

Sorption Potential of Epoxy/Pac Composite for the Removal of Cs⁺ ion from Aqueous Solutions

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Abstract

Simultaneous Gamma irradiation was used to prepare Epoxy/Pac porous resin. Characterizations of the polymer using Fourier Transform Infrared (FTIR), Thermogravimetric analysis (TGA), scanning electron microscope were performed. The sorption potential of polymer for removal of Cs⁺ from liquid solutions has been investigated. The influences of pH, contact time between liquid and solid phases, initial metal ion concentration, and temperature have been evaluated. Equilibrium isotherms were determined to assess the maximum sorption capacity of polymer for the studied ion. Desorption and durability measurements of the polymer confirmed their use from cost benefit point of view. The equilibrium sorption data were analyzed using Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherm models. All tested models fit the data reasonably well in terms of regression coefficients. Sorption studies were also performed at different temperatures to obtain the thermodynamic parameters of the process. The numerical value of ΔG° decreases with an increase in temperature, indicating that the sorption reaction of each ion is more favorable at higher temperature. The positive values of ΔH° correspond to the endothermic nature of sorption processes.

Keywords: Gamma irradiation; Porous resin; Sorption; Cesium ion; Thermodynamics

Introduction

A manifold enhancement in industrialization in many regions has raised the discharge of industrial wastes, especially those containing heavy metals, into natural water bodies or on land. Heavy metal contamination to various surface waters or ground water is great a concern because of the toxic effect of heavy metal ions to plants, animals and human beings [1-6]. Therefore, effective removal of heavy metal ions from water or various industrial effluents is very important and has attracted considerable research and practical interest. Many methods, such as chemical precipitation, ion exchange, reverse osmosis and sorption, etc., have been used to remove heavy metal ions from various aqueous solutions [3-5,7,8]. Among these methods, sorption has increasingly received more attention in recent years because the method is simple, relatively low-cost and effective in removing heavy metal ions, especially at medium to low metal ion concentrations and wastewaters [3-6,8,9].

Naturally-occurring cesium occurs in the environment mostly from the erosion and weathering of rocks and minerals. The mining and milling of certain ores can also release cesium to the air, water, and soil. Radioactive cesium is released to the environment during the normal operation of nuclear power plants, explosion of nuclear weapons, and accidents involving nuclear power plants or nuclear powered satellites or submarines. Non-radioactive (stable) cesium can be neither created nor destroyed under typical environmental conditions, but can react with other compounds found in the environment and change into different cesium compounds. Radioactive decay decreases the concentration of ¹³⁴Cs and ¹³⁷Cs. Both stable and radioactive cesium are the same element and behave in a similar manner chemically and in the body. Cesium compounds can migrate long distances in the air before being brought back to the earth by rainfall and gravitational settling. In water and moist soils, most cesium compounds are very soluble. Cesium binds strongly to most soils and does not migrate far below the surface of the soil. Consequently, cesium is not readily available for uptake by vegetation through roots. However, radio-cesium can enter plants upon falling onto the surface of leaves. Animal testing may also be used to identify health effects such as cancer or birth defects.

Traditional techniques for cesium removal have certain disadvantages such as higher operational cost, requiring additional chemical, high energy consumption, and residual metal sludge disposable. Due to forbidding cost of these processes, the uses of resin have been received with considerable attention. In recent years, a number of commercial resin such as Lewatit TP-207 [10], Amberlite IR-120 [11], Amberlite IRC-748 [12], Lewatite S-100 [13] Lewatit CNP-80 [14], Amberlite IRC-718 [15] have been used to remove heavy metals from wastewater. There still exists a need to develop a low-cost and efficient adsorbent material for the removal of pollutants. Recently, a biological method of heavy metal removal, termed biosorption, has been suggested as a cheaper and more effective alternative to existing treatment techniques [16].

Biosorption has gained important credibility during recent years because of its eco friendly nature, excellent performance, and low cost domestic technique for remediating even, heavily metal loaded wastewater. New approaches of developing various microbial sources, seaweed, aquatic plants and leaf based adsorbents as cost effective and efficient biosorbents have been reported by various investigators [17]. Among them, PAC have proved to possess high metal binding capacities

However, activated carbons are by far more effective in this application due to some specific characteristics that enhance the use of activated carbon for the removal of contaminants including heavy metals from water supplies. Activated carbons are extremely versatile adsorbents used in major industrial applications and in a wide range

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of processes concerned principally with the removal of undesired species from the gaseous or liquid phase in order to effect purification or the recovery of chemicals [18]. If the sorption process is to be used as an alternative in wastewater treatment, the sorbent regeneration may be crucially important to keep low processing costs and open the possibility to recover the extracted metals from the liquid phase.

The desorption process give up metals in a concentrated form, which facilitates disposal and restores sorbent for effective reuse. The desorption process give up metals in a concentrated form, which facilitates disposal and restores biosorbent for effective reuse [19,20]. The desorption mechanism is similar to ion exchange, where metals are eluted from the adsorbent by an appropriate solution to give a small concentrated volume of metal containing solution. The biomass stripping can be achieved with a relatively inexpensive acid such as HCl, HNO₃ and H₂SO₄

In this study insertion of Powdered Activated Carbon (PAC) on the matrix of epoxy with different ratios for synthesise of porous PAC/Epoxy resin was carried out. Investigations of the synthesized polymer thermally, physically and chemically were performed. Batch experiment was used to study the sorption of the Cs⁺. Different parameters were studied well such as temperature, pH and different concentrations of the solutions. Desorption using different methods such as Gamma irradiations and chemically were investigated. Durability of the polymer was evaluated by measuring the desorptions-adsorptions for three times to evaluate the loss of the potential sorption of the polymer. Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherm models were applied to study the mode of sorption. Thermodynamic parameters of the process was measured and well discussed.

Experimental

Chemicals and reagents

Materials: Commercial grade of phenyl epoxy, Powdered Activated Carbon were used in the preparation of the porous composite. Commercial hydrogen gas was used for foaming of the composite. cesium chloride were used to make a simulated waste; was of analytical grade purchased from Merck co. bidistilled water was used for preparation the desired concentration of simulated waste All the chemicals and gas were purchased from OPT. Co. (Cairo, Egypt) and used without further purification.

Preparation of porous resin: Epoxy/PAC was mixed to realize the optimum ratio which has good structure and hydrophilic character. 2%, 5%, 10% and 12 % by weigh of PAC were mixed with Epoxy and its solidifying agent. Heating the mixture at 80°C for 30 minuets to reach

the maximum compatibility and then reduce the temperature of the composite to 15°C for reaching a very viscous state. Foaming of the blend for 5 hours till solid form attained to achieve a highly porous blend. Irradiation of different doses; 5, 10, 20 and KGy by Gamma cell (⁶⁰Co) was carried out to realize high porous and hydrophilic properties. Milling of the solid porous blend using agate mortar and pestle was performed to attain small bead with different diameter.

Water uptakes studies: Water uptake / swelling behavior of different porous resin was studied in water as a function of different doses (KGy), different composition. Some factors were studied such as; contact time and pH. Swollen polymer were wiped off with tissue paper to remove surface water and then weighed immediately to know the swelling percent or water uptake percent, which was calculated as:

$$\text{Water uptake\%} = \frac{\text{Weight of swollen resin} - \text{Weight of dry resin}}{\text{Weight of dry resin}} \times 100 \quad (\text{A.1})$$

Scientific equipments

- FTIR characterization:** The functional groups of the prepared hydrogels were studied using Mattson 1000, PYE-Unicam, England.
- Scanning electron microscope:** Investigation and magnification of the polymer surface was carried out by SEM, JEOL-JSM-5400; Japan.
- Thermal gravimetric analysis:** Shimadzu TGA -50, Japan was used to characterize the thermal stability of the copolymer hydrogel.
- Atomic absorption analysis:** Pye Unicam model 939, England used for evaluation of Cs⁺ concentration.

Sorption isotherms: Batch sorption studies of cesium ions were performed at different temperatures (25, 40 and 60 °C) to obtain the equilibrium isotherms. For isotherm studies, a series of 25 ml test tubes were employed. Each test tube was filled with 10 ml of metal ion solution of varying concentrations (10⁻⁵ to 10⁻⁴ M) and a known amount of polymer (100 mg) was added into each test tube and agitated for a sufficiently long time (~3 hr) required to reach equilibrium.

The amount of Cs(I) in the solid phase, q_e (mmol/Kg), was calculated by using the equation

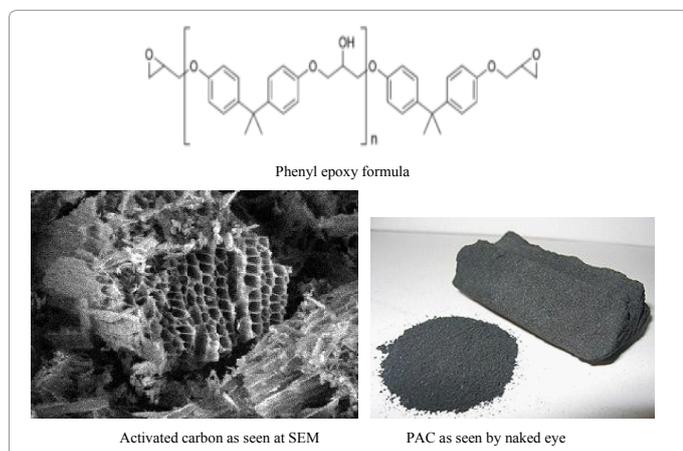
$$q_e = (C_o - C_t) V/m \quad (\text{A.2})$$

where C_o and C_t are the amount of initial and retained Cs (Kg) ion in the solution at time t (mmol/l), respectively, V is the solution volume (l) and m is the weight of adsorbent (Kg).

All experiments were carried out in triplicate and the mean values are presented. The value of sample solutions was always done for a period of time to have a mean value which lies within ±1-2% statistical accuracy.

Desorption and porous resin durability: Radio-desorption: desorption was carried out using Gamma irradiation with 1, 2 5, 10 and 12KGy, 1 g. of adsorbed porous resin was immersed in 100 ml of bi-distilled water and expose to the mentioned doses in a closed ampoule.

Withdrawing the adsorbent while measuring the cesium level using atomic absorption technique. Measuring the radio-desorption percent by applying equation Eq.A.3. Chemi-desorption: For the desorption study, 1.0 g porous resin was contacted with 50 ml Cs⁺ solution (100 mg/l). After adsorption experiment, the porous resin was collected by filtration and washed with distilled water for three times, to remove residual Cs⁺ on the surface. Then it was transferred to 50 ml



desorbing solutions: deionizer water, 0.1 M HCl. The mixtures were shaken overnight, then the filtrates were analyzed to determine the concentration of Cs⁺ after desorption. Desorption ratio was given as the following [21-23].

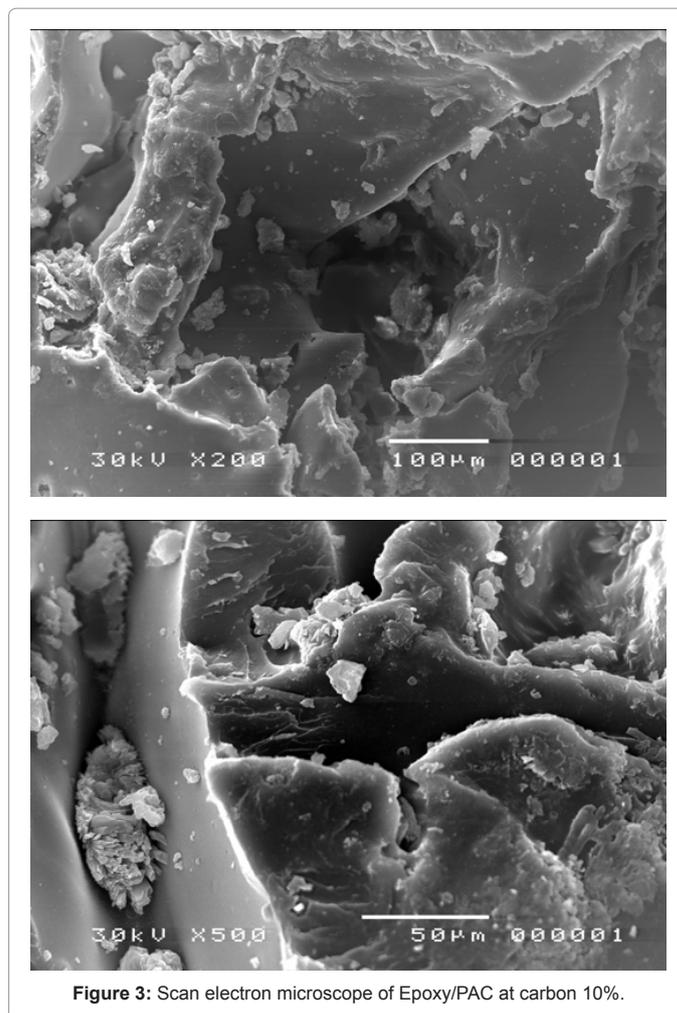
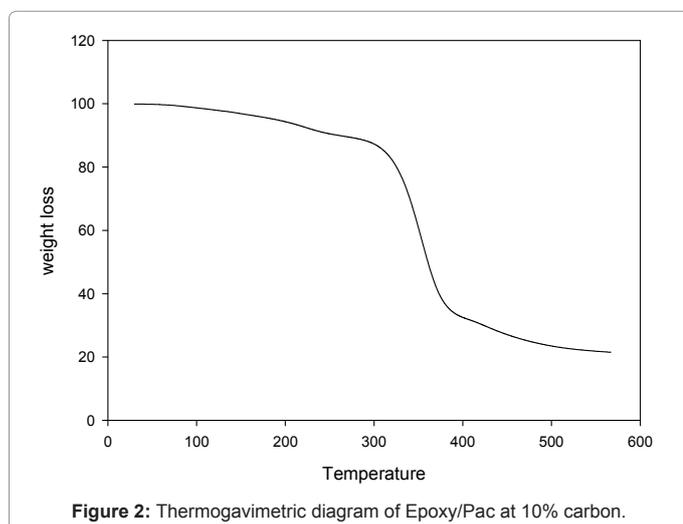
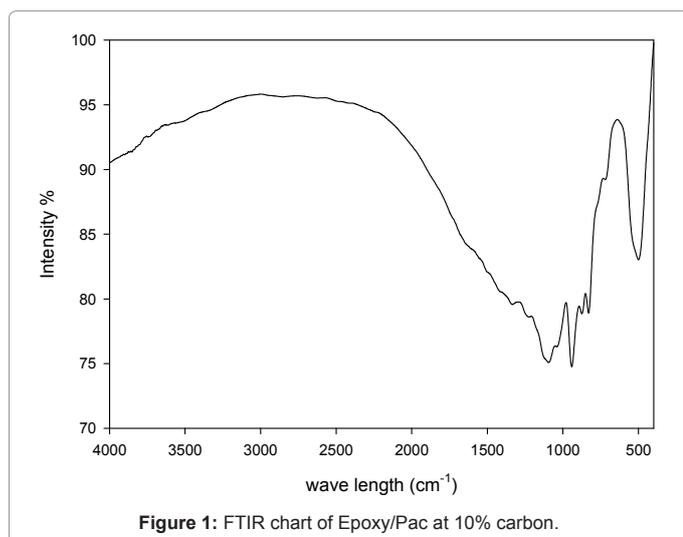
$$\text{Desorption ratio} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100 \quad (\text{A.3})$$

Results and Discussion

Characterizations of the resin

FTIR characterization: Evidence of homogenous of Epoxy / PAC porous resin and network formation has been provided by the characterization of porous resin synthesized. The peaks at 945 cm⁻¹ as evidence of presence of epoxy were obviously appeared. The spectral band observed at 1044 cm⁻¹ is attributed to the deformation of aliphatic carbons in C=CH₂ [24,25]. The peaks between 1340-1100 are as bending of C-C-C (1300-1100 cm⁻¹) [24] which may attempt the chemical incorporation of some carbon atoms (PAC) into the polymer matrix.

TGA Characterization: (Figure 1) Thermal resistance is a description of the chemical stability of the polymer at high temperature



in vacuum, air in an inert atmosphere. The determination of this loss in weight is the principle of different variant of thermogravimetric analysis (TGA). The temperature at which the loss in weight occurs is considered to be the thermal resistance of polymer. An improvement of thermal characteristic was shown as insertion of PAC and foaming of epoxy has been carried out. The thermogram can be divided into four divisions according to range of temperature. First division discuss the thermal resistivity of the composite at range of 0°C -220 of °C, at which loss of weight reached to 8% from the original weight, it may explained by evolving of non bounded water. Second division study the thermogram from 220°C to 280°C, at which it could be seen that 6% loss of weight that may as release of volatile products formed as PAC insertion into epoxy net-matrix. Third division reviewed the thermal resistivity through temperature range 300 °C -380 °C, through which maximum loss of weight have seen reached to 44% (it means 66% loss of weight from the original weight) it may be due to almost decay of the polymer trunk of the composite. Fourth division discussed the loss of weight through the temperature range of 380 °C to 580 °C via which complete decay have been seen reached to 88% from the original weight. The thermogram showed compatibility of the composite as no terminal beak was seen (Figure 2).

SEM characterization

(Figure 3) In order to be able to judge damage to polymeric material surfaces, it is necessary to be familiar with the surface

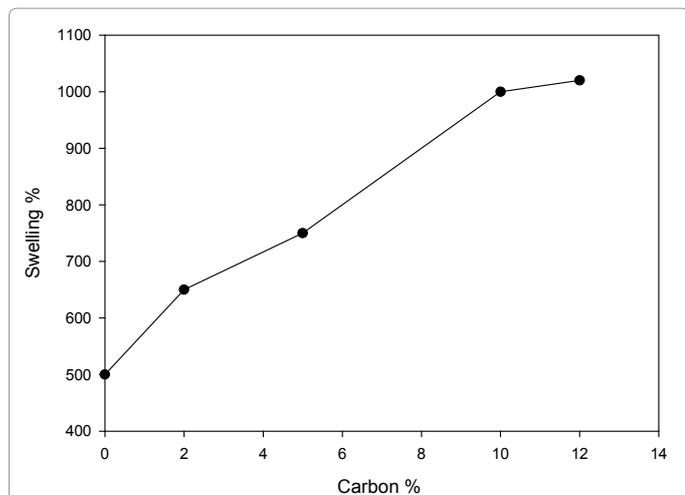


Figure 4: Effect of powdered activated carbon % of Epoxy/PAC on water swelling percent.

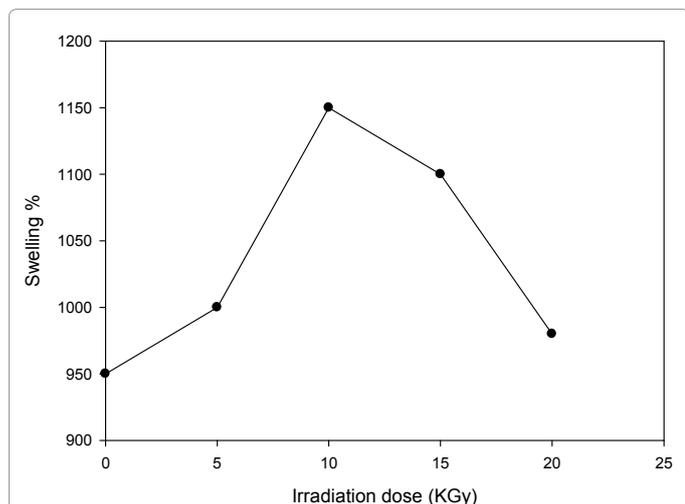


Figure 5: Effect of Gamma irradiation (KGy) of Epoxy/PAC on water swelling percent.

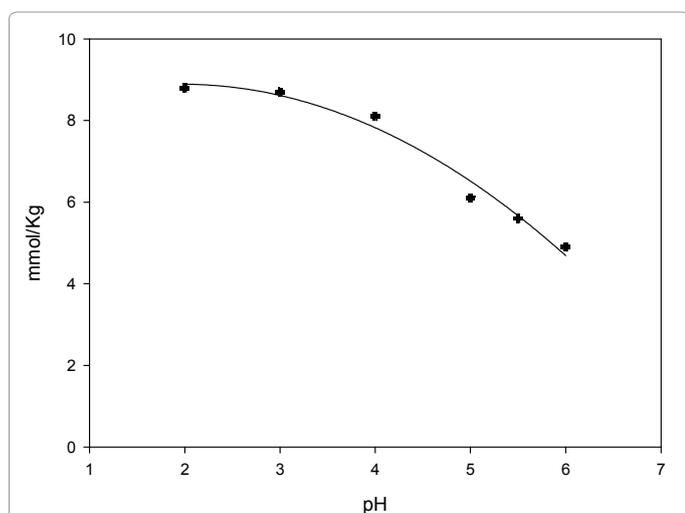


Figure 6: Effect of pH on the amount sorbed of Cs⁺ ion onto Epoxy/PAC at 10% carbon.

textures that are caused by the synthesis process. Figure 3 showed scattered gaps obviously seen due the foaming of the blend, forming a big cavity distributed in a regular manner which is an evidence of achieving homogenous porous resin. Regular distribution of small particles with different color tend to be whitish, it can be explained by PAC distribution through the epoxy foam matrix. Wide channels and cavities have seen, attempt increasing pore number and size and therefore the active sites that; give good chance for potential adsorption of the synthesized porous resin.

Water uptake: Incorporation of hydrophilic properties by hydrogen foaming and insertion a powdered activated carbon groups via network formation assess a very good swelling behavior. Increase powdered activated carbon ratio performed an increase in swelling character to about ten folds (1000%) as it seen in Figure 4. The optimum irradiation dose was 10 kilo gray as it seen in Figure 5 at which water uptake raised to about 1150%. While raising the irradiation dose reduced the water swelling which may due to more irradiation terminated the reaction between the polymer network and active hydrogen. These additives anchored by the resin formation are active to metal ions, backbone structure of the needles resin also opened up and different ratio of carbon and pores present on. It also become available to act as active sites to bind the metal ions (Figure 5).

Application of the porous resin for Cs⁺ adsorption

Effect of pH: Figure 6 presents the effects of initial pH on the removal of Cs⁺ by polymer. It is clear that; the sorption of cesium ion onto the polymer resin was examined from solutions at pH values covering range of 2-6. The sorption of metal ion by the prepared resin decreased with increasing pH. The sorption of metal ion is primarily affected by the surface charge on the sorbent, which in term is influenced by solution's pH. The low sorption at high pH may be explained by the less ability of ions motion towards the resin active site (The metal ion solubility is increase with decrease of pH). It could be attributed to the tendency of metal ions to be precipitated by combination with hydroxyl group (precipitation at high of pH is predominant technique more than adsorption). less availability of H⁺ to compete with these metals for adsorption sites of the composite may affecting on the adsorption reduction [25,26]. Earlier workers [27-29] have suggested that main adsorption sites deprotonated at pH range 3.5-5.5 and attract the positively charged metal ions to facilitate metal binding. The sorption at pH above 6 showed a decreasing trend because of the formation of hydroxyl complexes of cesium ion leading to precipitation of ions. Hence, in subsequent studies, experiments were performed in the solution pH value 2-6.

Effect of contact time: Figure 7 shows plots of the amount sorbed

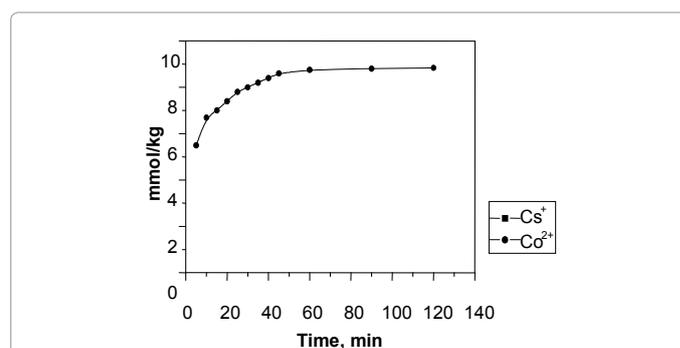


Figure 7: Effect of contact time on the amount sorbed of Cs⁺ ion onto Epoxy/PAC at 10% carbon.

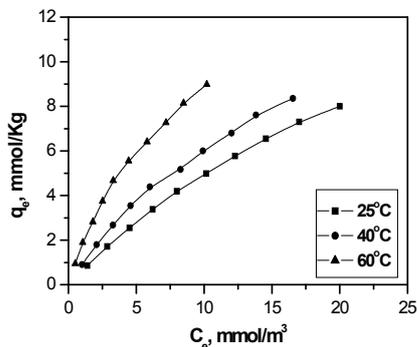


Figure 8: Effect of temperature on the amount sorbed of Cs⁺ ion onto Epoxy/PAC at 10% carbon.

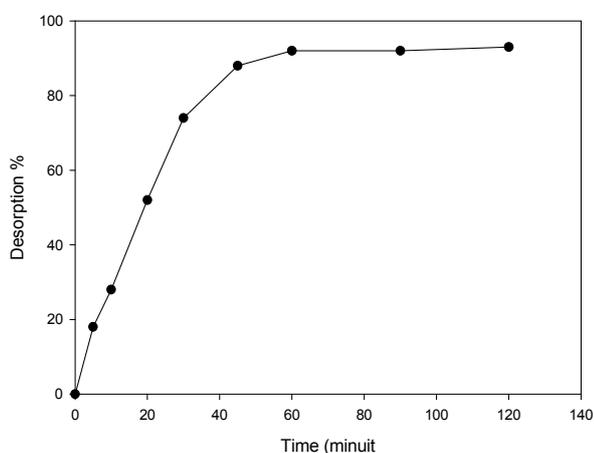


Figure 9: Effect of time (minutes) on desorption of Cs⁺ from Epoxy/PAC at 10% carbon by chemical method.

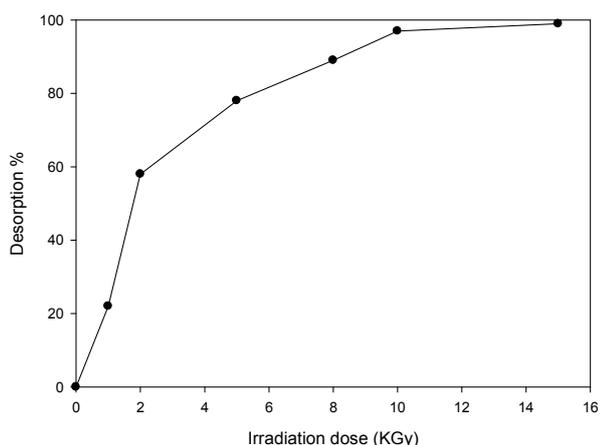


Figure 10: Effect of Gamma irradiation (KGy) on desorption of Cs⁺ from Epoxy/PAC at 10% Carbon.

of Cs⁺ ions from aqueous solutions onto polymer granules, at initial metal ion concentration of 10⁻⁴ M and at room temperature (25 ± 1°C), as a function of contact time. The figure shows a high initial rate of removal within the first 45 minutes of contact (70 - 80% removed) followed by a slower subsequent removal rate that gradually

approached an equilibrium condition in about two hours. The rapid uptake of both metal ions by both studied polymer may be due to adsorption and / or exchange of the ions with some ions in the surface of the polymer. It should be noted that the diffusion of metal ions onto the composite lattice is a time and a temperature dependent. Therefore pseudo equilibrium is attained when the contact time is lengthened. On the basis of these results, three hours of equilibration time was chosen as the optimum period to ensure equilibrium conditions.

Sorption isotherms: Sorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature and pH. An adsorption isotherm describes the relationship between the amount of adsorbate on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. In this concern, the sorption isotherms for removal of Cs⁺ ions from aqueous solutions onto polymer at three different temperatures were determined as shown in Figure 8. The isotherms are regular, positive. The convex isotherms at high concentrations indicated that sorption was reduced [30]. The initial rapid sorption gives way to a slow approach to equilibrium at higher ion concentrations. These results reflect the efficiency of polymer for the removal of Cs⁺ ions from aqueous solution in a wide range of concentrations. The uptake of ions increased with the increase in temperature thereby indicating the process to be endothermic.

Desorption and durability

(Figure 10) Desorption and / or regeneration of metal ions from the studied adsorbent has great economical significance for its reuse adsorbent for several times and recovery of metal ions sorbed especially when it have an economical value in industry or human health. It was reviewed that 0.1 N of hydrochloric acid for 2 hours at room temperature is enough for complete desorption which is agreed well with the results showed in Figure 9 [31,32]. Gamma irradiation was reported also that it used in the regeneration of PAC and also increase their efficiency which may due to degradation of organic traces which may originate through their manufacture and so activate their active sites. Gamma irradiation proved to be more efficient for desorption of metal ions as seen in Figure 10 and also gamma irradiation play a very important role for maintain the capacity of the adsorbent as it seen in the Table 1.

Freundlich isotherm model [33]

Freundlich equation is derived to model the multilayer sorption and for the sorption onto heterogeneous surfaces. The logarithmic form of Freundlich equation may be written as:

$$\log q_e = \log K_f + (1/n) \log C_e \quad (B.1)$$

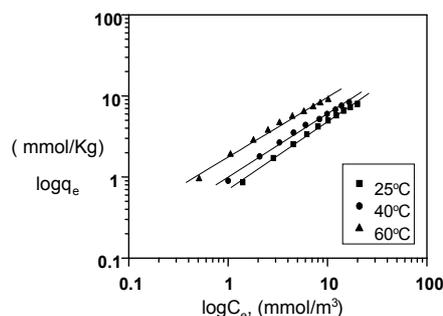


Figure 11: Freundlich isotherm plots for sorption of Cs⁺ ions sorbed onto polymer at different temperatures.

Adsorption Period	Δ adsorption after chemical desorption	Δ adsorption after Irradiation desorption
1	3%	0.5%
2	7%	1%
3	12%	2%
4	17%	2.8%

Table 1: Comparative study of chemical and irradiation for desorption of Cs⁺ from Epoxy/PAC at 10% of carbon.

Temp., °C	1/n	K _f , mmol/kg	R ²
	Cs ⁺	Cs ⁺	Cs ⁺
25	0.837	3.78	0.9985
40	0.782	4.83	0.9964
60	0.735	7.78	0.9953

Table 2: Freundlich isotherm parameters of Cs⁺ ions sorbed onto polymer.

Temp., °C	Q ^o , mmol/kg	b, l/mmol	R ²	R _L
	Cs ⁺	Cs ⁺	Cs ⁺	Cs ⁺
25	78.20	41.5	0.9981	0.194
40	86.10	55.73	0.9939	0.152
60	94.35	105.87	0.9969	0.086

Table 3: Langmuir isotherm parameters of Cs⁺ ions sorbed onto polymer.

Temp., °C	β, mmol ² /kJ ²	X _m , mmol/kg	R ²	E, kJ/mol
	Cs ⁺	Cs ⁺	Cs ⁺	Cs ⁺
25	-0.00564	390.63	0.9995	9.43
40	-0.00465	412.22	0.9982	10.36
60	-0.00373	480.77	0.9980	11.58

Table 4: D-R isotherm parameters of Cs⁺ ions sorbed onto polymer.

Temp., °C	K _c	-ΔG ^o , kJ/mol	ΔH ^o , kJ/mol	ΔS ^o , J/mol.K
	Cs ⁺	Cs ⁺	Cs ⁺	Cs ⁺
25	3.25	2.92	26.86	99.35
40	4.80	4.08		
60	10.00	6.37		

Table 5: Values of thermodynamic parameters for sorption of Cs⁺ onto polymer.

where, q_e is the amount of metal ion sorbed per unit weight of polymer (mmol/kg), C_e is the equilibrium concentration of metal ion in equilibrium solution (mmol/l), K_f is a constant indicative of the relative adsorption capacity of the porous resin (mmol/kg) and $1/n$ is a constant indicative of the intensity of sorption process. The pictorial illustration of q_e vs. C_e is shown in (Figure 11), which suggests that sorption of Cs⁺ onto polymer obeys Freundlich isotherm over the entire range of sorption concentration studied. The numerical values of the constants $1/n$ and K_f are computed from the slope and intercepts, by means of the linear least square fitting method, and given in Table 2. The $1/n$ value is usually dependent on the nature and strength of sorption process as well as on the distribution of active sites. The numerical values of K_f represent sorption capacity of Cs⁺ sorbed onto polymer of a narrow sub- region having equally distribution energy sites towards metal ions.

Langmuir isotherm model [34]: Langmuir sorption isotherm models the monolayer coverage of sorption surfaces and assumes that sorption occurs on a structurally homogeneous adsorbent and all the sorption sites are energetically identical. The linearized form of the Langmuir equation is given by the following formula:

$$(C_e / q_e) = (1/Q^o b) + (1/Q^o) C_e \quad (B.2)$$

where, Q^o is the monolayer adsorption capacity (mmol/kg) and b is a constant related to the free energy of adsorption ($b \propto e^{-\Delta G/RT}$).

The graphic presentations of C_e/q_e vs. C_e give straight lines for Cs⁺

ions sorbed onto polymer as represented in Figure 12, confirming that this expression is indeed a reasonable representation of chemi-sorption isotherm. The numerical value of constants Q^o and b evaluated from the slope and intercept of each plot are given in Table 3. The value of saturation capacity Q^o corresponds to the monolayer coverage and defines the total capacity of the polymer for a specific metal ion. The Langmuir constants Q^o and b for sorption of ions onto polymer increased with temperature showing that the sorption capacity and intensity of sorption are enhanced at higher temperatures. This increase in sorption capacity with temperature suggested that the active surfaces available for sorption have increased with temperature [35]. High values of regression coefficients between the sorbate and sorbent systems for both Langmuir and Freundlich models (around 0.95) indicated the applicability of this resin system for Cs⁺ removal in both monolayer sorption and heterogeneous surface conditions, but the values of R_L for Langmuir adsorption isotherms are lesser than that of Freundlich isotherms represents a slightly better fit to the experimental data than the langmuir and conducting higher applicability.

One of the essential characteristics of the Langmuir model could be expressed by dimensionless constant called equilibrium parameters R_L [36].

$$R_L = 1 / (1 + K_L C_o) \quad (B.3)$$

where, C_o is the highest initial metal ion concentration (mmol/l). The value of R_L indicates the type of isotherm to be irreversible ($R_L=0$), favorable when (Figure 12) ($0 < R_L < 1$), linear ($R_L=1$), or unfavorable ($R_L > 1$). All R_L values as seen in Table 3 were found to be less than 1 and greater than 0 indicating the favorable sorption isotherms of metal ions onto polymer.

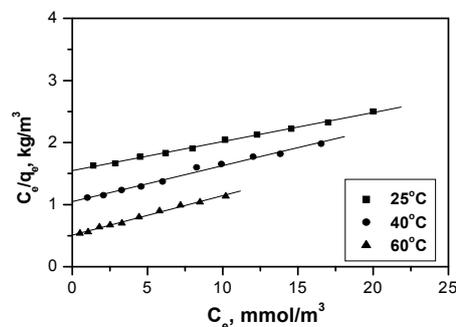


Figure 12: Langmuir isotherm plots for sorption of Cs⁺ ions onto polymer at different temperatures.

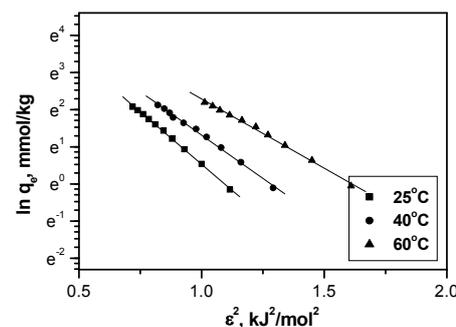


Figure 13: D-R isotherm plots for the sorption of Cs⁺ ions sorbed onto polymer at different temperatures.

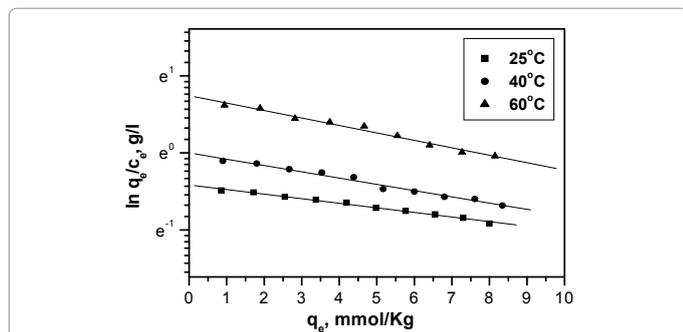


Figure 14: Plot of $\ln(q_e/c_e)$ versus q_e for sorption of Cs⁺ ions onto polymer at different temperatures.

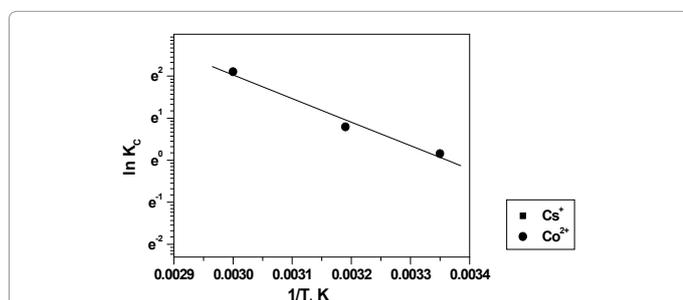


Figure 15: Plot of $\ln K_c$ versus $1/T$ for sorption of Cs⁺ ions onto polymer.

Dubinin-Radushkevich (D-R) isotherm model: D-R isotherm describes sorption on a single type of uniform pores. In this respect, the D-R isotherm is an analogue of Langmuir type but it is more general because it does not assume a homogeneous surface or constant sorption potential [37]. The D-R isotherm is given with the following equation:

$$\ln q_e = \ln q_m - \beta \xi^2 \quad (B.4)$$

where, q_m is the maximum amount of ion that can be sorbed onto unit weight polymer i.e., sorption capacity (mmol/kg), β is a constant related to the sorption energy (mol^2/kJ^2); and ξ is the Polanyi potential which is equal to $RT \ln(1 + 1/C_e)$, where R is the gas constant ($\text{kJ}/\text{mol.K}$), and T is the absolute temperature. The mean free energy of sorption is the free energy change when one mole of ion is transferred to the surface of the polymer from infinity in the solution, and it is calculated from:

$$E = (-2\beta)^{-1/2} \quad (B.5)$$

The magnitude of E can be related to the reaction mechanism. If E is in the range of 8-16 kJ/mole, sorption is governed by ion exchange [38,39]. In case of $E < 8$ kJ/mole, physical forces may affect the sorption mechanism.

The D-R plots of $\ln q_e$ versus ξ^2 for sorption of both ions onto polymer at different temperatures are given in Figure 13, these linear plots indicate that the D-R isotherm expression is followed for each metal ion. Linear regression analysis using paired of $\ln q_e$ and ξ^2 resulted in derivation of q_m , β , E and the correlation factor (R^2). The correlation factor is a statistical measure of how well the data points fit the regression line. These D-R parameters, evaluated for sorption of both ions at different temperatures, are presented in Table 4. The maximum sorption capacities (q_m) are in the ranges of 390.6 – 480.8 mmol/kg for Cs⁺ ions. The values of the mean free energy, E , of sorption in all cases is in the range of 8-16 kJ/mol, which are within the energy ranges of ion exchange reaction which agree with the results obtained from freundlich isotherm.

Effect of temperature: Temperature has two major effects on adsorption processes. Increasing temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in velocity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [35]. In order to gain insight into the thermodynamic nature of the sorption process, several thermodynamic parameters for the present systems were calculated. The Gibbs free energy change, ΔG° , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity.

The free energy of the sorption reaction is given by the following equation:

$$\Delta G^\circ = -RT \ln K_c \quad (B.6)$$

where K_c is the sorption equilibrium constant, R is the gas constant and T is the absolute temperature. The values of thermodynamic equilibrium constant at different studied temperatures were determined by plotting $\ln q_e/c_e$ against q_e and extrapolating to zero q_e according to the method of Khan and Singh [40] as shown in Figure 14. The variation of K_c with temperature by applying equation Eq.[B.6] interpreted that K_c values increase with increase in sorption temperature, thus implying a strengthening of adsorbate-adsorbent interactions at higher temperature. Also, the obtained negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of the sorption processes with preference towards Cs⁺ ions (Figure 14).

(Table 5) Other thermal parameters such as enthalpy change (ΔH°), and entropy change (ΔS°) were calculated using the relationship:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (B.7)$$

The values of enthalpy change (ΔH°) and entropy change (ΔS°) calculated from the slope and intercept of the plot of $\ln K_c$ versus $1/T$ (Figure 15) are also given in Table 5. The change in ΔH° for both ions in polymer was found to be positive confirming the endothermic nature of all the sorption processes. ΔS° values were found to be positive due to the exchange of the metal ions with more mobile ions present on polymer, which would cause increase in the entropy during the sorption process. In the case of physio-sorption, which may also contribute to the total sorption process, water molecules released from the hydrated metal ions or from the sorption surface may also cause an increase in the entropy.

Conclusion

For increase up the applicability of the powdered activated carbon (PAC), it could be inserted into the epoxy foam matrix. The reactivity of the PAC have confirmed by FTIR, TGA which approved the applicability of the composite through wide range of temperature reached to 220°C. While homogeneity of the sample have been assured by scan electron microscope. Hydrophilicity of the composite has measured by water uptake evaluation which reached to 1000%. Mode of action of the composite adsorption availability for Cs⁺ have discussed by applying Freundlich, Langmuir and Dubinin-radushkevich (D-R) isotherm, that attempt adsorption obeyed all models used. While Adsorption tend to fit with freundlich more than langmuir isotherm specially at higher temperature. Measurements of ΔG° is a negative value confirmed the adsorption reactions occurred spontaneously at a given temperature.

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