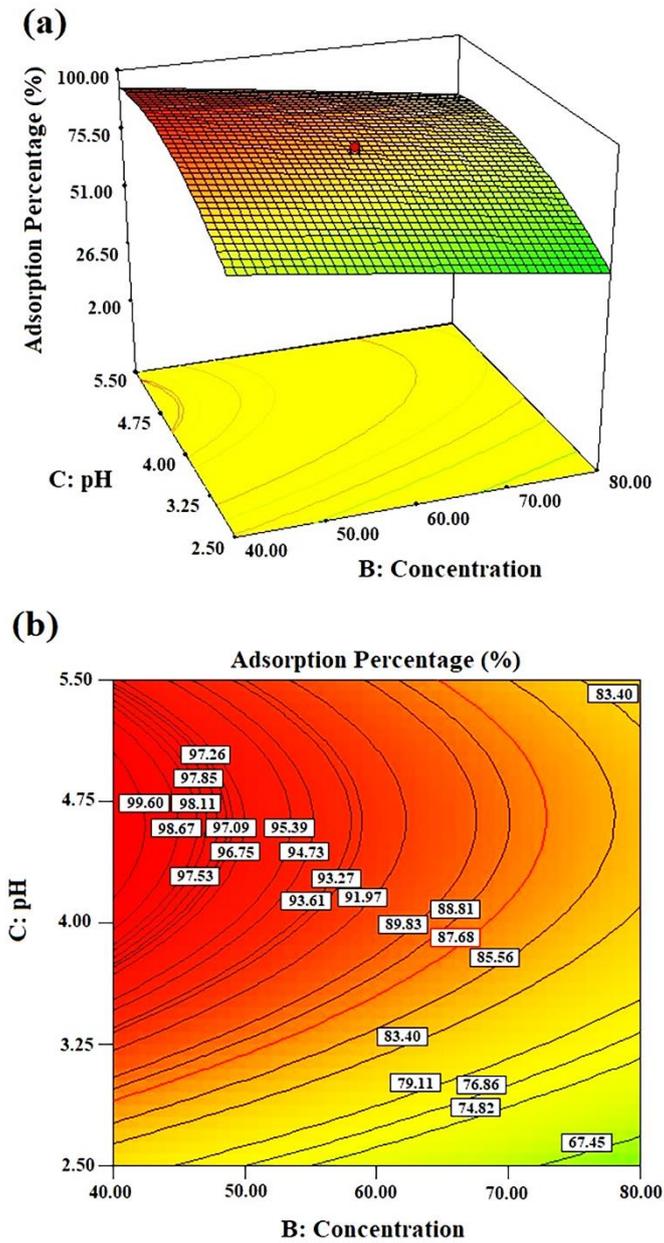


Fig.8. (a) 3D plot and (b) contour plot showing effect of solution concentration and pH on percentage adsorption of cobalt (II) ions (gram of adsorbent=0.06 g; time=130 min)

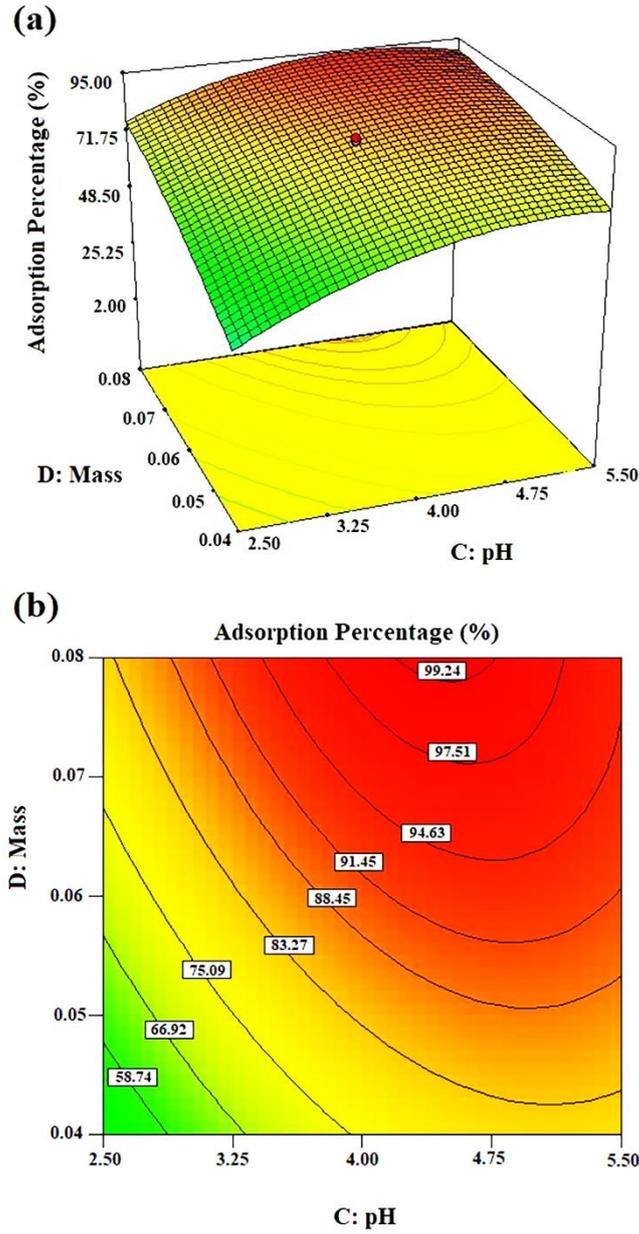


Fig.9. (a) 3D plot and (b) contour plot showing effect of adsorbent mass and pH on percentage adsorption of cobalt (II) ions (time=130 min; Co(II) ions in aqueous solution=60 ppm)

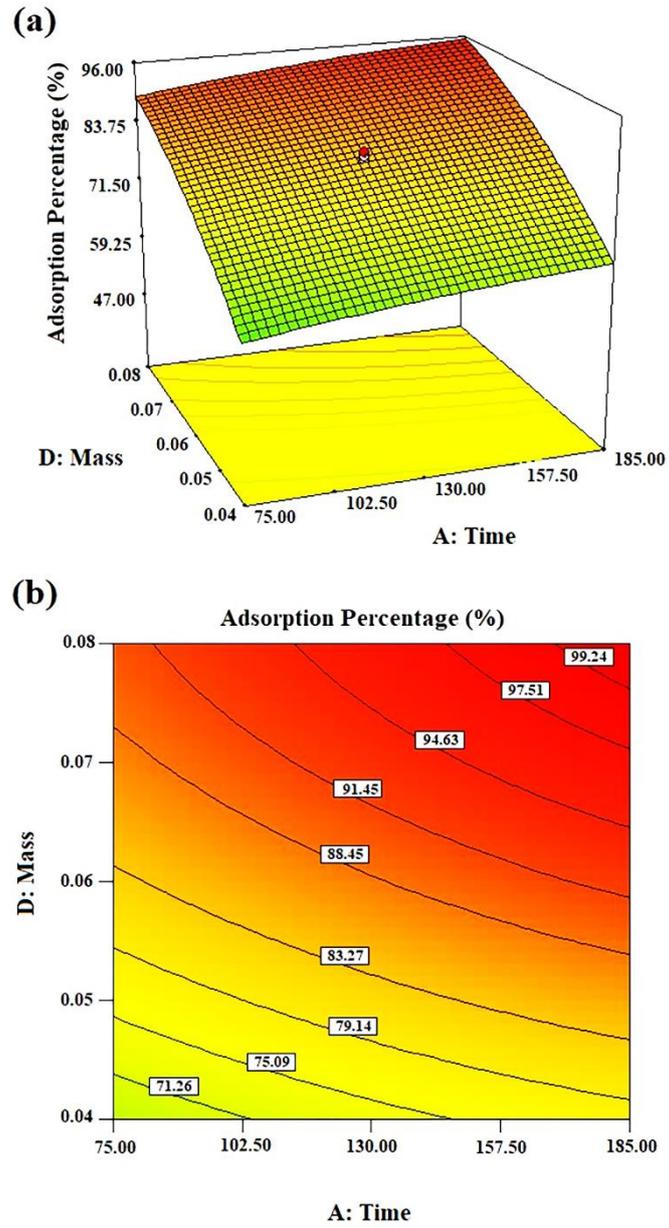


Fig.10. (a) 3D plot and (b) contour plot showing effect of adsorbent mass and adsorption time on percentage adsorption of cobalt (II) ions (pH=4; Co(II) ions in aqueous solution=60 ppm)

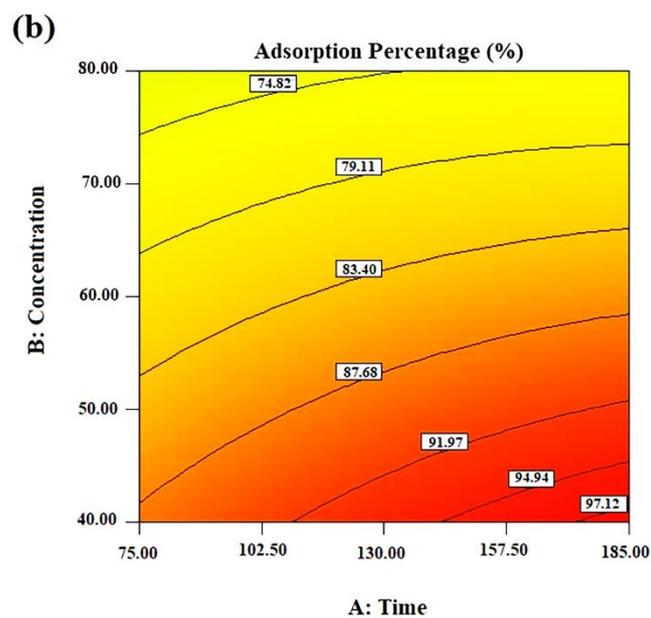
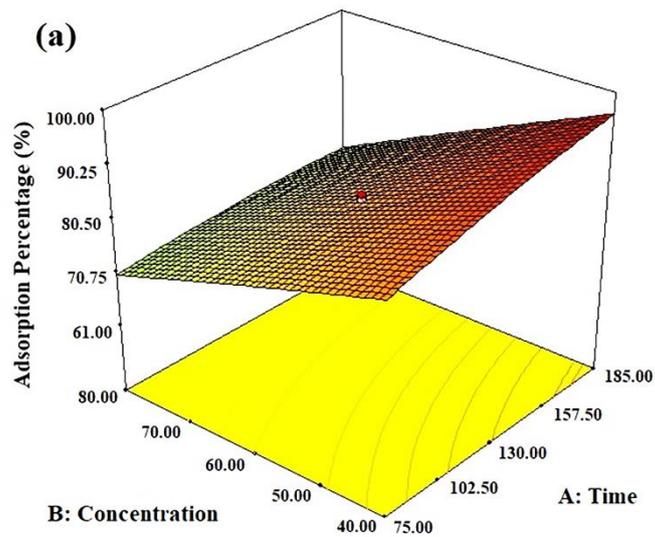


Fig.11. (a) 3D plot and (b) contour plot showing effect of concentration and adsorption time on percentage adsorption of cobalt (II) ions (pH=4; gram of adsorbent=0.06 g)

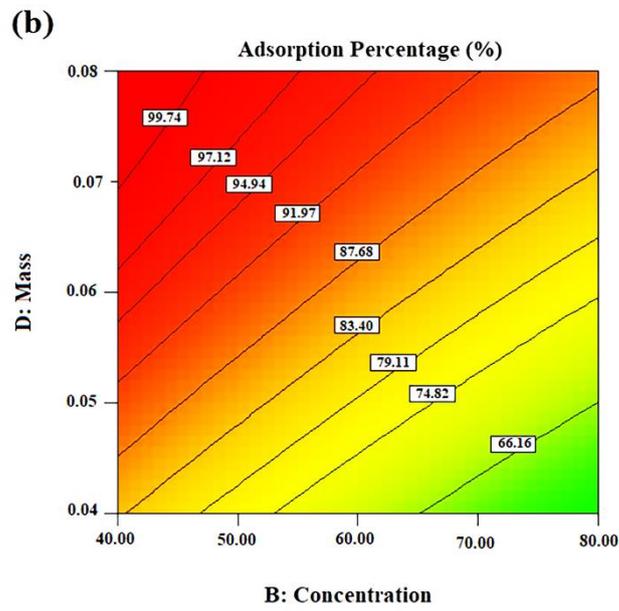
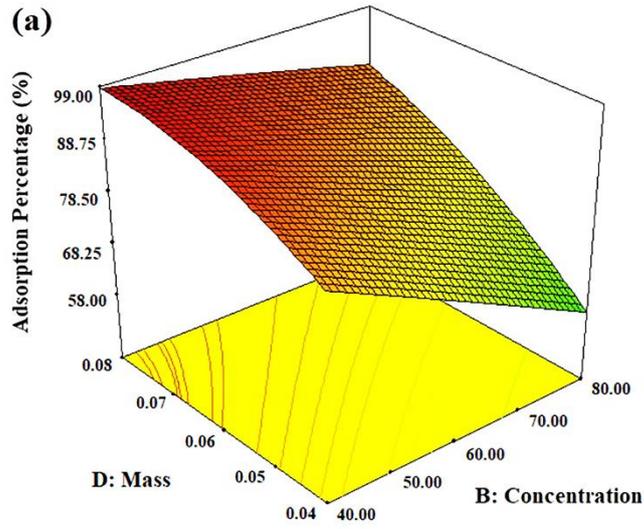


Fig.12. (a) 3D plot and (b) contour plot showing effect of concentration and adsorbent mass on percentage adsorption of cobalt (II) ions (pH=4; time=130 min)