Selective Adsorption of 2-nitrophenol, Phenol, Hydroquinone on Poly (Vinyl Alcohol) Crosslinked Glutaraldehyde-β-cyclodextrin Polymer Membrane

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Abstract The aim of this paper is to use poly (vinylalcohol) polymer membrane as an adsorbent for the removal of 2-nitrophenol, phenol, hydroquinone from aqueous solutions through the batch experiments. In order to obtain efficient adsorbent, cross-linked poly(vinyl alcohol)/glutaraldehyde-β-cyclodextrin membranes were prepared. Synthesized membranes were characterized by infrared spectroscopy and swelling measurements. Then, influence of pH, temperature on the adsorption process was investigated. As results, β-cyclodextrin is completely mixed into the PVA polymer without covalent bond formation. And absorption level of PVA/GA membranes is significantly improved by the presence of β-cyclodextrin. Adsorption capacity increases with increasing amount of cyclodextrin, and it reached the highest value at pH<pKa; the change in adsorption capacities may be due to the structure effect, weight molecular of phenolic compounds. Therefore, results of adsorption isotherms indicated that the Freundlich isotherm model was more appropriate, the low temperature is favourable for adsorption and the negative value of free energy indicated the spontaneous nature process and easy regeneration of polymeric materials.

Keywords: poly (vinyl alcohol), β-cyclodextrin, swelling, adsorption, 2-nitrophenol

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1. Introduction

Water pollution by organic and inorganic contaminants is of immense public concern. A typical group of organic contaminants is the phenols and its derivative; these are important environmental pollutants because of their toxic effect, ubiquitous presence, and carcinogenic character towards life in the aquatic environment [1].

Phenol and its derivatives are some of the most refractory contaminants, which may occur in the environment due to its widespread use in agriculture, petrochemical, textile, paint, dyes, industrial resins, plastics, adhesives, and paper industries, medical and health products, electrical industries [2]. These substances have been categorized into the priority pollutants by US Environmental Protection Agency (USEPA) and need to be eliminated with the specific treatment [3].

The regular treatment methods for water containing phenol are flocculation, solvent extraction, adsorption, advanced oxidation, photocatalytic oxidation, and electrochemical degradation [4]. The adsorption process by solid adsorbents is widely used for treatment of industrial wastewater, it has advantages over the other methods; because of simple design and can involve low investment in term of initial cost. In recent years, the search for low-cost adsorbents that have pollutant binding capacities has intensified. Many materials such as synthetic resin, green macro alga, and bagasse fly ash have been used in phenol removal from aqueous solution. However, Adsorption of organic pollutants onto cyclodextrin-based polymer (CDPs) is an efficient technique with the advantages of specific affinity, low cost and simple design, and high selectivity [5].

Hydrophilic polymer materials are widely used in the adsorption processes for their high resistance to organic solvents [6]. Polyvinyl alcohol (PVA) is a water-soluble synthetic biopolymer, biodegradable, and readily available low-cost. It can be crosslinked by chemical or physical methods to form membrane or hydrogel with specific properties such as adsorption, good biocompatibility, bioadhesive, good mechanical properties, and high degree of swelling and ease of processing. However, to improve the functionality of PVA, this polymer is often combined with nanoparticles and other synthetic and natural polymers, such as polyacrylic acid [7], polyethylene glycol, poly (N-isopropylacrylamide), poly (vinyl pyrrolidone), chitosan, gelatin and cyclodextrin [8].

Cyclodextrins can play a major role in environmental science in terms of enrichment and removal of organic pollutants and heavy metals from soil, water and atmosphere by inclusion complex formation. Especially, with aromatics and heterocycles [9].

The aim of this work is to increase the importance of the chemical modification of polymer membranes in order to get a material with improved absorbency and efficient phenolic compounds removal.

In experimental, various amounts of β-cyclodexrin were embedded in crosslinked poly (vinylalcohol) glutaraldehyde polymer membranes (PVA/GA). Modified membranes (PVA/GA/β-cyclodextrin) were characterized by infrared analysis (FTIR), the treated polymers showed interesting behavior in swelling. Adsorption of 2-nitrophenol, phenol, hydroquinone on polymer membranes (PVA/GA) and (PVA/GA/β-cyclodextrin) was consequently studied using UV-Vis spectroscopy.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) MM 50000 from LABOSI, hydrated β-cyclodextrin $C_{42}H_{72}O_{36}.H_2O$ (Aldrich), Glutaraldehyde (25wt% in water solution) from Panreac Chemical, Chloride acid HCl (Aldrich), All the chemicals used in the study were of analytical reagent grade.

Phenol C_6H_6O, M_m=94.11 gmol^{-1}, 2-nirorophenol $C_6H_5NO_3$, M_m= 139.11 gmol^{-1}, and hydroquinon $C_6H_4(OH)_2$, M_m=110.11gmol^{-1} were obtained from Merck, and used without further purification.

2.2. Synthesis Procedure

Amount of PVA/β-cyclodextrin mixture (weight ratio β-cyclodextrin to PVA was 0.02, 0.04, 0.06 and 0.08) was dissolved in 20 ml of hot water into a two necks round bottom flask at 363 K and under stirring. After about 2 hours, a clear transparent solution was obtained, and then 1 ml Glutaraldehyde and 0.4 ml HCl (catalyst) were added into the flask with continuous stirring at room temperature. After 1 h, the solution was filtered; and then the resulting homogeneous solution was poured into glass plate and allowed to dry at room temperature for 1-2 days. Finally, the obtained membranes were washed several times with distilled water to remove any remaining reagent, dried at room temperature and then treated at 393 K for 3 h.

2.3. Swelling Measurement of the Polymer Membranes

The swelling properties of PVA membranes were determined by conventional water uptake measurements. The membranes were completely dried under vacuum at 303 K for 24 h, and then weighed [10]. The dried membranes were then immersed in distilled water and weighed at regular time intervals until equilibrium was reached. The evaluation of swelling is performed by measuring the amount of liquid absorbed by the material as a function of time; up to saturation. The swelling rate is determined as follows:

$$Swelling\ rate = \left[\frac{Wwet - Wdry}{Wdry}\right] \times 100 \qquad (1)$$

Where W_{wet} and W_{dry} are the weights of dry and swollen sample respectively.

2.4. Adsorption Experiments

Adsorption experiments were carried out by the batch equilibrium technique with 0.1g PVA/GA/β-cyclodextrin membrane with 4 cm^2 of dimension and 25ml organic pollutant solution with an initial concentration of 100mg·L^{-1} in a conical flask. In the kinetic experiments, separating flasks were prepared and shaken at regularly stirring for equilibrium time 24 h, at natural pH and room temperature 294 K. Then, effect of solution pH was studied by adjusting the pH at 3,6,12 using dilute HCl and NaOH solutions. The effect of temperature (294 K, 303 K, 313K, and 333 K) on phenolic compounds removal was also investigated.

Residual pollutant concentration was analyzed after measurements of absorbance values with Shimadzu Model UV-1202 spectrophotometer at wavelengths of 270, 340, 292 nm for phenol, 2- nitrophenol, and hydroquinone respectively [11].

The adsorption capacity of phenolic compounds Q (mg g^{-1}) was calculated by the following equation:

$$Qe = \frac{(Co - Ce)}{W} \times V \qquad (2)$$

Where Qe is the amount of adsorbed per mass unit of adsorbent (mg g^{-1}), C_0 and Ce are the initial and equilibrium solution concentrations respectively (mg L^{-1}), V is the volume of pollutant solution (L), and W is the amount of adsorbent (g).

Blank sample PVA/GA polymer membrane without β-cyclodextrin was used for the comparison under the same conditions.

Langmuir isotherm

Langmuir models predict that adsorption occurs uniformly on the specific sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at this site. Therefore a saturation value is reached (monolayer coverage). The Langmuir model equation is:

$$Qe = K_L \times \frac{Ce}{(1 + a_L Ce)} \qquad (3)$$

Where Qe is the equilibrium concentration of adsorbate (mg g^{-1}); Ce is the equilibrium adsorbate in the solution (mg L^{-1}), K_L (L g^{-1}) and a_L (L mg^{-1}) are Langmuir constant, being K_L/a_L is the theoretical monolayer capacity q_{max}. The linear form of the Langmuir isotherm can be represented by the following equation:

$$\frac{Ce}{Qe} = \frac{1}{K_L} + \frac{a_L}{K_L} \times Ce. \qquad (4)$$

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimension less separation factor (R_L) which is defined by:

$$R_L = \frac{1}{(1 + K_L Co)} \qquad (5)$$

Where C_0 is the initial solute concentration (mg L^{-1}). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [12].

Freundlich isotherm

The empirical model was shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surface [13]. The empirical equation is:

$$Qe = \text{Ln}K_F + K_F Ce^{1/n_F} \qquad (6)$$

Where K_F is the Freundlich constant (L g^{-1}) and $1/n_F$ is the heterogeneity factor. If $n_F > 1$, the adsorption is favourable. From a linear fit of Eq. 6, these empirical values were obtained.

$$\text{Ln}\,Qe = \frac{1}{n_F}\text{Ln}Ce + \text{Ln}K_F. \qquad (7)$$

The standard free energy of adsorption DG_0 (kJ mol^{-1}), can be obtained using Eq. 8, where K_L is constant in terms of L mol^{-1}:

$$\Delta G = -RT\text{Ln}\,K_L \qquad (8)$$

Where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T=294 K.

3. Results and Discussion

3.1. FTIR Membrane Characterization

The infrared spectrum of membranes exhibits several bands characteristic of stretching and bending vibrations of poly (vinyl alcohol) (Figure 1):

- A strong band was observed at 3400 cm^{-1} corresponding to the O-H stretching frequency, which indicate presence of hydroxyl groups of PVA [14], and bands observed at 2900 cm^{-1} and 1429 cm^{-1} indicates an asymmetry in stretching mode of CH$_2$ group.

- Bands at 1600 cm^{-1} and 1700 cm^{-1} corresponded to stretching mode of carbonyl groups (-CO-); that confirms the crosslinking of poly(vinyl alcohol) by glutaraldehyde.

-The bands at 1157 cm^{-1} represented on Figure 1 (b) are characteristic of cyclodextrin (C-O-C), these bands were also observed by B. George [15] and J. Zhang [16]. On the other hand spectra (a) and (b) show no new bands related with cyclodextrin, this indicates that there is no covalent bond formation between PVA and β-cyclodextrin: cyclodextrin is completely mixed into the PVA matrix polymer [17].
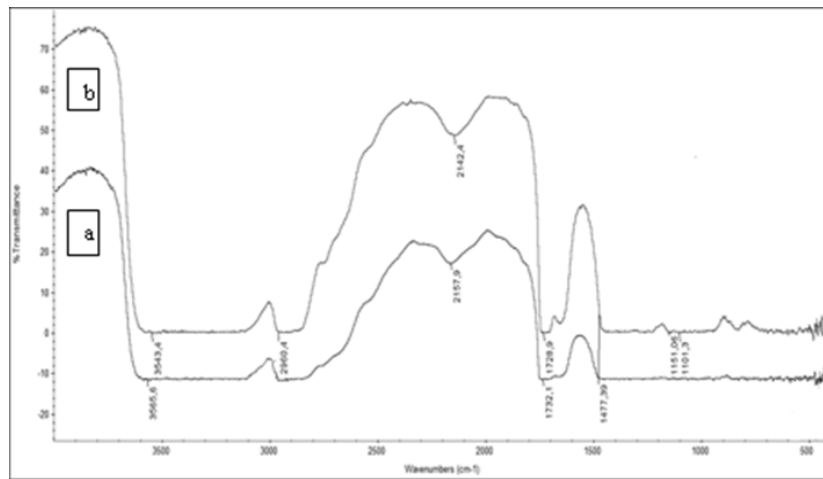

Figure 1. FTIR spectra of PVA/GA (a) and PVA/GA/β-cyclodextrin (b) polymer membrane

3.2. Swelling Behavior of the PVA/GA and PVA/β-cyclodextrin/GA Polymer Membranes

The data of swelling measurement represented on Figure 2, shows that absorption level of PVA/GA membranes is significantly improved by the presence of β-cyclodextrin. The swelling ratio obviously increased with increase of β-cyclodextrin amount (for 2% β-cyclodextrin, swelling ratio increased from 58% to 80% and for 8% β-cyclodextrin it increase from 58% to 100%) for a period time of 200 min; this implying that the PVA/GA/β-cyclodextrin is more hydrophilic than the PVA/GA membrane alone [10].
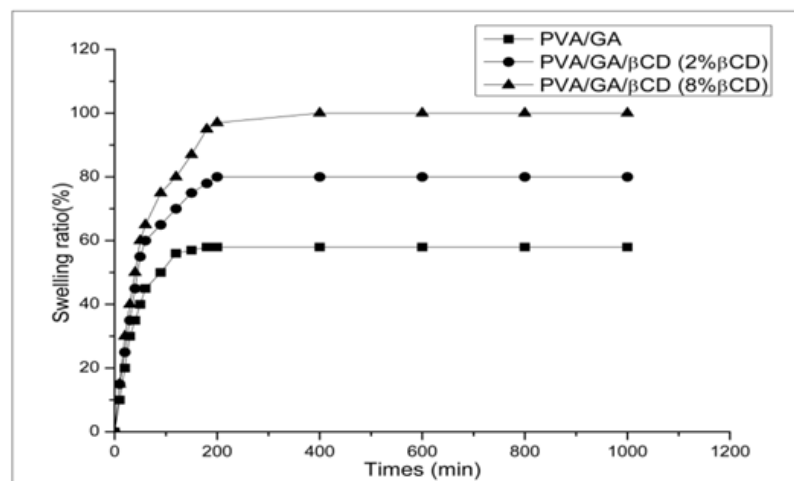

Figure 2. Swelling measurement of the membranes PVA / GA and PVA / GA / β-cyclodextrin (2% and 8% β-cyclodextrin) in distilled water (T=294K, pH =7)

Retention properties of PVA/GA membrane is due to its hydrophilic structure; that confirm a wider use of hydrophilic membrane based PVA for the deshydratation of organic liquids in pervaporation domain.

The Increase in swelling ratio of the PVA/GA/β-cyclodextrin polymer membranes result first, from the interaction between hydroxyl groups of PVA and secondary hydroxyl groups of cyclodextrin and liquid molecules, Then, probably from the increase in free volume in presence of β-cyclodextrin. Also, apolar cavity of the cyclodextrin plays a very important role in water retention of polymer membrane.

3.3. Equilibrium Adsorption of Phenolic Compounds

The results of adsorption equilibrium of 2-nitrophenol, phenol and hydroquinone on PVA/GA and PVA/GA/β-cyclodextrin polymer membranes are shown in the isotherms presented in Figure 3, Figure 4, and Figure 5 respectively where it is plotted Qe (mg g^{-1}) of phenolic compounds adsorbed per g of dry membrane, versus Ce final equilibrium concentration in solution expressed in mg L^{-1}.
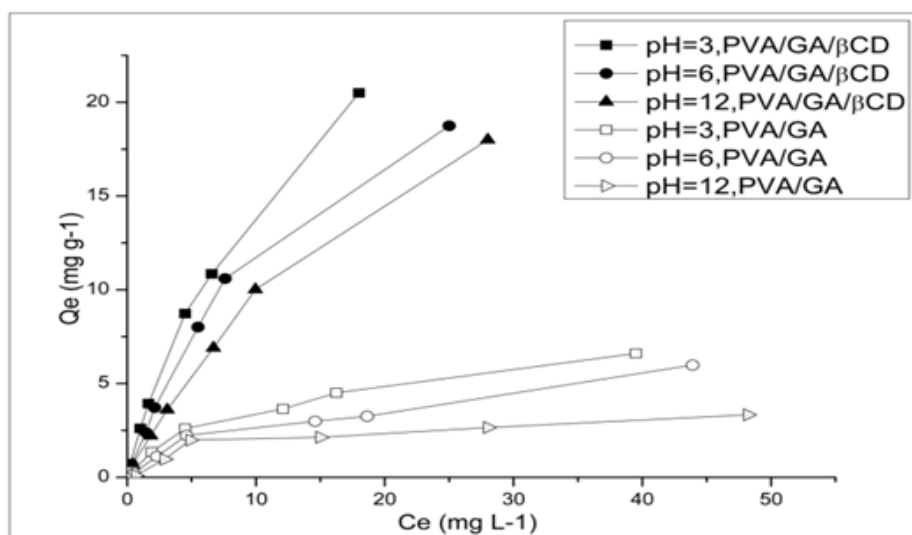
Figure 3. Equilibrium adsorption of 2- Nitrophenol on PVA/GA/β-cyclodextrin and PVA/GA at various pH (3, 6, 12) (T=294K, C_0=100mg L^{-1}, 8% β-cyclodextrin content)
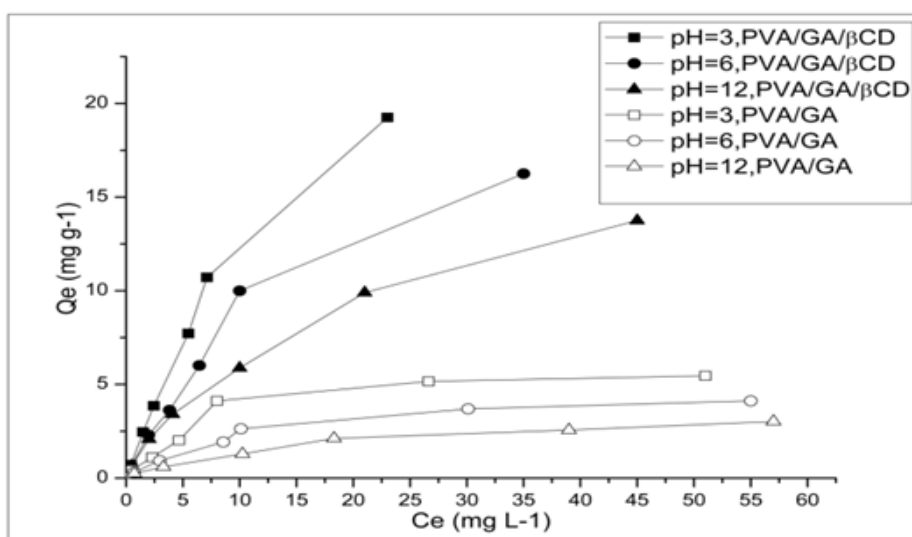
Figure 4. Equilibrium adsorption of phenol on PVA/GA/β-cyclodextrin and PVA/GA at various pH (3, 6, 12) (T=294 K, C_0=100mg L^{-1}, 8% β-cyclodextrin content)

From the data, we observed that for three phenolic compounds, the adsorption capacity value increased with increase in the β-cyclodextrin content on the PVA/GA membranes, signifying that membrane with higher β-cyclodextrin content (8%) had an excellent performance for the phenolic compounds adsorption; these results confirms that cyclodextrin plays a very important role in adsorption process thanks to its internal cavity, also, β-cyclodextrin can typically complex aromatics and Heterocycles [18].

The adsorption isotherms shape indicates behaviour of L2 type of Giles and Smith classification. Most of the adsorption isotherms of phenolic compounds reported in the literature are the same type L_2 of isotherms [19].

The curves shape were indicative of a high affinity between the PVA/GA/β-cyclodextrin surface and molecules of phenolic compounds. We observed a rapid adsorption then equilibrium. The rapid adsorption probably due to the abundant availability of active sites on the polymer membrane surface and with the gradual

occupancy of these sites; the adsorption became less efficient, therefore, at low initial concentration this membrane effectively eliminates the pollutant, but at higher concentrations the isotherms reach a maximum. The increase in adsorption capacity with increasing pollutants concentration could be due to higher probability of collision between phenol molecules and adsorbent surface [20]. Similar results were reported for the adsorption of phenols on garlic peel [21].
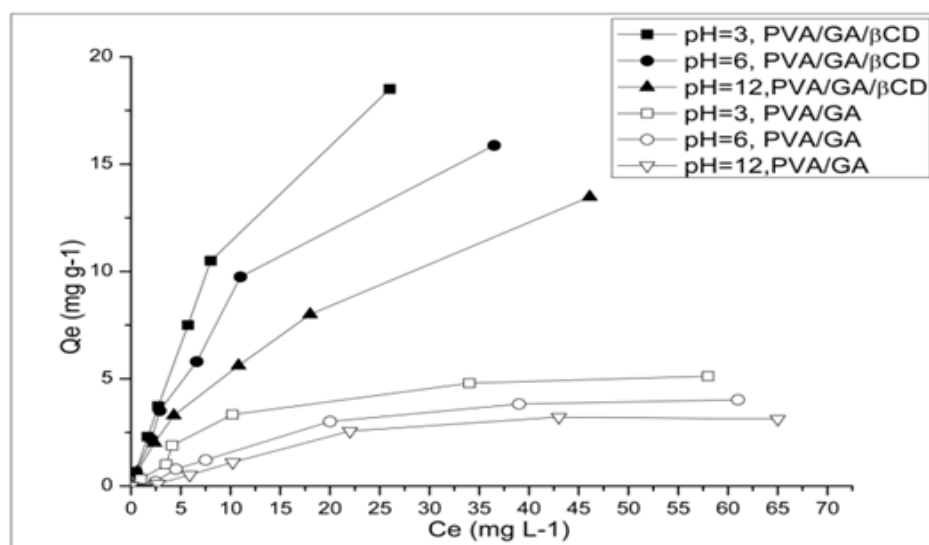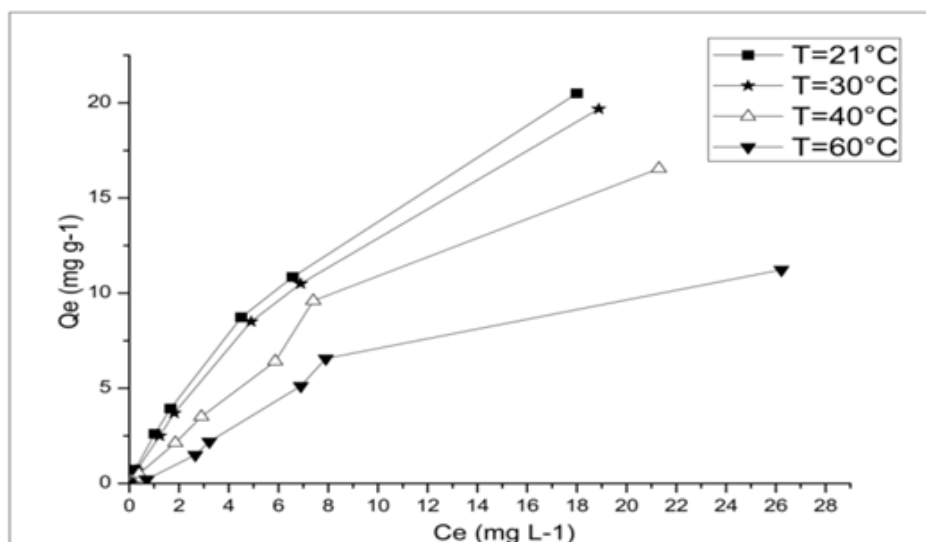

Figure 5. Equilibrium adsorption of hydroquinone on PVA/GA/β-cyclodextrin and PVA/GA at various pH (3, 6, 12) (T=294 K, C_0=100mg L^{-1}, 8% β-cyclodextrin content)

However, when comparing results, we observe that adsorption of 2-nitrophenol is higher than phenol, and hydroquinone; this is due to dipolar moment (presence of NO_2^- and OH^- groups); the phenol is more polar than the 2-nitrophenol; which effect the inclusion complex formation [9]. And lipophilic cavity of cyclodextrin molecules provides a microenvironment, into which appropriately sized non-polar moieties can enter to form inclusion complexes. No covalent bonds are formed during formation of the inclusion complex. The main driving force of complex formation is the release of enthalpy-rich water molecules from the cavity, van der waals and hydrophobic interactions, hydrogen bonding [22].

On the other hand, adsorption of phenol is higher than hydroquinone, probably because of the lower molecular weight of phenol, then, inclusion complex formation of cyclodextrin is a function of the size of the guest molecule or certain key functional groups within the guest, and of the thermodynamic interactions between the different components of the system (cyclodextrin, guest, solvent) which confirms selectivity of cyclodextrin.

1. Effect of Temperature

In our experiment, effect of temperature on the adsorption capacities was investigated. Results were shown in Figure 6, Figure 7 for 2-nitrophenol and phenol respectively.

Figure 6. Equilibrium adsorption of 2- Nitrophenol on PVA/GA/β-cyclodextrin at various temperature (294, 303, 313, 333 K) (C_0=100mg L^{-1}, 8% β-cyclodextrin content, pH=3)
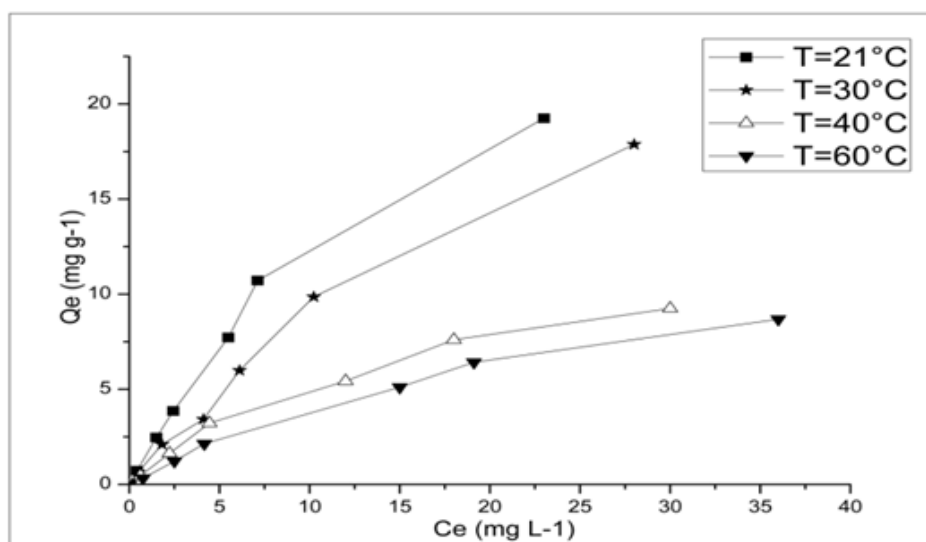
Figure 7. Equilibrium adsorption of phenol on PVA/GA/β-cyclodextrin at various temperature (294, 303, 313, 333 K) (C$_0$=100mg L^{-1}, 8% β-cyclodextrin content, pH=3)

The data indicated that with increasing temperature from 294 K to 303, 313, 333 K, adsorption capacities decrease for all pollutants (decrease over 70% at T=333K), similar results implies that the low temperature is favourable for adsorption of phenolic compounds. [23]. The decrease in adsorption with increase in temperature; is partly due to the weakening of the attractive forces between the phenolic compounds and adsorbent. It could also be attributed to the enhancement of thermal energies of the adsorbate, thus making the force between adsorbent and adsorbate insufficient to retain the adsorbed molecules at the binding sites.

2. Effect of pH

In order to optimize the pH to achieve maximum removal efficiency, experiments were conducted in a wide range of pH, from 3 to 12. The data presented in Figure 3,

Figure 4, Figure 5 indicated that, for three pollutants, adsorption capacity reached the highest value at pH =3, whereas it decreased greatly with pH increase; for 2-nitrophenol, the maximum adsorption capacity decreased from 39,370 mg g^{-1} at pH=3 to 29.325mg g^{-1} at pH=12 (Table 1), and for phenol from 36.901mg g^{-1} at pH=3 to 18,587 mg g^{-1} at pH=12 (Table 2), and for hydroquinone From 35.8423 mg g^{-1} at pH=3 to 17.4216 mg g^{-1} at pH=12 (Table 3). The behavior can be explained with the adsorption mechanism interaction adsorbent/adsorbate/solvent. Generally, the pH of the solution plays an important role in the whole adsorption process, influencing not only the solution phenolic compounds chemistry, but also the surface charge of the polymer [24]. The polymer contains hydroxyl groups (at alkaline pH these groups are deprotonated). In alkaline medium, the surface of polymer becomes negatively charged.

Table 1. Isotherms constants and correlation coefficients from Langmuir and Freundlich isotherms models for 2-Nitrophenol adsorption by PVA/GA/β-cyclodextrin polymer membrane

pH	Langmuir isotherm						Freundlich isotherm			
	K_L	a_L/K_L	q_{max}	R^2	R_L	$\Delta G_{ads}(J)$	K_F	$1/n_F$	n_F	R^2
3	2.694	0.0254	39.370	0.9409	0.1275	-2422.927	2.4823	0.7731	0.4028	0.9944
6	2.000	0.0331	30.211	0.9872	0.1312	-1694.271	1.8615	0.7843	1.2750	0.9848
12	1.400	0.0303	29.325	0.9647	0.1908	-822.968	1.4294	0.7970	1.2547	0.9949

Table 2. Isotherms constants and correlation coefficients from Langmuir and Freundlich isotherms models for phenol adsorption by PVA/GA/β-cyclodextrin polymer membrane

pH	Langmuir isotherm						Freundlich isotherm			
	K_L	a_L/K_L	q_{max}	R^2	R_L	$\Delta G_{ads}(J)$	K_F	$1/n_F$	n_F	R^2
3	1.811	0.0271	36.901	0.9703	0.1694	-1451.628	1.7059	0.8419	1.1877	0.9840
6	1.323	0.0394	25.380	0.9565	0.1610	-684.168	1.3494	0.7606	1.3147	0.9806
12	1.075	0.0538	18.587	0.9908	0.1473	- 176.774	1.1864	0.6799	1.4708	0.9910

Table 3. Isotherms constants and correlation coefficients from Langmuir and Freundlich isotherms models for hydroquinone adsorption by PVA/GA/β-cyclodextrin polymer membrane.

pH	Langmuir isotherm						Freundlich isotherm			
	K_L	a_L/K_L	q_{max}	R^2	R_L	$\Delta G_{ads}(J)$	K_F	$1/n_F$	n_F	R^2
3	1.5559	0.0279	35.8423	0.9506	0.1872	-1080.520	1.4693	0.8547	1.1700	0.9796
6	1.3036	0.0416	24.0384	0.9817	0.1557	-648.060	1.3086	0.7591	1.3173	0.9762
12	0.9273	0.0574	17.4216	0.9751	0.1582	-184.492	1.0488	0.6953	1.4382	0.9919

However, the effect of pH on the removal efficiency could be explained by considering the presence of ionic and molecular forms of phenolic compounds in aqueous

solutions. The phenolic compounds considered in this study: 2-nitrophenol, phenol, hydroquinone, have pKa values of 7.23, 9.9, and 9.96 respectively, suggesting that

phenol is a weak acid; hence, they only exist as anions at high pH values. Phenolic compounds are proton donors, so they become anions at a certain pH (%50 in the anion form at pH= pKa).

In acidic solutions, the molecular form dominates, while in alkaline mediums (pH >pKa), the anionic form (phenolate anions) is the predominant species, and the surface charge on the PVA/GA/β-cyclodextrin membrane becomes negative, which probably leads to a lower electrostatic attraction between the phenolate anions and the anionic functional groups of PVA membrane surface [25]. Also, β-cyclodextrin selected the molecular form then the anionic form of the guest. Therefore, phenolic

compounds effectively adsorbed on to the adsorbent as molecules but not phenolate ions [26].

3. Adsorption isotherm

Adsorption data were fitted to Langmuir and Freundlich isotherm in the form expressed in Eqs. 4 and 7. Figure 8 and Figure 9 show linear plots of 2-nitrophenol to Langmuir and Freundlich model respectively, and Figure 10 and Figure 11 are similar for phenol. Table 1, Table 2 and Table 3 summarize the values of Langmuir and Freundlich parameters for 2-nitrophenol, phenol, hydroquinone respectively.
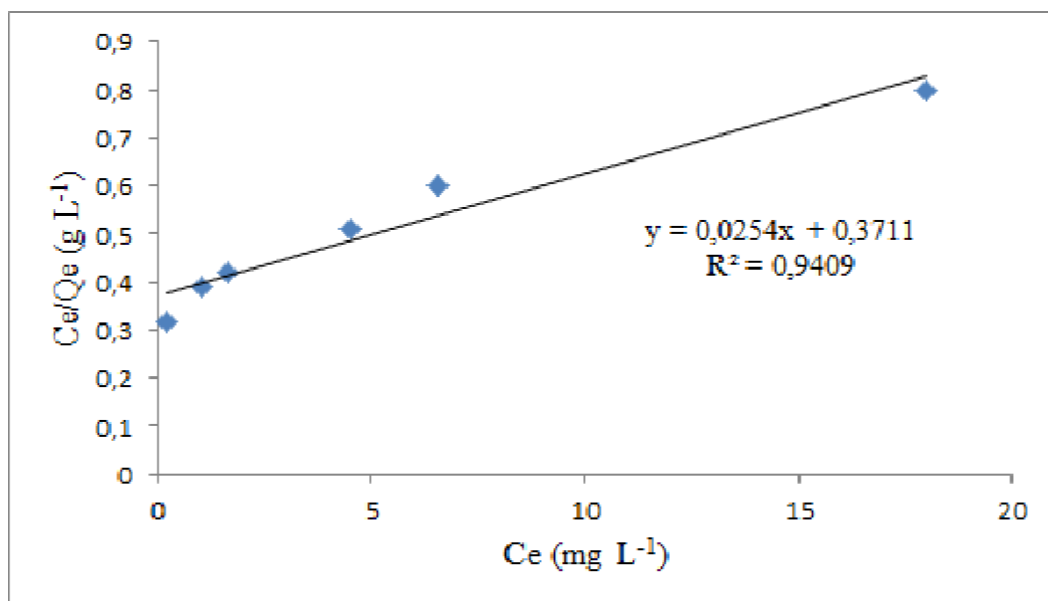

Figure 8. Linear fit of adsorption data of 2-nitrophenol on PVA/GA/β-cyclodextrin polymer membrane to Langmuir model at pH=3

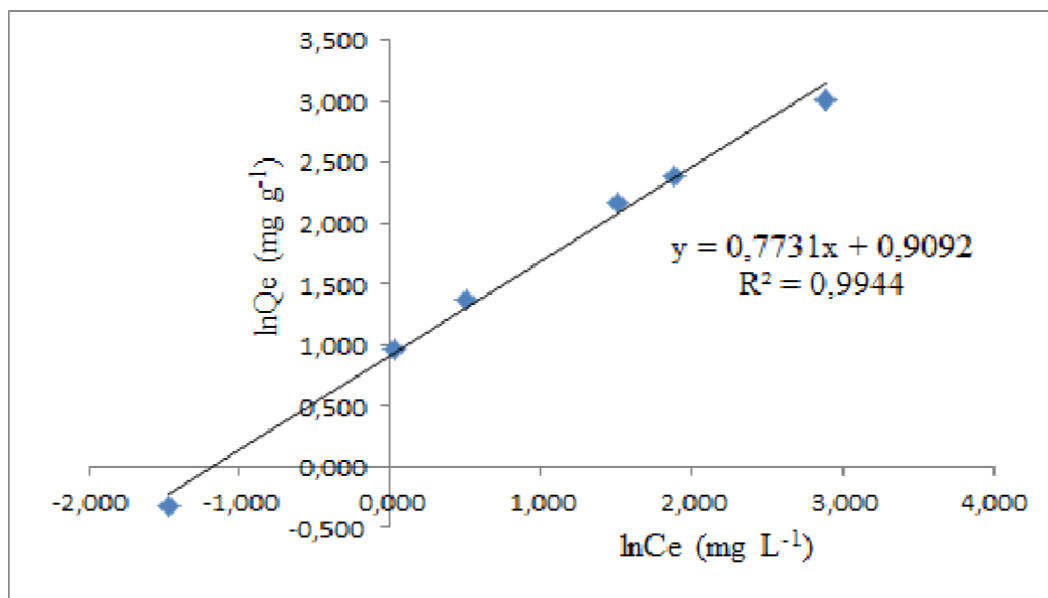**Figure 9.** Linear fit of adsorption data of 2-nitrophenol on PVA/GA/β-cyclodextrin polymer membrane to Freundlich model at pH=3

The linearization of equilibrium data (Figure 8, Figure 9) showed that the adsorption of 2-nitrophenol on the PVA/GA/β-cyclodextrin membrane complied with both Langmuir and Freundlich isotherm model. Nevertheless, the R^2 value >0.98 (Table 1) of Freundlich model was higher than that of Langmuir model (there is good correlation), so the Freundlich isotherm model was more

appropriate for 2-nitro phenol adsorption on the membrane. Similar results were found for phenol and hydroquinone (Table 2 and Table 3).

However, Results indicated that, values of the parameters K_L, and q_{max} are higher for 2-nitrophenol than for phenol and hydroquinone; which confirmed high affinity between 2-nitrophenol and PVA/GA/β-cyclodextrin

membranes (Figure 3, Figure 4, Figure 5); the results might be explained as the inclusion of cyclodextrin was influenced by the structure molecule size, and the dipole moment. Moreover, the nitro group and the hydroxyl groups interacting with the secondary hydroxyl of β-cyclodextrin [27].
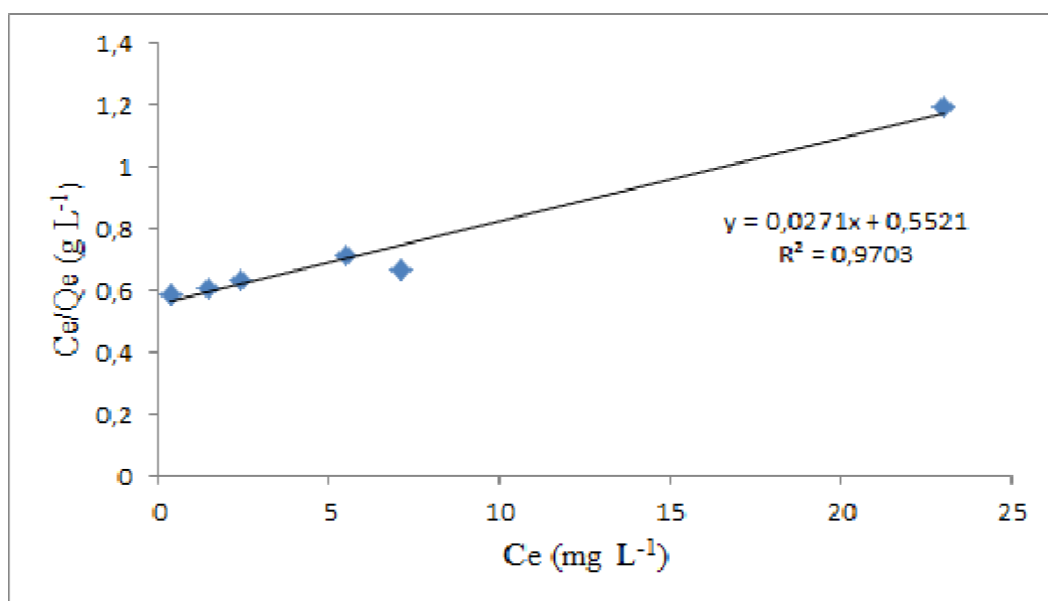

Figure 10. Linear fit of adsorption data of phenol on PVA/GA/β-cyclodextrin polymer membrane to Langmuir model at pH=3
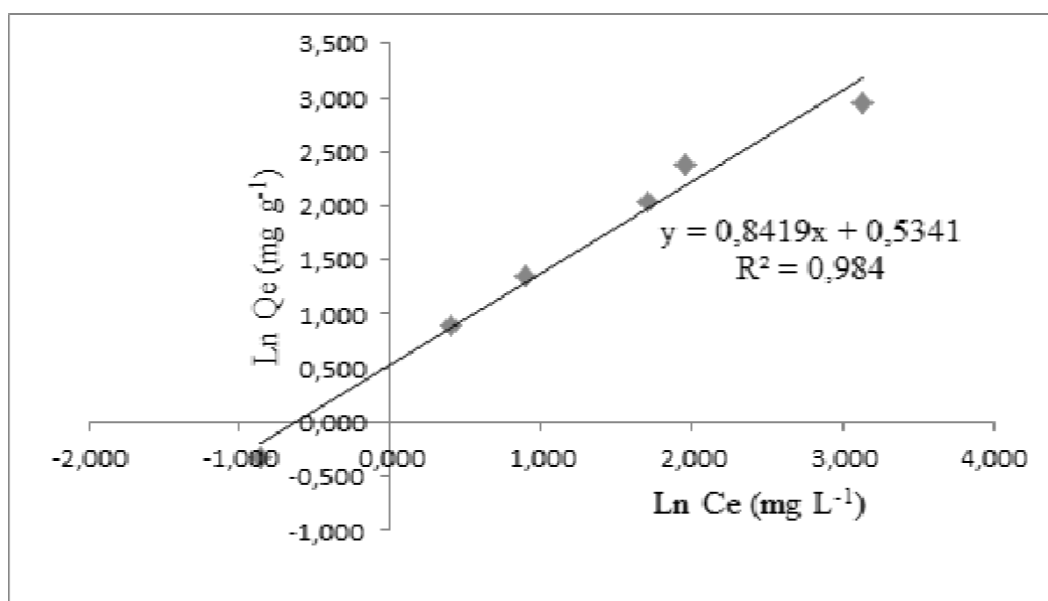

Figure 11. Linear fit of adsorption data of phenol on PVA/GA/β-cyclodextrin polymer membrane to Freundlich model at pH=3

Results show also, that for three phenolic compounds, the value of R_L is between 0 and 1, confirming the favorable pollutants adsorption process [12]. And $n_f > 1$, suggesting that the adsorption process was favorable under the studied conditions and, $1/n_F$ values close to 1 suggests a favorable adsorption of the adsorbent surface rather homogeneous (Table 1, Table 2, Table 3).

From the data, we observed that the high adsorption capacities q_{max} decreased with pH increase, this is confirmed by the decrease in the value of K_L constant, which indicating a less favorable adsorption with increasing pH for all pollutants (Table 1, Table 2, Table 3). This large reduction can be attributed to the electrostatic repulsion between negatively charged of PVA/GA/β-cyclodextrin polymer membrane surface and phenolate anions in basic medium, and selectivity of cyclodextrin. So, it confirmed that the adsorption process is based on the electrostatic interaction and the phenomenon of inclusion in the internal cavity of the β-cyclodextrin [9].

Finally, Gibbs free energy (ΔGo) was small and negative, and its value decreased with increasing pH; which confirm that the adsorption processes could be enhanced with acidic medium. Negative value indicates a physical and spontaneous adsorption process and easy regeneration of these materials due to no covalent bonds formation between interacting molecules and PVA/GA/β-cyclodextrin membrane polymer.

4. Conclusion

Modified polymer adsorbents were prepared for the removal of organic pollutants from wastewater. The study on the behaviors of 2-nitrophenol and phenol,

hydroquinone adsorption from the aqueous solutions onto crosslinked poly (vinylalchol) glutardaldehyde with and without β-cyclodextrin proved that the adsorption was obviously affected by chemical structure of phenolic compound, temperature, and solution pH.

As a result, crosslinked poly (vinylalcohol)/glutaraldehyde membrane exhibits a lower adsorption capacity. In this case, adsorption mechanism is based only on physical adsorption in porous membrane and hydrogen bonding formation between hydroxyalkyl groups of PVA polymer and phenolic compounds.

However, PVA/GA/β-cyclodextrin polymer membrane exhibited an effective adsorption capacity due to the presence of the electrostatic attraction between hydroxyls group of PVA polymer and secondary hydroxyls group of β-cyclodextrin and molecules of pollutants, and inclusion phenomena in apolar cavity of β-cyclodextrin. Therefore, the inclusion process was influenced mainly by molecular weight, size, and polarity of guest molecules.

Adsorption of 2-nitrophenol, phenol, and hydroquinone from aqueous solution has been favored in acidic medium at pH< pKa, and the low temperature is favourable for adsorption.

Then, the swelling of the PVA/GA/β-cyclodextrin polymer membranes in distilled water was found to increase with increasing content of β-cyclodextrin, implying that the polymer is more hydrophilic than the PVA/GA membrane.

However, Gibbs free energy (ΔGo) was small and negative, indicates a physical and spontaneous adsorption process and easy regeneration of these materials; no covalent bonds are formed during the complex formation.

The Freundlich isotherm model was more appropriate for adsorption of three phenolic compounds on the PVA/GA/β-cyclodextrin membrane.

Finally, PVA/GA/β-cyclodextrin polymer membranes were a potential and promising adsorbent for removal of phenolic compounds from wastewater, and they can be regenerated.

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