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Original Research

Elimination of Polyethylene Glycol from Aqueous Solution Using Activated Carbon

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Abstract

The present study looks at the adsorption of polyethylene glycol onto activated carbon with the different molecular weight. The amount of PEG adsorbed on activated carbon depends on temperatures and pH. The adsorption capacities were determined through the adsorption isotherms. The results of the adsorption isotherm and kinetic studies show that the adsorption process can be well described with the Langmuir model. After linearization of the Arrhenius equation the activated energy had been estimated.

Keywords: polyethylene glycol, isotherm, granular-activated carbon, activated energy

Introduction

Polyethylene glycol (PEG) is a water-soluble, waxy solid that is used extensively in the cosmetic, textile and toiletry industries. As the molecular weight of PEG increases, viscosity and freezing point increase. Therefore, polyethylene glycols are presented in wastewater as a surfactant constituent [1-3] or as catabolic products of these [4].

There are two principal processes for physico-chemical removal of PEG in water and wastewater: destructive processes such as ozonation [5, 6], ozonation/UV [7] or H_2O_2/UV oxidation, and processes such as adsorption into activated carbon [8, 9]. Chang et al. [9] examined the adsorption equilibrium of PEG with large molecular weight (average 6000) from copper electroplating solutions on activated carbon at 288-313 K, and investigated the feasibility of removing the organic additive from the bath.

In particular, adsorption of polyethylene glycol with different molecular weights (MWs) in the aqueous solutions on activated carbon reported by Zhao et al. [10], indicated the large adsorption capacities of PEG on the activated carbon,

Polarity of PEG weakens and the affinity of PEG to water molecules decreases with the increase of its molecular weight [10]. There is no universal activated carbon which is ideal for every application, so it is important to match the properties of the activated carbon with the performance requirements of the process. This paper presents the characterization of the adsorption process of PEG onto activated carbon to evaluate its applicability with wastewater.

Materials and Methods

Materials

Commercial-activated carbon GAC 207 EA with the particle size 12x40 supplied by B.M.D. S.r.l., (Bagni di Tivoli,

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Italy) has been used after washing by distilled water to remove the crushed carbon. Polyethylene glycol standards for adsorption experiments were purchased from Aldrich. The general formula of PEG is $H(OCH_2CH_2)_nOH$ and in particular experiments were performed with 1450, 3350 and 8000 molecular weight, respectively. For pH, 0.1 M and 1 M NaOH and 0.1 and 1 M HCl were used.

Methods

The adsorption equilibrium of PEG was attained by using a fixed solution volume (0.1 dm^3) with the different initial concentration of PEG ranging from 0.2-3.0 $g \cdot L^{-1}$ and mixed with 500 mg of adsorbent. Filtration of the samples through 0.45 μm pore-diameter filter has been performed to remove the activated carbon before PEG concentration determination by a VARIAN TECHTRON DMS 200 spectrophotometer at 192.4 nm wavelength. The calibration curves have been prepared for all types of PEG in the range 0.2 $g \cdot L^{-1}$ to 3.0 $g \cdot L^{-1}$.

Results and Discussion

Effect of Initial Concentration

To elucidate the times needed to reach adsorption equilibrium with different PEG initial concentrations, tests were performed with different MWs at 20°C (Fig.1.). For PEG-1450 smaller initial concentrations took longer to reach equilibrium. For-PEG 3350 the time to reach equilibrium was almost the same for all initial concentrations and for PEG-8000, higher concentrations took longer to reach equilibrium, but not much more material was adsorbed.

Adsorption Isotherm

To determine the maximum adsorption capacity of PEG onto activated carbon, a study of adsorption models (Fig.2.) was achieved comparing the commonest models, therefore data were analyzed using the Langmuir (1) and Freundlich (2) model [11]. The Langmuir isotherm is as follows:

$$q_e = Q^0 b C_e/(1+bC_e) \text{ or, linearized}$$
$$1/qe = (1/Q^0 b)(1/C_e) + 1/Q^0 \quad (1)$$

where q_e is the amount of element adsorbed per unit weight of adsorbent, $[mg \cdot g^{-1}]$

Q^0 – is the solid phase concentration corresponding to complete coverage of available sites (limiting adsorption capacity) $[mg \cdot g^{-1}]$

C_e – is the residual liquid phase concentration at equilibrium $[g \cdot L^{-1}]$

b – adsorption coefficient

Linearized Freundlich equation in logarithmic form:

$$\log q_e = \log Kf + 1/n \log C_e \quad (2)$$

where Kf $[mg \cdot g^{-1}]$ and 1/n are characteristic constants determined, respectively, by the intercept and slope of the Freundlich equation on logarithmic plot and representing sorption capacity and adsorption intensity, respectively.

According to the Freundlich model, slope 1/n, ranging between 0 and 1, is a measure for the adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/n below one indicates a normal Langmuir isotherm while 1/n above one is indicative of cooperative adsorption [11]. A plot of log q_e vs log C_e susceptible to determine the empirical constant Kf and 1/n from the intercept and slope of linear regression. Table 1 presents the Langmuir and Freundlich parameters. The results obtained from the Langmuir model give a satisfactory correlation between the model predictions and experimental data. According to the Langmuir model a maximum uptake of 188.68 $mg \cdot g^{-1}$ for PEG-1450, 126.58 $mg \cdot g^{-1}$ for PEG-3350 and 81.30 $mg \cdot g^{-1}$ PEG-8000 was achieved. The values of exponent 1/n are for all studied PEG's below zero to confirm for better description of polyethylene glycol adsorption suits the Langmuir model.

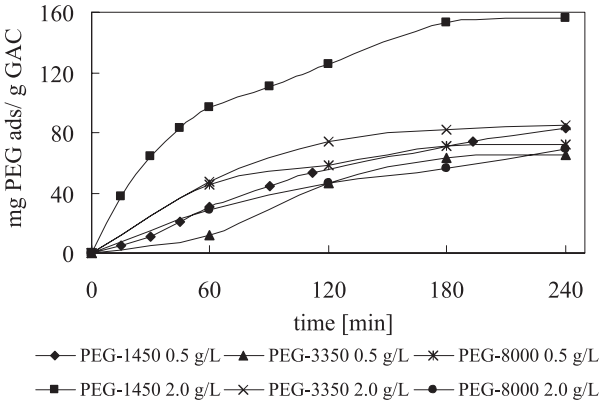

Fig.1. Kinetic curve for PEG at the various initial concentration at the pH = 5.2 – 5.5 and at the temperature 20°C.

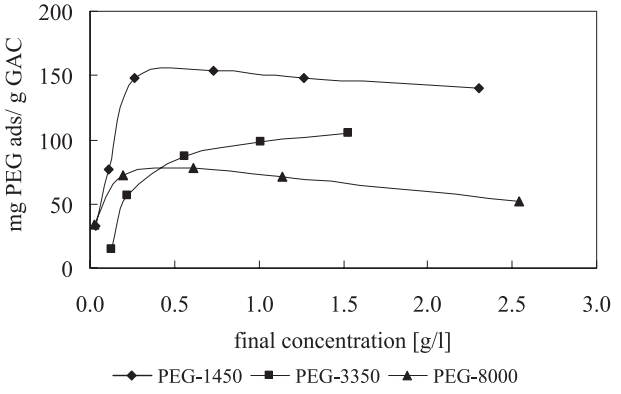

Fig.2. Sorption isotherms of PEG-1450, PEG-3350 and PEG-8000 in water solution on the activated carbon at the pH = 5.2 and at the temperature 20°C.

The breakthrough curve obtained with the PEG-1450 at the initial concentration 3.0 g·L^{-1} and pH 3.55 shows that 26-28 bed volumes (BV) can be treated before reaching the breakpoint (Fig.3.). The adsorption in the fixed bed reactor (FBR) was designed to operate in down-flow direction. Factors which affect the actual shape of the breakthrough curve include the adsorbate concentration, pH, rate-limiting mechanism for adsorption, nature of the equilibrium conditions, particle size of the adsorbent, depth of the column or the bed, and flow rate. In general, the time of breakpoint for a specific type of adsorbent and a given adsorbate is decreased by increased particle size of adsorbent, increased concentration of adsorbate in solution, and increased flow rate [11].

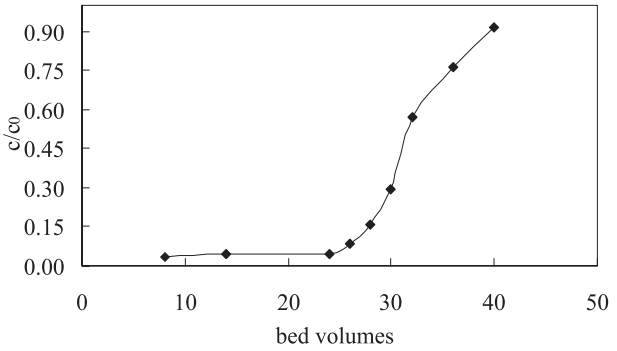

Fig.3. Breakthrough curve for PEG-1450 passing through GAC in the fixed-bed reactor with the dawn-flow direction. Initial concentration of PEG-1450 3.0 g·L^{-1}, pH = 3.55, flow rate 0.6-0.8 ml.min^{-1} and BV = 50 ml.

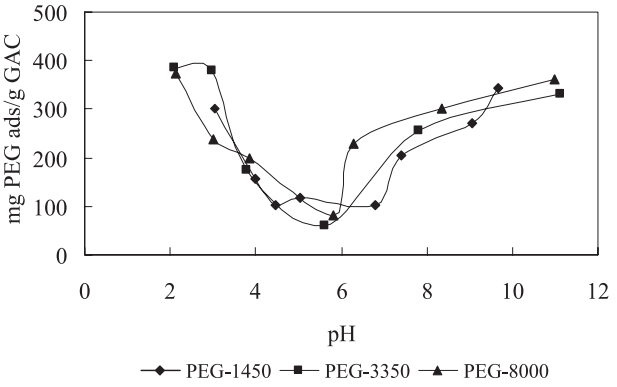

Fig.4. PEG adsorption with different molecular weight at different pH.

Effect of the pH on the Adsorption PEG

Adsorption of the PEG with the different molecular weight at the pH range of 2 to 11 was studied and the results are reported in Fig. 4.

According to the obtained results we achieved the adsorption of polyethylene glycol is strongly dependent on the pH and the best pH for adsorption process with activated carbon is in the range 2-3 and 10-12. How the properties of the activated carbon change with pH have not been studied.

Effect of Temperature on Adsorption of PEG

The amount of PEG adsorbed on activated carbon depends on temperature and for the PEG with the lower molecular weight, the effect of temperature is smaller than for the PEG with the higher molecular weight, probably due to the diffusion control mechanism.

The activation energy is the amount of energy required to ensure that a reaction happens. According to the Arrhenius equation:

$$\log k = -Ea/(2.303*R*T) + cost \qquad (3)$$

where k is the rate coefficient, A is a constant, E_a is the activation energy, R (8.314 J.mol^{-1}.K^{-1}) is the universal gas constant, and T is the temperature (in degrees Kelvin), we found activated energy for PEG-1450, PEG-3350 and PEG-8000.

After linearization of the Arrhenius equation we achieved the values of the activated energy for PEG-8000 17.23 J.mol^{-1}, PEG-3350 12.95 J.mol^{-1} and for PEG-1450 7.93 J.mol^{-1} (Fig. 5).

According to the results, the amount of PEG adsorbed on the activated carbon increased with an increase of temperature. As is widely agreed, the adsorption is a spontaneous exothermic process but according to the results PEG adsorption increase with the increase of temperature and moreover the effect is higher for the PEG-8000. Has been suggested that in aqueous solution PEG forms a hydrated complex containing till six water molecules attached to each ethylene glycol unit [12] and therefore a decreasing in PEG-water hydrogen bonding with increase of temperature can explain the higher adsorption capacity.

Table 1. Isotherm model parameters for adsorption process of PEG onto activated carbon. See Fig. 2 for the curve explanation.

	Langmuir			Freundlich		
Curve	Q_0 [mg/g]	b	R^2	Kf [mg/g]	1/n	R^2
PEG-1450	188.68	5.33	0.9836	144.97	0.3396	0.7328
PEG-3350	126.58	3.16	0.9744	79.82	0.5905	0.7801
PEG-8000	81.30	24.60	0.9849	81.99	0.2104	0.7826

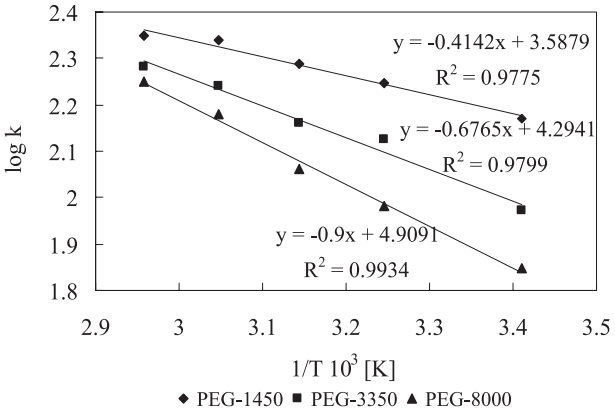

Fig.5. Adsorption of PEG's at the different temperatures, pH = 5.2 –5.5. Linearization of the Arrhenius equation.

Five temperatures were conducted for the experiment and the results show that the amount of PEG adsorbed on the activated carbon is markedly affected by temperature.

After comparing the deviation of mg PEG adsorbed on the activated carbon at the lowest (20°C) and highest (65°C) temperatures we can predict behavior of polyethylene glycols with different molecular weights. Deviation between the mg of PEG adsorbed on GAC at the highest and lowest temperature is almost two times higher for PEG-8000 than for PEG-1450.

Conclusions

This work shows that polyethylene glycols at different molecular weights can be effectively removed from the water solution by adsorption onto activated carbon. The adsorption process in particular fits the Langmuir isotherm model as reflected by correlation coefficients which ranged from 0.97 to 0.98. The time for reaching equilibrium at lower initial concentrations of PEG is less than that with the higher initial concentration for all PEGs. Adsorption of polyethylene glycol is strongly dependent on pH, the best results of adsorption have been achieved in the range of pH 2-3 and 10-12.

The effect of temperature is also significant for the adsorption process of PEG and depends on the molecular weight of PEG (with the lower molecular weight the effect of temperature is smaller than for the PEG with higher molecular weight). Activated energy for PEG with the higher MWs are higher. The results of this research were found to be in agreement with those for similar adsorption systems, *e.g.* the PEG-zeolite system [13].

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