# Removal of Ag<sup>+</sup>, Co<sup>++</sup> and Cs<sup>+</sup> From Wastewater Using Porous Resin Blend (Epoxy/PVA)

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**Abstract:** In this study, removal of silver, cobalt and cesium from aqueous solutions under different experimental conditions using a prepared porous resin blend (Epoxy/Polyvinyl alcohol) was investigated. Blending of Epoxy with PVA and thereafter foaming in a viscous state were carried out to attain the optimum hydrophilicity. Gamma rays were used in the preparation process to control the granular size and the compatibility of the blend. Characterization of the blend after milling was reported using thermogravimetric analysis (TGA), Fourier transform infra red (FTIR) and scan electron microscopy (SEM). The adsorption of Ag(I), Co(II) and Cs(I) ions from aqueous solution by the prepared porous resin blend was examined by batch equilibration technique. The effects of initial ion concentration, temperature, pH and shaking time on the adsorption of metal ions were investigated. The adsorption amount of ions increased with the increase of shaking time, temperature, metal ion concentration and pH of the media. The results showed that metal ion adsorption followed the order Ag<sup>+</sup>>Co<sup>++</sup>>Cs<sup>+</sup>. The amount of metal ion adsorbed at equilibrium for Ag<sup>+</sup>, Co<sup>++</sup> and Cs<sup>+</sup> at pH 5 was 9.8, 9.4 and 9.1 mg/g. It was found that the adsorption isotherm of the ions fitted Langmuir isotherms.

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Key Wards; Blend, - irradiation, metal ion, porous resin, adsorption, contaminated water

#### 1. Introduction:

Heavy metals are often problematic environmental pollutants, with well-known toxic effects on living systems. Nevertheless, because of certain useful physical and chemical properties, some heavy metals, including silver, cobalt, and cadmium are intentionally added to certain consumer and industrial products such as batteries, electroplating. Cobalt was once widely used in pharmaceutical products and agricultural chemicals while cesium has taken more importance after nuclear reactor construction has been expanded. (1,2) Large amount of any of them may cause acute or chronic toxicity. (3-5) Heavy metals in human body tend to bioaccumulate, which may result in damaged or reduced mental and central nervous function, and damage to blood composition, lungs, kidneys and liver. Notably, it has been declared that the regulatory levels of health metals in drinking water level often not exceed 10  $ug/L^{(6-8)}$ .

The removal of heavy metal ions from aqueous solutions, either for pollution control or for raw material recovery, has been taking on increasing importance in recent years. Different treatment techniques, such as chemical precipitation, coagulation–precipitation, adsorption and ion exchange, have been progressively developed to remove heavy metals from contaminated water <sup>(9-11)</sup>

Coagulation–flocculation and chemical precipitation are perhaps the most widely used, however, they both have the drawbacks of difficult sludge disposal and more importantly the diminished effectiveness when treating water with low heavy metal levels<sup>(12)</sup>.

Membrane filtration and reverse osmosis were also reported (13). However, these methods usually involve expensive materials and high operation costs. Other methods. such as electrodialysis, membrane electrolysis and electrochemical precipitation, have also investigated, however, their applications have been limited due to the high energy consumption (14) On the other hand, as a cost effective method, ion exchange process normally involves low-cost materials and convenient operations, and they have been proved to be very effective for removing contaminants from water such as ammonia and heavy metals (15-17). Moreover, ion exchange is particularly effective for treating water with low concentration of heavy metals which is very common in practice (18). The development of potential low-cost adsorbents with high exchanging levels is essential to facilitate the application of ion exchange processes for heavy metal removal. Various materials, including natural and synthetic zeolites and polymeric resins, have been studied for this purpose (19).

The aim of the present work is the preparation and characterization of cationic porous resin by blending a functional polymer, namely polyvinyl alcohol with epoxy, acting as carrier. Batch technique was used to study the sorption of  $Ag^+$ ,  $Co^{++}$  and  $Cs^+$ . Different parameters, such as temperature, pH of the solution, different concentrations of metal ion and effect of shaking time were manifested.

## 2. Experimental Approach:

#### 2.1. Materials

The samples were prepared using propyl epoxy commercial grade and partially hydrolyzed polyvinyl alcohol and a commercial hydrogen gas was used in foaming the blend purchased from Optco, Egypt. The PVA powder was dissolved into magnetically stirred distilled water for 3 hours at 80 °C getting a solution with the concentration of 20 %. Cobalt chloride, silver chloride and cesium chloride were used as a simulated waste; all salts employed were of analytical grade purchased from Merck Co. bidistilled water was used for the simulated waste solutions: 200 ppm, 100 ppm, 50 ppm and 25 ppm.

# 2.2. Scientific Equipments

A Fourier transform infrared (FTIR) spectrophotometer from Mattson 1000, Pye-Unicam, England was used to analyze the chemical and/or physical interactions in the wave number range 400–4000 cm–1. The concentrations of the metal ions were measured with an Ati Unicom (Model 929) atomic absorption spectrophotometer. The pH values of the buffer solutions were determined with a Ø50 pH meter (Beckman, Beckman Instrument). TGA - 50, Japan was used to characterize the polymer resin thermally. Atomic absorption Spectrophotometer (Perkin-Elmer 2380) using lamps for Ag, Co and Cs were used for measuring all adsorption process. Merck atomic absorption standard solutions of these metals were used for calibration process.

# 2.3. Methods of preparation

PVA/Epoxy was mixed to realize the optimum ratio which has good structure and best hydrophilic character: 5%, 10%, 20% and 30 % by weigh of PVA were mixed with Epoxy. Heating of the mixture to reach the maximum compatibility and then reduce the temperature of the mixture blend till reach a very viscous state. Foaming of the blend was for more than 5 hours till solid form performed to achieve a highly porous blend. Irradiation of different doses; 5, 10, 20 and 2 KGy by Gamma cell (<sup>60</sup>Co) was carried out to attain better porosity and best hydrophilicity. Milling of the solid porous blend using agate mortar and pestle was performed to obtain small bead with different diameter.

#### 2.4. Water uptake

Water uptake/swelling behavior of different resins formed was studied in water as a function of the applied dose for different composition. Swollen polymers were wiped off with tissue paper to remove surface water and then weighed immediately to know the percent swelling/ percent water uptake, which was calculated as:

Water uptake  $\% = [(W-W_0)/W_o]x100$  (1) Where, W, Wo are the weight of swollen blend resin and dry blend resin, respectively.

### 2.5. Adsorption experiments

Adsorption experiments were carried out using a batch wise method. Dried samples (0.1 g each) of blend resin were added into 100 cm $^3$  Erlenmeyer containing volume of 30 cm $^3$  of each metal ion solution (50 ppm) and adjusted to desired pH. The mixture solution was stirred at 25  $^0$ C. After filtration of the solution, the ion concentration of the filtrates was analyzed with an atomic adsorption spectrophotometer. The amount of metal ions adsorbed on the adsorbent at adsorption equilibrium,  $q_e$  (mg/g) was calculated according to the following equation

Where  $C_o$  and  $C_e$  are the initial and equilibrium metal ion concentration (mg/l), respectively, V is the volume of solution (l), and W is the weight of the resin (g).

#### 2.6. Desorption experiments

The elution of heavy metals is the most common elimination method of the exhausted sorbent, allowing both recovery of metal ions at higher concentration and recycling of the sorbent for subsequent uses. For an effective recycling process, adsorbed metal ions should be easily desorbed without destroying the adsorbent materials under the suitable conditions. The adsorption was performed with the same procedure mentioned above. On the other hand, desorption was examined as follows: 1 g of the blend resin loaded by Ag(I), Co(II) and Cs(I) from the previous metal adsorption study was put into a 250 ml Erlenmeyer flask containing 100 ml (0.1 N HCl). The mixture was then shaken with the shaker at 100 rpm at room temperature. Samples of the solution were taken every 5 min until steady state (about 30 min) was achieved. The metal concentration was then determined by the Atomic absorption Spectrophotometer (Perkin-Elmer 2380). The adsorption and desorption processes were

repeated for three cycles using the same adsorbent to evaluate the effect of regeneration on the capacity of re-adsorption of Ag(I), Co(II) and Cs(I) on the prepared epoxy blend resin.

#### 3. Results and Discussion:

# 3.1. Characterizations of the resin 3.1.1 FTIR

Evidence of blending and network formation has been provided by the characterization of the synthesized porous resin. The use of IR spectroscopy is a well-known method for the identification of the chemical groups. The IR spectra of the synthesized porous resin, prepared by blending propyl epoxy, commercial grade, with partially hydrolyzed polyvinyl alcohol, are given in Fig. 1. Polyvinylalcohol is produced by the reaction of polyvinylacetate with methanol. The spectrum should be a fairly simple combination of methylene and hydroxyl vibrational peaks. The resulting hydrogen bonding between hydroxyl groups produces a wide hydroxyl stretch at 3400 cm<sup>-1</sup>. Three successive peaks at 670, 1300 and 1650 cm<sup>-1</sup> were recorded which of manifest the presence The C-O stretch appears at 1095 cm<sup>-1</sup>, is for secondary alcohols. Sometimes typical polyvinylacetate peaks are seen at 1739 and 1239 cm<sup>-</sup> when hydrolysis is not complete. Thus bands at 1746 and 1246 cm<sup>-1</sup> due to methyl acetate byproducts are sometimes discernable.

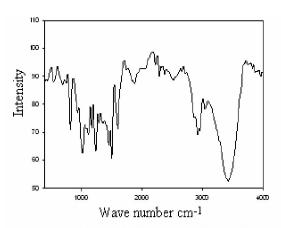


Figure (1): FTIR of Epoxy/PVA blend resin

## 3.1.2 TGA

Temperature at which the loss in weight occurs is considered to be the thermal resistance of polymer (21, 22). An improvement in the thermal characteristics was detected as a result of blending

PVA with epoxy. The blend showed high thermal resistance up to 360 °C above which loss of weight could be detected while complete decay was noticed close to 400 °C. From ambient to 350°C, a gradual weight decrease was reported, this loss of weight does not exceed 10% evidencing the evaporation of non bounded water. Meanwhile, the abrupt change in weight, was recorded within the 55%, temperature range 350 - 400 °C. The third division, as shown in Fig.2 exhibits the change in weight (loss of 17%) over the temperature raise up to 580 °C. No step peak has been seen manifesting the polymer-polymer compatiblization (foam component) all over the applied range of temperature from ambient to 580 °C.

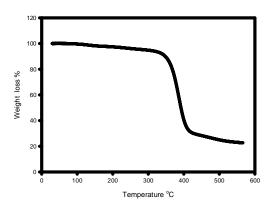


Figure (2): Thermogravimetic analysis of porous resin blend (Epoxy/PVA)

## 3.1.3. SEM

Scan electron microscopy was applied to distinguish between primary textures due to the synthesis process and those due to subsequent treatment of surface, <sup>(23)</sup>. Figure 3 showed scattered gaps as a result of foaming the blend, forming large cavities distributed in a regular manner. This may provide an evidence of forming homogenously distributed porous resin upon synthesis.

# 3.2. Water uptake

Water uptake of the porous blend resin was studied as a function of composition and gamma irradiation. 20 % PVA blend showed maximum water uptake, as shown in Fig. 4. It was found that a dose of 10 KGy was the proper dose for at most water uptake as obviously demonstrated by Fig. 5. Foaming of blend remarkably improved water uptake. This may be accounted for an increase in pore number, pore size and/or increase in dimensions of the formed foam, i.e. increase in the allowed surface area of the net matrix.

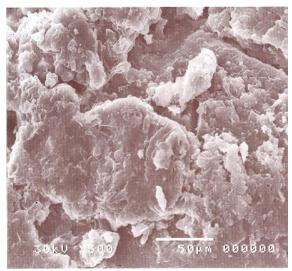
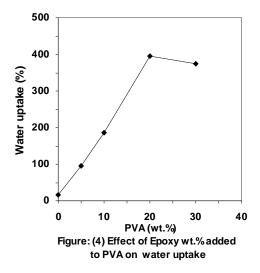


Figure 3: Scan Electron Microscope of Epoxy/PVA blend foam



# 3.3. Adsorption of metal ion3.3.1 Effect of metal ion concentration:

The adsorption of metal ion by the synthesized porous resin blend was conducted in different initial concentrations ranging from 25 ppm to 200 ppm. Figure 6 shows the relationship between the initial concentration of metal ion and the adsorption amount. It is clear from the figure that, the adsorption amount of metal ion increased with increasing initial ion concentration untill reached a plateau value at a concentration of ~100 ppm. This is attributed to the chelating sites capacity of the prepared (Epoxy/PVA) porous resin blend which becomes saturated as concentration nearly reached 100 ppm. The removal percent can be arranged in the following manner Ag<sup>+</sup>>Co<sup>++</sup>>Cs<sup>+</sup>, which can be largely accounted for the ionic radius and charge of the metal ion.

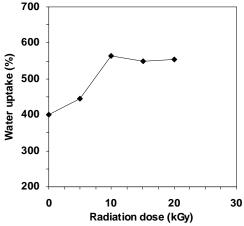


Figure (5): Effect of radiation dose on water uptake of Epoxy/PVA blend resin; PVA 20 wt. %

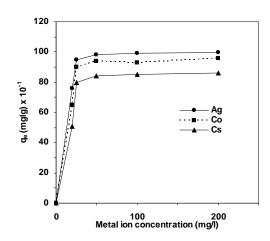


Figure (6): Effect of metal ion concentration (mg/l) on the removal of silver, cobalt and cesium from their aqueous solution using porous resin blend (Epoxy/PVA); pH 6; 30 °C; 2h.

## 3.3.2. Effect of temperature

The effect of the temperature on the adsorption amount of ion onto the prepared porous resin blend was studied within the range 25–60  $^{0}$ C, where the initial concentration being kept at 50 ppm at pH 5, the results are shown in Fig. 7. From this figure it is clear that with increasing temperature, the adsorption amount of metal ion slightly increased. This may be either due to accelerating of some originally very slow adsorption steps or due to creation of some new active sites on the surface of adsorbent  $^{(24)}$ . Also, it is quite possible that a diffusion process takes place and is partly contributing to the rate of adsorption  $^{(25)}$ .

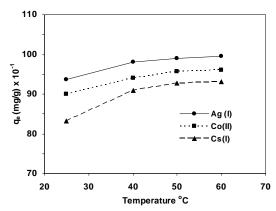


Figure (7): Effect of temperature on the removal of silver, cobalt and cesium ions from their aqueous wastes by porous resin blend (Epoxy/PVA); pH 5, concen. 50 ppm; t= 2h.

## 3.3.3. Effect of pH

The effect of the initial pH value on metal ion removal by the prepared porous resin was investigated within the pH range 2-6 taking into account the precipitation pH value of metal ions (26,27). At different pH values, the protonation and deprotonation behaviors of acidic and basic groups would be influenced. The surface structure of the porous resin blend and the metal ions would exist in different forms. The experimental results for the effect of pH on the non-competitive adsorption of metal ions are shown in Fig. 9. It can be seen that adsorption significantly increased with the increase of pH (within pH 3–5), reaching a value of 9.8, 9.4 and 9.1 mg/g, for Ag(I), Co(II) and Cs(I), respectively. At low pH values, the high hydrogen ion concentration at the interface electrostatically repels the positively charged metal ions and prevents their approach to the resin blend surface (28).

## 3.3.4. Effect of contact time

Removal of Ag(I), Co(II) and Cs(I) from their aqueous solutions by Epoxy/PVA resin blend with time was carried out at pH 5 and the effect of contact time on the sorption of these metal ions are presented in Fig. 9. As may be seen from Fig. 9, the binding of Ag(I), Co(II) and Cs(I) on Epoxy/PVA resin blend from the solution increases very rapidly with agitation time. The investigations indicated that the binding of Ag(I), Co(II) and Cs(I) was found to be about 7.3, 6.6 and 6.2 mg/g, respectively within the initial 15 min. Later, the percentage sorption of Ag(I), Co(II) and Cs(I) reached about 9.8, 9.4 and 9.1 mg/g respectively and attained equilibrium by the end of a contact period of 60 min. The increase of contact time further from 60 to 120 min had no significant effect on the percentage sorption of all metal ions. Therefore, a contact time of 60 min was applied for all other subsequent experiments. Initial rapid binding of Ag(I), Co(II) and Cs(I) occurs initially due to easily available exchangeable sites located on surface of the Epoxy/PVA resin blend. The subsequent slow process suggests that intrapore diffusion was also involved in the sorption process. It was previously stated that the plateau portion of the curve corresponds to pore diffusion where as the linear portion of the curve reflects surface layer diffusion (29).

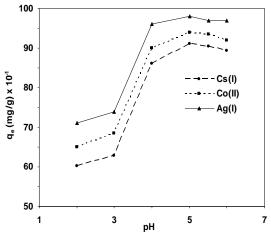


Figure (8): Effect of pH on the adsorption amount of Ag(I), Co(II) and Cs(I) from aquous waste using porous resin blend (Epoxy/PVA); metal ion conen. 100 ppm; t=2h; temp. 30 °C.

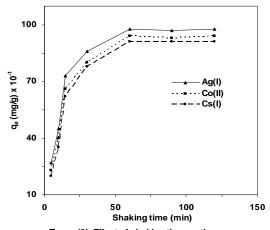


Figure (9): Effect of shaking time on the adsorption amount of Ag(I), Co(II) and Cs(I) from aquous solution usings porous resin blend (Epoxy/PVA); metal ion conc. 100 ppm; pH 5; 30 °C

#### 3.4.5. Adsorption kinetics

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior

between solute and adsorbent. The popularly used Langmuir isotherm is expressed by the linear Eq. (3) (30,31).

$$C_e/q_e = C_e/Q_o + 1/bQ_o \qquad .... \qquad 3$$

where  $q_e$  is the amount of metal ion adsorbed per unit mass of adsorbent (mg/g),  $C_e$  is the equilibrium concentration of metal ions(mg/l),  $Q_o$  is a measure of adsorption capacity of adsorbent (mg/g) and b is the Langmuir isotherm constant (l/mg) related to the energy of adsorption. A plot of  $C_e/q_e$  versus  $C_e$  exhibits a straight line of slope  $1/q_o$  and intercept  $1/bQ_o$  as shown in Figure 10

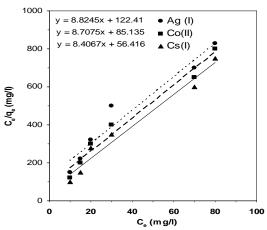


Figure (10): Linearized Langmuir for the adsorption of metal ions (Ag+, Co++ and Cs+) using Epoxy/PVA blend resin

From the value of the Langmuir constant and the coefficient obtained, it can be concluded that the Langmuir equation gives better fit to the experimental data. The theoretical Langmuir isotherms of  $Ag^+$ ,  $Co^{++}$  and  $Cs^+$  on porous resin are depicted in Figure 10. The  $q_o$  values calculated from Langmuir model are fairly close to the experimental results.

### 3.4.6. Desorption experiment

Table 1 shows the Ag(I), Co(II) and Cs(I) adsorption and desorption of intact blend resin compared with regenerated blend resin adsorbent. The adsorption capacity of regenerated blend resin decreased with increasing cycle times. This may be explained by the fact that esopores of adsorbent prevent metal ions from desorption which results in reduction in the number of active sites and consequently in the adsorption capacity.

Table 1. Adsorption and desorption of Ag(I), Co(II) and Cs(I) per mass of Epoxy/PVA blend resin at each cycle of regeneration

Cycle	Ag(I)		Co(II)		Cs(I)	
number	Adsorbed (mg/g)	Leached (mg/g)	Adsorbed (mg/g)	Leached (mg/g)	Adsorbed (mg/g)	Leached (mg/g)
1 <sup>a</sup>	9.8	9.1	9.4	8.5	9.1	8.1
2	9.4	8.5	8.7	7.7	8.5	7.4
3	8.9	8.0	8.3	7.2	7.9	6.8
4	8.2	7.1	7.7	6.5	7.4	6.3

1<sup>a</sup> Intact blend resin adsorbent was used in cycles number 1 whereas regenerated blend resin adsorbent was used in cycle number 2, 3, and 4 consecutively.

## 4. Conclusions:

A porous resin blend (Epoxy/Polyvinyl alcohol) was synthesized with PVA at different weight ratios for removing Ag(I), Co(II) and Cs(I) ions from aqueous solutions. The FTIR spectra reveal the hydrogen bonding between hydroxyl groups represented by a wide hydroxyl stretch at 3400 cm<sup>-1</sup>. Three successive peaks at 670, 1300 and 1650 cm<sup>-1</sup> were recorded which manifest the presence of epoxy. All the adsorption processes tended toward equilibrium after

a contact time of 60 min and the percentage sorption of Cs(I), Co(II) and Ag(I) reached 9.1, 9.4 and 9.8 mg/g, respectively. The adsorption increased significantly with the increase of pH (within pH 3–5), reaching the values 9.8, 9.4 and 9.1 mg/g, for Ag(I), Co(II) and Cs(I), respectively. By increasing adsorption temperature, the adsorption amount of metal ion slightly increased. Furtherly, adsorption amount of metal ion increased with increasing initial

ion concentration and reached a plateau value at a concentration of~100 ppm.

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