Removal of Some Hazardous Materials from Their Solutions Using Active Carbon-Filled Poly Vinyl Alcohol/*N*-vinyl Pyrrolidone Membrane Subjected to Freeze–Thawing and Gamma Irradiation

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ABSTRACT: Carbon membrane consisting of a mixture of powdered activated carbon and poly vinyl alcohol/*N*-vinyl pyrrolidone was made by single freezing and thawing followed by gamma-ray irradiation. The prepared membrane was characterized by X-ray diffraction, scanning electron microscopy, and gel content. The membrane was applied for adsorption of some hazardous wastes (acid dye, basic dye, heavy metal ions such as Co and Ni, dichromate anion, and phenols) from their solutions. From the results, it was found that the prepared membrane possesses greater efficiency toward removal of heavy metal ions than powdered activated carbon, whereas their adsorption capacity toward dyes and phenol is almost the same as active carbon. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 149–156, 2009

Key words: activated carbon; *N*-vinyl pyrrolidone; poly vinyl alcohol; freeze–thawing; gamma irradiation

INTRODUCTION

The use of carbons results primarily from their big specific surface area, high pore volume, microporosity, etc. However, a further advancement in the application of porous carbons, and more specifically activated carbons, in adsorption, catalysis, or electrochemical processes make use of their surface chemistry.[1–3] The strategy of polymer coating is widely utilized to modify the surface properties of activated carbons to improve their dispersibility in water.[4] Various types of carbon membranes have been prepared from polyvinylidene chloride-acrylate terpolymer,[5] acrylonitrile-methylmethacrylate copolymer,[6] and polypyrrolone.[7] In the case of activated carbons, the chemistry is mostly related to the nature and concentration of heteroatoms, which can be both substituted for carbon in the graphene layer and/or attached at the layer edges as functional groups. Some authors[8] consider a pyrone-like structure as the most important basic functionalities in common porous carbons.

The main interest in enrichment of porous carbons in nitrogen is to induce basicity to the surface. The basic nitrogen sites contribute essentially to the superior characteristics of activated carbons when used in the adsorption of transition metal cations.[9]

The use of polyvinyl pyrrolidone (PVP) was justified by the thermal stability of nitrogen and the expected affinity of *N*-vinyl pyrrolidone (NVP) to aromatics in nature pitch components.[10] Many authors used poly vinyl alcohol (PVA) to encapsulate the pulverized carbon black particles because of its special water solubility–temperature relationship.[4] Grafting of polymers onto the surface of carbon has been proved to be an effective method for surface modification of activated carbon: Tsubokawa[11–13] reported a series of approaches for grafting of polymers onto carbon surface.

In this study, we have prepared a series of activated carbon-filled PVA/NVP membranes synthesized by "freezing and thawing" procedure and radiation crosslinking process, where the prepared membrane was evaluated for removal of acidic dye, basic dye, Cr from potassium dichromate, heavy metal ions (Co and Ni), and phenols from their solutions.

MATERIALS AND METHODS

Materials

PVA with a molecular weight of 17,000 kDa and saponification degree of 99.85% was supplied by D-MiD Gel Koysna (Monofiya, Egypt). NVP was supplied by Aldrich. Powdered activated carbon (PAC; 100–150 mesh size) was supplied by EL-gomohoria (Cairo, Egypt). Preliminary experimenting showed

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that the employed active carbon sample contains <1%. This finding was reached by burning a known weight of this active carbon sample at 800°C in an open atmosphere for 5 h. The ash left was found to be negligibly small (<0.01%).
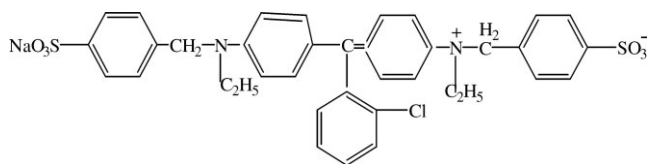
Basic dye

Basic Violet 7 (Astrazon Red 6B), molecular formula ($C_{24}H_{30}N_2Cl_2$), molecular weight (416), was supplied by Dystar (Cairo, Egypt).
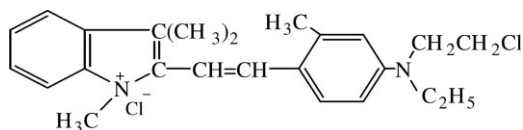
Acid dye

Acid (Acid Green B)

Ni(NO_3)$_2$·6H_2O and Co(NO_3)$_2$·6H_2O, $K_2Cr_2O_7$·7H_2O were supplied by EL-gomohoria. Phenol is Gc grade supplied by Merck (Germany).

Preparation of activated carbon PVA/NVP membranes

A mixture of equimolar proportions of PVA/NVP was dissolved in distilled water followed by heating at 90°C to achieve 15% polymer solution.[14] Then, a given amount of activated carbon (4, 6, 8, and 10 wt %) was added with continuous stirring at room temperature to form a homogeneous mixture. The mixture was poured into Petri dishes to a height of 3 mm, and then the dishes were sealed with parafilm. The freezing and thawing method involved freezing aqueous PVA/NVP activated carbon mixture in mold for 1 h in the freezer at −40°C and then allowing it to thaw at 25°C for 1 h. The PVA/NVP/activated carbon gel formed through "freezing and thawing" was exposed to [60]Co γ-rays at ambient temperature.

Techniques

Measurements of gel content

To measure the gel content, the prepared activated carbon PVA/PVP samples irradiated to different

irradiation doses and activated carbon composition were placed in 200-mesh stainless steel net and washed with distilled water three times after extraction in distilled water at 80°C for 24 h. The remaining gel was dried to constant weight. The gel content was measured gravimetrically as follows:

$$\text{Gelation } \% = \frac{W_d}{W_0} \times 100,$$

where W_d is the weight of dry sample after extraction, and W_0 is the initial weight of carbon membrane.

X-ray diffraction

X-ray diffraction (XRDs) of different solids calcined at 400 and 600°C were performed by using a Bruker diffractometer (Bruker D8 advance target). The patterns were run with Cu Kα with a second monochromator (λ = 1.5405 Å) at 40 kV and 40 mA at a scanning speed of 2° and 2θ min^{-1}.

Scanning electron microscopic measurements

The scanning electron microscopic (SEM) images of the prepared carbon membrane were recorded by using a JEOL SEM-25 (Japan) at the required magnification.

Spectrophotometric analysis of different substrates

The concentration of dichromate anion, acid dye, and basic dye was determined by measuring the absorbance at wavelengths of 540, 540, and 636 nm, respectively. Optical density measurements were performed against blanks of individual solvent at room temperature (25°C). The instrument with a double-beam ultraviolet visible spectrophotometer Unicam UV2 was used.

Gas chromatographic analysis

Hewlett Packard 5890 gas with an HP, 30-m capillary column, injector 150°C, oven, 60°C isotherm, flame ionization detector 150°C, and nitrogen as carrier gas flowing at a rate of 20 mL min^{-1} was used for analysis of phenol at concentrated 500 mg L^{-1}. The investigated samples were introduced in microquantity (1.2×10^{-3} cm^3) by the aid of a microsyringe in the form of pulse into the instrument. The reaction was transferred directly by inert gas (nitrogen) to the gas chromatograph.
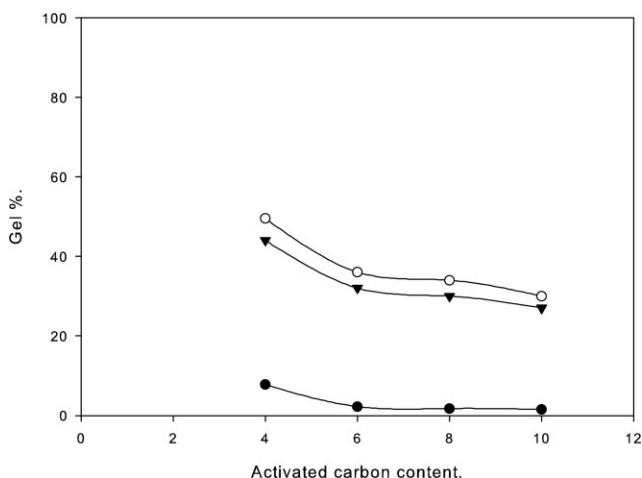
Figure 1 Gel content of PVA/PVP membranes as a function of the activated carbon concentration (4, 6, 8, and 10%) under different irradiation doses after freezing and thawing.

Determination of dichromate removed from its aqueous solution by the investigated activated carbon PVA/PVP

The sample (1 mL) containing different concentrations of Cr(VI) was mixed with 3.3 mL of 0.2M H$_2$SO$_4$, and 1 mL of 1,5 diphenyl carbazide was prepared by dissolving 250 mg in 50-mL acetone stored in a brown bottle and discarded when solution becomes discolored. After 10 min, the pink-violet color solution was analyzed for Cr^{6+} ions at 540 nm.[15]

Hazardous pollutants measurements

Stock solutions of the dyes, dichromate, and heavy metal ions containing 1000 mg L^{-1} in bidistilled water were prepared, whereas phenol was dissolved in ethanol. Dried, prepared activated carbon membranes of 0.1 g weight were immersed into 10 mL volume of the pollutants of different concentrations

at 25°C for 24 h. The amounts of dye adsorbed (acid, basic dye) and dichromate were determined from the initial and final concentration of the solutions, calculated from the measured absorbance after the desired treatment period. The concentration of heavy metal ions was determined by using atomic absorption, whereas the concentration of the phenol was determined by gas chromatography.

RESULTS AND DISCUSSION

Crosslinking behavior of the activated carbon PVA/PVP membrane

Figure 1 shows gelation behavior of the prepared membranes as a function of activated carbon content for membranes exposed to different doses of γ-rays. It is seen from Figure 1 that the increases in the amount of active carbon in the membrane from 4 to 8 wt % much decreases the gel content. The increase in the concentration of active carbon above this limit up to 10 wt % resulted in no measurable carbon in the gel content. It can be also seen from Figure 1 that the exposure of the membranes investigated to a dose of 20 kGy led to a considerable increase in the gel content, which decreases slightly by a dose of 30 kGy. It is known that "freezing and thawing" of PVA results in the formation of crystallites, which serve as physical crosslinks to render the material insoluble in water.[14] The irradiation and "freezing and thawing" induced physical crosslinking of PVA/PVP. This is thought to be cause for high gelation of PVA/PVP. The activated carbon composition was found to affect the degree of gelation, because high activated carbon concentration resulted in the formation of viscous medium, which restricts grafting and consequently crosslinking of PVA/PVP and finally led to a low degree of gelation at high radiation dose. Furthermore, the carbon particles may dissipate γ-radiation energy leading to decrease in the intensity of γ-radiation doses on the membrane.
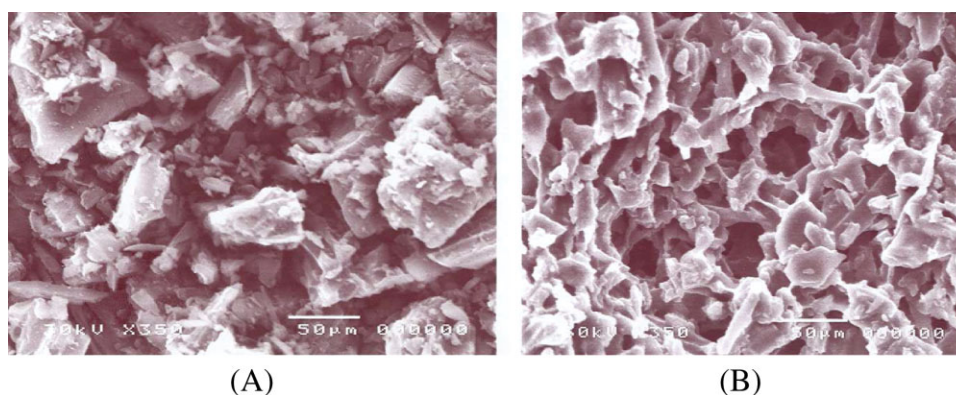

Figure 2 SEM of (A) PAC and (B) activated carbon PVA/PVP membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
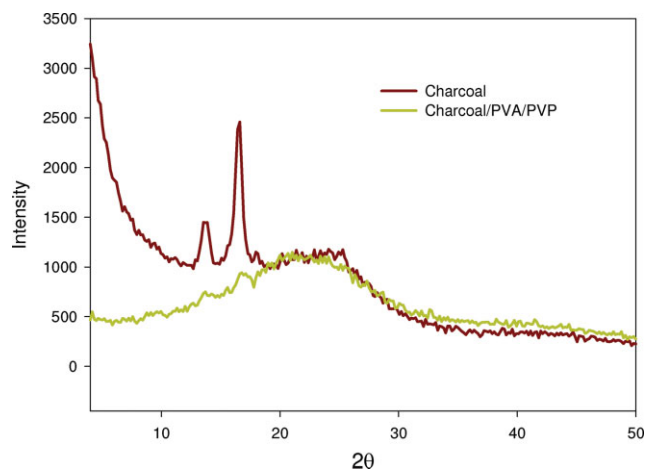
Figure 3 XRD of charcoal, charcoal/PVA/PVP membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Characterization of activated carbon PVA/PVP membrane

SEM

The SEM photograph of activated carbon [Fig. 2(A)] shows that carbon has a sponge-like structure due to the very high value of the fractal dimension; on the other hand, activated carbon PVA/PVP shows fractional and fragmented walls of the pores [Fig. 2(B)]. The PVA/PVP makes the interior of the pores expand uniformly and enhance the micropore area and hence the surface area.

XRD

The ash-free activated carbon should be amorphous in nature; its crystallization takes place by heating at an elevated temperature, around 3000°C, forming graphite. The fact that diffraction peaks were detected in the diffractogram of the employed activated carbon sample that has not been subjected to heating at an elevated temperature is indicative to the presence of some crystalline inorganic substrate having a crystalline structure. The identification of these substrates could be easily done via chemical analysis of the ash present in the carbon sample or directly by Edx analysis of the active carbon sample itself.[16] Figure 3 shows the disappearance of crystalline structure from the diffractogram with complete amorphous region, which indicates the substitution of pyron ring with inorganic substrate on the surface of carbon. This result was confirmed with Edx measurements, which showed the disappearance of sodium peak for the prepared membrane, which may be because of the complete substitution of pyran ring with sodium on the surface of activated carbon. In fact, it can be easily shown from Table 1 that the Edx results indicate the relative atomic abundance of

TABLE I
Edx Measurements for PAC and Active Carbon Filled with PVA/NVP

Sample	Na (at %)	P (at %)	Ca (at %)	Cu (at %)	Zn (at %)
PAC	24.3	46.96	4.79	14.24	9.78
Membrane	–	49.33	6.22	24.83	19.62

different elements present in activated carbon sample and the membrane contain active carbon filled with PVA/NVP. Examination of the results given in the table shows the following.

(1) The presence of active carbon in the prepared membrane led to complete disappearance of sodium as a result of a possible substitution of pyrron ring with sodium species. (2) The membrane formation did not affect the phosphorous content. (3) On the other hand, the membrane formation in the presence of active carbon led to a measurable increase in the concentration of Cu, Zn, and Ca species. It seems that the preparation of active carbon-containing film might be accompanied by a significant weight loss. This weight loss is normally followed up by an increase in the different cationic species present.

Adsorption of hazardous pollutants by PAC

Figure 4 shows the removal percentage of acid dye, basic dye, dichromate, phenol, Co, and Ni of initial concentration 500 mg L^{-1} by using powder-activated carbon. The results showed that the removal percentage of acid and basic dye was 80% and 85% at pH 3 and 10, respectively, whereas the removal percentage of dichromate was 12% at pH 3 and that of cobalt and nickel was 60% and 66% at pH 6, respectively, and the removal percentage of phenol was 95%.
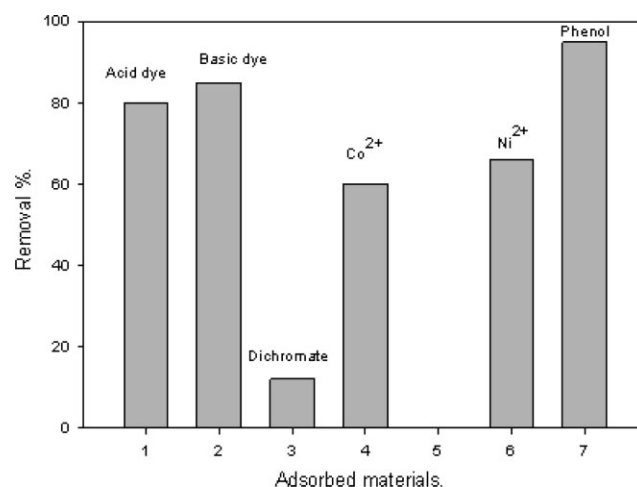

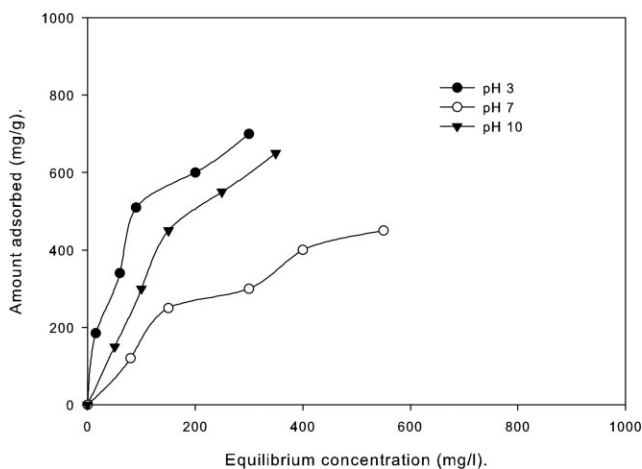**Figure 4** Removal percent of different pollutants by using powder-activated carbon.

Figure 5 Equilibrium isotherm for basic dye adsorption on activated carbon PVA/PVP at different pH values.

Adsorption of hazardous pollutants by activated carbon PVA/PVP

Several researchers have studied the liquid phase adsorption of high molecular weight compounds on mesopores carbons and demonstrated that the presence of mesopores together with microporous inactivated carbon enhances their adsorption capacities, particularly for large adsorbates.[17–21] These studies indicated that the pore size distributions of activated carbons are the key factor in determining how these materials are suitable for removal of giant molecules from water. The membrane medium-coated activated carbon was revealed to work well because adsorbed molecules of different pollutants can easily go into the membrane, as they diffuse in bulk water. This relatively rapid mass transfer is possible because of the small volume fraction of constituent PVP chains at a fully swollen state. For further improvement, mechanical durability of the membrane should be increased.

For the present purpose, PVA was expected to be suitable because PVA forms stable physically cross-linked gel simply by freezing and thawing, as previously reported.[22–24]

This study also aimed at the evaluation of sorption abilities of activated carbon PVA/PVP membrane (6% charcoal at 20 kGy) toward basic dye, acid dye, Co, Ni, dichromate anions, and phenol.

Adsorption of basic dye

Figure 5 shows the relationship between equilibrium concentration C_e (mg L^{-1}) and amount adsorbed (mg g^{-1}) at different pH values (pH 3, 7, 10). The dye sorption data are correlated with the theoretical model of Freundlich:

$$q_e = KC_e^{1/n},$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent (mg g^{-1}), and C_e is the equilibrium concentration of solute in the bulk solution (mg L^{-1}). The constants K and n can be related to the strength of the adsorptive bond and the bond distribution, respectively.[24] From Figure 5, it can be seen that the adsorption of basic dye increases at lower pH (pH 3) than at a higher pH value (pH 10). This behavior may be explained that the ionization of basic dye in acidic medium is higher than alkaline medium, resulting in bond formation with the C=O group of PVP. There can be many possible mechanisms for the adsorption of dyes, phenol, and heavy metal ions on the prepared activated carbon membrane: (a) ion dipole interaction; (b) the surface C=O group of the PVP and ─OH group of the phenol may form a hydrogen bond (Scheme 1); (c) CH─O─R bonding may be possible (Scheme 2);
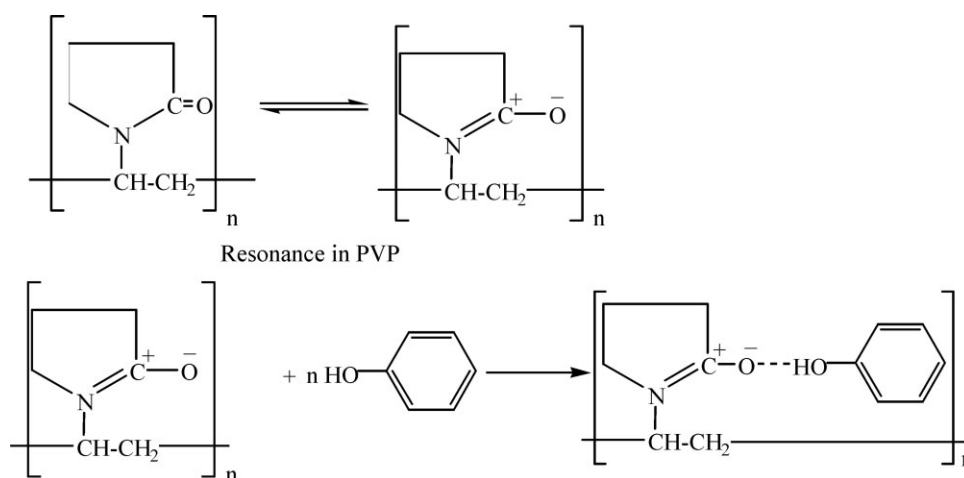
Scheme 1 Represents the resonance structure of NVP and the suggested mechanism for adsorption of phenol by NVP.
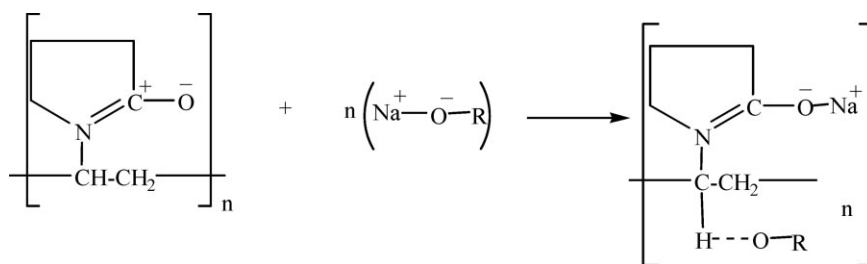
Scheme 2 Represents the suggested mechanism for adsorption of the dye by NVP.

and (d) the N atom in amide can make hydrogen bonds with the ─OH group of the phenol, but this mechanism is much less likely than the others.[25]

Adsorption of acid dye

Figure 6 shows the adsorption capacity of acid dye of initial concentration 1000 mg L^{-1} at different pH values (pH 3, 7, and 10). The maximum dye removal was 400, 550, and 750 mg L^{-1} at pH 3, 7, and 10, respectively. The high removal percent at pH 10 may be because of high ionization of sulfonate groups of the dye with the formation of hydrogen bonding with water molecules in the PVP hydrated shell[26] or by mechanism illustrated in Scheme 2. Furthermore, it was found that the equilibrium data for the adsorption of acid dye onto prepared membrane follow the Freundlich equation.

Adsorption of dichromate

Figure 7 shows the adsorption isotherm of Cr(VI) onto activated carbon PVA/PVP at different initial concentrations in the range of 100–500 mg L^{-1} and at different pH values (pH 3, 7, and 9). From this figure, it can be seen that the adsorption of Cr(VI) decreases with increasing initial concentrations and

the removal percent at 200 mg L^{-1} was 85%, whereas at a higher initial concentration of 500 mg L^{-1}, the removal percent was 10%. Therefore, the uptake of Cr(VI) is strongly concentration dependant and it can be seen that this uptake is higher for activated carbon PVA/PVP than that for PAC, due to its high degree of hydrophilicity, which allows better contact of the solute with the membrane surface.

Effect of pH on adsorption of Cr(VI). The effect of pH on the removal of Cr(VI) is investigated by testing three values of pH 3, 7, and 9 at a temperature 25°C ± 1°C and for all the experiments. The experimental results are presented in Figure 7. From this figure, it can be seen that the maximum adsorption of Cr(VI) occurs at the lowest pH value (pH 3). Indeed, pH has a strong effect on the removal of Cr(VI). This finding has been reported by several investigators,[27–29] who have found that Cr(VI) adsorption by activated carbon is enhanced in the acidic range of pH. As mentioned by Rao et al.,[29] the favorable effect of pH can be attributed to the neutralization of negative charge on the surface of adsorbents by excess hydrogen ions, thereby facilitating the diffusion of hydrogen chromate ions (HCrO$_4^-$) and their subsequent adsorption. Besides, according to diagram of Benefield et al.,[30] HCrO$_4^-$ is the dominant anionic form of Cr(VI) between pH 1.0 and 4.0. This
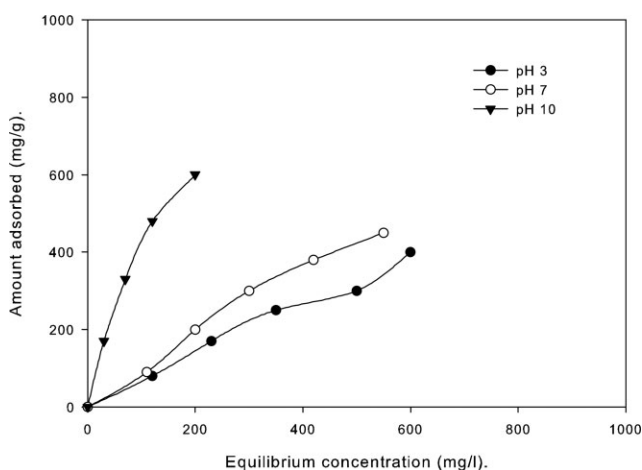

Figure 6 Equilibrium isotherm for acid dye adsorption on activated carbon PVA/PVP at different pH values.
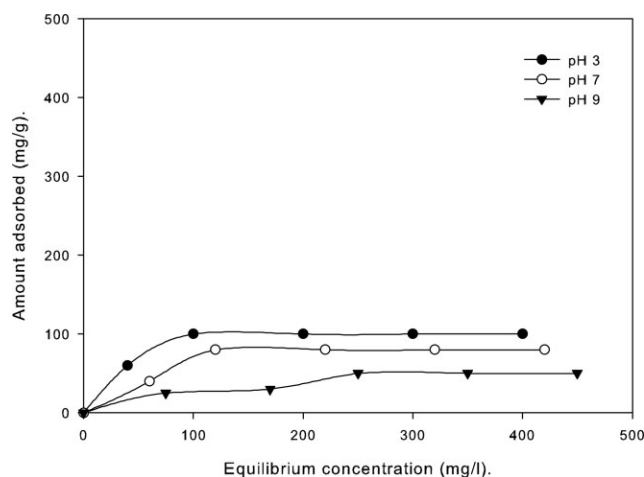

Figure 7 Equilibrium isotherm for Cr(VI) adsorption on activated carbon PVA/PVP at different pH values.
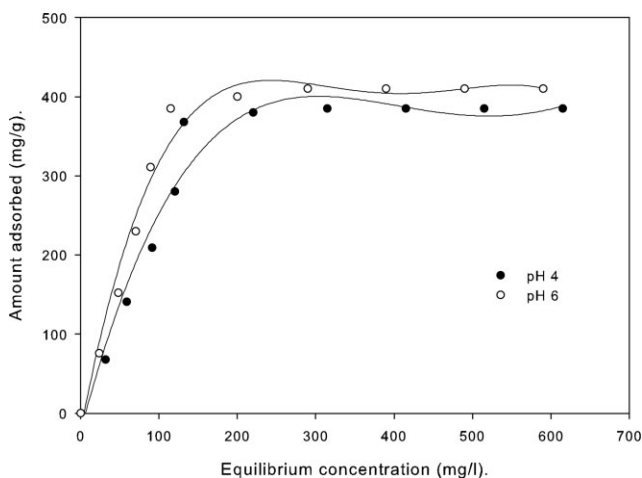
Figure 8 Equilibrium isotherm of adsorption of Ni(II) onto activated carbon-filled PVA-NVP membrane at different pH values.

ionic form was found to be preferentially adsorbed on the surface of carbon.[26] Maximum adsorption at pH 3 indicates that it is the $HCrO_4^-$ form of Cr(VI), which is adsorbed on carbon.

Adsorption of heavy metal ions

Figures 8 and 9 show the adsorption isotherm of Co and Ni onto activated carbon PVA/NVP at different initial concentrations in the range of 100–500 mg L^{-1} at pH values 4 and 6. From these figures, it can be seen that the adsorption capacity of Co and Ni onto activated carbon PVA/PVP membrane is higher than that of PAC because of the role of PVP on the adsorption of heavy metal ions. Oxygen of the carbonyl groups of PVP is responsible for the interaction of the metal ions with the adsorbent. Because the mobile π electrons are pulled strongly toward
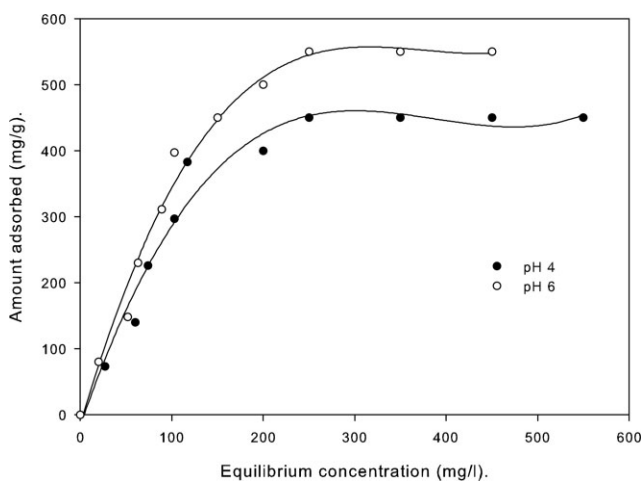
oxygen, carbonyl carbon is electron deficient and carbonyl oxygen is electron rich, and metal ion acts as an electron acceptor and is taken by the coordination to the donor oxygen.[31] Besides, the adsorption of the metal ions is because of the presence of amide group that could act as electron donor.[32] Thus, the nitrogen electron present in the amide groups can establish dative bonds with Ni^{2+} and Co^{2+} ions. Furthermore, the metal uptake will eventually undergo bond complex formation between metals and hydroxyl groups present in PVA of the prepared membrane.

Effect of pH of feed solution. From Figures 8 and 9, it can be seen that increasing the pH value is accompanied by a detectable increase in the percentage value for metal ions under investigation. This reduction may be attributed to formation of protonated nitrogen of PVP group and increasing its cationic character. So, no interaction occurs between the N-atom and heavy metal ions, as well as hydrolysis of the metal ions at higher pH values.[33]

Adsorption of phenol

Activated carbon PVA/PVP membrane shows high removal percentage of phenol ($\cong$98%) and removal of initial concentration (500 mg L^{-1}). The equilibrium isotherm for adsorption of phenol onto this membrane was shown in Figure 10. As already described, the activated carbon has been developed by introduction of polar functional group (amide group) onto activated carbon, which can be used in the sorption of polar compounds. This can be attributed to an increase in the surface polarity, which enables the adsorbed sample to make a better contact with the membrane surface.[34] The amount of phenol adsorbed on PAC and activated carbon PVA/PVP membrane is almost the same. $1/n$ and k
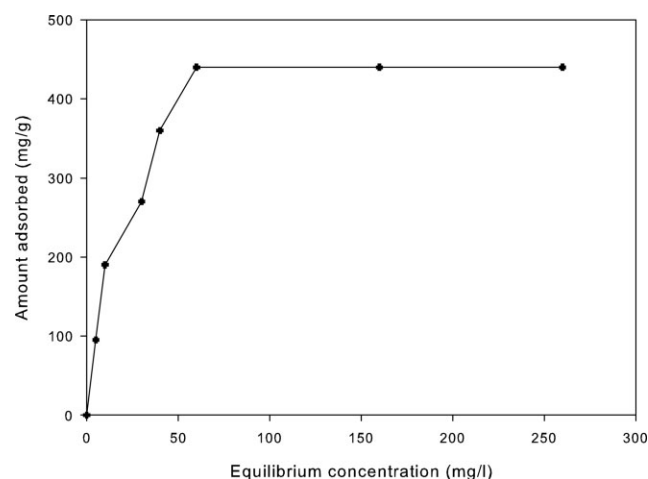

Figure 9 Equilibrium isotherm of adsorption of Co(II) onto activated carbon-filled PVA-NVP membrane at different pH values.

Figure 10 Equilibrium isotherm for phenol adsorption on activated carbon PVA/PVP at different pH values.

TABLE II
1/n and k Parameters from Adsorption Data of Different Hazardous Wastes onto Activated Carbon PVA/PVP Membrane at Different pH Values

Hazardous waste	1/n	k	pH
Acid dye	0.46	39.8	10
Basic dye	0.55	17.7	3
Dichromate	0.23	31.6	3
Co^{2+}	1.3	1.12	4
Ni^{2+}	1.25	1	4
Phenol	0.6	31.6	—

parameters from adsorption data of different hazardous wastes onto activated carbon PVA/PVP membrane were shown in Table II.

CONCLUSION

Membranes from a mixture of activated carbon and PVA/NVP made by single "freezing and thawing" followed by γ-irradiation were synthesized to modify the surface of activated carbon by introducing a pyrron ring, which enhances the adsorption efficiency of activated carbon. The prepared membrane was applied for the removal of different hazardous pollutants from aqueous solution [e.g., acidic, basic dyes, dichromate anion, heavy metal ions (Co and Ni), and phenol]. The prepared membrane showed high efficiency for the removal of Co and Ni than for commercial activated carbon. A slight difference was found, when it was applied for removal of acid, basic dyes, whereas the removal of phenol was the same as commercial PAC. The adsorption isotherm for all hazardous pollutants was found to be in agreement with the Freundlich model.

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