Optimization of adsorption removal of ethylene glycol from wastewater using granular activated carbon by response surface methodology

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ABSTRACT

Wastewater reuse has been attracted a lot of attention in recent years especially in places with low water availability. The effluents that were considered to be discharged are now could be used as potential sources of reusable water. In this study, variables affecting the removal of ethylene glycol (EG) by adsorption on granular activated carbon (GAC) from the synthetic wastewater solutions were optimized by response surface methodology (RSM) using a central composite design. The investigated factors were temperature, EG concentration, contact time, activated carbon amount and granular size. Adsorption kinetic was also studied and an acceptable correlation between Langmuir model and experimental data was observed. As a result, a modified third degree equation was proposed and used to find the optimized condition. The maximum adsorption was achieved at 27.7 ºC with 0.8 g of 30 mesh activated carbons for an EG feed concentration of 135 mg/L at 210 minutes.

1. Introduction

The water management in dry areas of the world has been a critical challenge for the centuries, which is caused by limitations on water availability. Critical point refers to the condition when the balance between the usable water and the demand cannot be maintained. In most areas affected by drought or low water accessibility, all-out industrialization, urbanization and high growth rate of population, increase the need to address the serious pressure on available water resources. Furthermore, climatic changes are envisaged to have more negative effects on natural water resources and their water quality, emphasizing the urgency of this severe problem (Meyer et al. 2009; Sowers et al. 2011). Reusing of wastewater is one of the most popular strategies of water management employed to handle these situations (Pereira et al. 2002). Generally, the industries with large share of wastewater consumption are more likely to have a wide choice when it comes to water reuse strategies. Depending on the usage, different practices could be employed. In the most cases, after physical and chemical treatments, the wastewater achieves required standards for general maintenance applications i.e. washing floors or cooling purposes (Rehun and Engel, 1988; Mohsen and Jaber, 2003; Farahani et al. 2016).

In recent years, with realization of fresh water resources limitation and depletion, water recycling and reuse has become one of the major priorities of the industrial and urban communities (Petrinie et al. 2015). Researchers have concluded that ecological footprint of water and wastewater system can be dropped for about 25% just by benefiting from recycled wastewater in water management (Anderson 2003). In order to use the wastewater as a valuable water resource, some typical treatments are required to improve the water quality. On the other hand, treatment costs rise drastically for higher qualities (Feng and Chu, 2004).

Mono-ethylene glycol (MEG) is an odorless and colorless clear liquid, which is miscible with water and it is known for its low volatility (Eisenreich et al., 1981). In 2004, worldwide MEG production was roughly about 18500 kilotons. Although it might be known for its use as a common coolant, it’s also being used in a variety of industries from deicing fluids for airstrips to being a component of beauty products. With these amounts of consumption, there is a considerable volume of wastewater generated in these industries contaminated with MEG (Staples et al., 2001; Devlin and Schwartz, 2014).

Ethylene glycol (EG) in its effluent form typically after being used as a runway deicing agent or as an industrial wastewater has high mobility and therefore, it has high potential to contaminate the soil and any water bodies that it comes into contact with. Also, it undergoes an approximately 2-days photo-chemical degradation process in atmosphere. Its degradation in soil and water occurs under both aerobic and anaerobic conditions, which range from a day to about a few weeks depending on the environmental conditions. The EG as a component of wastewater stream increases the effluents biological oxygen demand; therefore contaminated aqua-ecosystems will have higher chance to be disrupted (Carnegie and Ramsay, 2009). The EG as a sole pollutant has low level of toxicity. But once it’s metabolized by the microorganisms present in the environment, it breaks down to different types of toxic components. It is considered toxic to central nervous system. However, since its adsorption through human skin happens at a very slow rate, it is very unlikely to reach toxic dosage (Dye 2001).

Although aerobic digestion of EG has been the subject of numerous research articles (Gonzalez et al. 1972; Staples et al. 2001; Revitt and Worrall, 2003), some suggest that acidogenesis in anaerobic digestion in soil is able to significantly degrade ethylene glycol and is more effective method comparing to aerobic techniques (McVicker et al. 1998).

The anaerobic digestion of ethylene glycol has been subjected to several researches but only fermentation (Straß and Schink, 1986; Elredy and Tawfik, 2015) and methanogenesis stages have been discussed in details (Dwyer and Tiedje, 1983). Dwyer and Tiedje (1983) proposed the anaerobic pathway, which methanogens utilize ethanol.
acetone and acetaldehyde for better treatments of ethylene glycol. McGahey and Bouwer (1992) have studied subsurface cases and reported degradation of EG by native consortium in soil and water bodies. They pointed out that efficiency of the process was highly dependent on oxygen availability, therefore ethylene glycol concentrations near surface drops more quickly.

Another technique for removal of EG is membrane processes. Polyamide and polypropylene thin film composite membranes was used for dehydration of ethylene glycol by pervaporation process. The results showed that temperature has a positive effect on permeation flux. The higher temperatures resulted in better separation when NaCl was present in the feed (Wu et al. 2015). There have been some approaches to the ethylene glycol oxidation in fuel cells. In one the recent studies, it was concluded that an effective promoter for Pd electro-catalysis of EG oxidation was a possible candidate for industrial ethylene glycol fuel cells (Yang et al. 2015).

Polyethylene glycol (PEG) is another abundant pollutant present in industrial wastewater which made its biodegradation interesting for many researchers (Haines J., Alexander, 1975; Huang et al. 2005; Cadar et al. 2012). The investigations include biological aerobic and anaerobic treatment of PEGs with different molecular weights (Huang et al. 2005), comparison of biodegradation of polyethylene glycols and polypropylene glycols (Zgola-Grzeskowiak et al. 2006), and anaerobic digestion of PEGs with different molecular weights (Bernhardt et al. 2008).

One of the most commonly used material for separating a wide spectrum of unwanted chemicals in liquid and gas phases is granular activated carbon (GAC) which can be produced using wood-like carbon rich materials (McCullum et al. 2018; Jaria et al. 2019). Generally, the term of activated carbon is used for a large group of carbonic material with high levels of porosity and surface area. In recent years, the activated carbon which has been used in chemical industries mostly in adsorption processes is used for environmental purposes (Bansal and Goyal, 2005). It is used to treat industrial wastewaters in order to meet the environmental standards that allow discharge of the effluent to receiving waters.

Recently, response surface methodology (RSM) has been used for modeling adsorption of different pollutants on activated carbon adsorbents (Hameed et al. 2009; Sahu et al. 2009; Anilkumar et al. 2011; Esfandiar et al. 2014; Hajati et al. 2015). The RSM based statistical analysis, which is extensively utilized to multivariable optimization studies (Wongkaew et al. 2016), is a collection of mathematical and statistical techniques. This statistical technique decreases the number of essential tests considerably without overlooking the interactions among the experiment variables (Vatanpour et al. 2017). Since it is important to understand the interaction effects between several factors, the RSM provides a better understanding of the process than the standard methods of experimentation. It can predict in a complex process how the inputs influence the outputs where different factors can interact among themselves.

In this study, the removal of ethylene glycol from wastewater was examined by adsorption on granular activated carbon. The investigated parameters were granular activated carbon amount and different meshes of it, retention time, temperature, and feed concentration of ethylene glycol. A statistical modeling was used to estimate the remaining concentration of EG. A series of central-composite-design based experiments were conducted using response surface methodology and conditions of the adsorption process were optimized. We used RSM for experimental design and investigated 5 effective parameters in three levels, which this report is comprehensive investigation of theses parameters in removal of ethylene glycol by the GAC.

<table>
<thead>
<tr>
<th>Independent variable</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Temperature (ºC)</td>
<td>-α 20.0 -1 23.8 0 27.5 +1 31.2 +α 35.0</td>
</tr>
<tr>
<td>(B) Feed concentration (mg/L)</td>
<td>90</td>
</tr>
<tr>
<td>(C) Granular activated carbon (g)</td>
<td>0.2</td>
</tr>
<tr>
<td>(D) Time (min)</td>
<td>120</td>
</tr>
</tbody>
</table>

2. Materials and methods

2.1. Materials and instruments

Ethylene glycol was obtained from Maroon petrochemical complex (Iran). Granular activated carbon processed from Coconut by Jacobi®. In order to take particle size into account GAC was screened into two mesh size categories 10-20 (841-2000 μm) and 20-30 (595-841 μm). NaOH and HNO3 from Merck were used for pH adjustment. HPLC-grade water was prepared by reverse osmosis de-ionizing apparatus (water purification system ultraclear direct, SG waters, Germany). A pH meter (Methrohm, Switzerland) and a balance scale (AND-HR200, Japan) were used to determine the solution pH and weigh the adsorbent, respectively. The samples were incubated for the duration of retention time in a shaken incubator (Labron, South Africa).

2.2. Measurement of EG concentration by high performance liquid chromatography (HPLC)

In order to measure the concentrations of EG during the adsorption process, HPLC analysis was applied. The HPLC (Waters, USA) was equipped with C18 column (250×4.60 mm, 10 micron) from Waters, μbondapakTM, Ireland, which attached to IR absorbance detector set at 254 nm. The mobile phase was pure water at a flow rate of 2 mL/min. The samples were injected in 20 μL duplicates. The peak areas for each compound were averaged and percent concentration was calculated by comparison to the peak areas.

Batch adsorption process was carried out in 250 mL Erlenmeyer flasks. Different concentrations of EG were obtained by dilution of a 1 g per liter stock solution of the ethylene glycol. Afterwards, certain amounts of GAC adsorbent were added to the solutions. The pH was adjusted in 7.0 and the samples were incubated at different temperatures. All samples were stirred at 170 RPMs.

2.4. Experimental design

Design of experiments is a procedure which allows the experiments to be carried out in a way that sufficient data for optimization is obtained from the minimum numbers of experiments. Therefore, defining a definite number of runs in a specific order according to number of variables is possible. There are different methods to use designing experiments. Among them, RSM is one of the most frequently used. Central composite design (CCD) is a robust and accurate design which falls into the RSM category. It comprises of 5-level design for each factor included in the model.

In this study, 52 experiments were carried out according to the CCD design. Table 1 illustrates the investigated factors affecting outlet concentration of ethylene glycol and their modified ranges. Since two different mesh sizes (10-20 and 20-30) of GAC were used and it was difficult to obtain specific values for it, therefore the GAC mesh sizes effect was tested as a categorical factor. In order to estimate remained concentration of ethylene glycol, final equation was derived from a raw cubic model which was a third degree polynomial and it was generally described as following:
In which $a_i$ is constant, $a_{ij}$, $a_{ik}$ and $a_{ij}$ are respectively coefficients for first, second and third degree terms of a factor. $a_{ij}$, $a_{ik}$, $a_{ij}$ represent interaction coefficients and $x_i$ is an independent parameter, which is called a factor, $k$ is the number of factors and $z$ is the associated model with the model (Mason et al. 2003).

$$R^2 = 0.928 \quad \text{adequate precision} = 28.765$$

3. Results and discussion
3.1. Analysis of variance (ANOVA)

Investigation of operation parameters which affect the adsorption process was conducted and the experiments were carried out according to the CCD design matrix. Table 2 shows design points and the relevant remained concentrations of ethylene glycol after adsorption process. Design of experiments was done in such a way that effect of uncontrolled factors was reduced and the experiments were generated in a random order by the Design Expert (Ver. 8.0.1). After analysis, a cubic equation which its coefficients were calculated by least-squares regression was found to be fit for representing the concentration of ethylene glycol in the remained solution. Third-order equations of ethylene glycol’s outlet concentration considering only the significant terms are shown in Eqs. 2 & 3.

EG' outlet (mesh of AC: 10-20) = $+1129.9 - 44.62 A - 12.96 B - 41.63C + 0.947 D + 0.537 AB + 0.0334 B^2 - 3.84 D^2 - 0.001 A^2B + 0.0022 A^2C + 0.0037 A^2D - 0.0012 B^2A$ (2)

EG' outlet (mesh of AC: 20-30) = $+1132.49 - 44.63 A - 12.98 B - 41.63C + 0.947 D + 0.537 AB + 0.0334 B^2 - 3.84 D^2 - 0.0013 A^2B + 0.0023 A^2C + 0.0037 A^2D - 0.0013 B^2A$ (3)

In constructing the model, a series of lack-of-fit tests should be performed in order to determine significance of the proposed model. The mentioned model has F-value of 34.33 shown in Table 3 accompanying with other analysis of variance (ANOVA) parameters. The p-value is an index that shows the significance of a term or a model and in this case terms with p-values less than 0.1 were considered significant and those with p-values more than 0.1 were considered insignificant and removed from the model manually. The p-value for the final model was less than 0.0001, which indicated that the model was significant. The lack-of-fit term for the remained concentration of ethylene glycol had a p-value of 0.1431.

Another parameter which indicates robustness and statistical importance of the proposed model is the adequate precision value which is a measure of "signal-to-noise ratio". In this case, the adequate precision was 28.765. The models with an adequate precision higher than 4 are more likely to make acceptable predictions in the central composite design defined space. The normal probability plot of residuals, which is shown in Fig. 1, indicated that error distribution was normal throughout the model. Another important plot that can illustrate the quality of the model is the predicted vs. actual diagram. As it is shown in Fig. 2, data points were located close to the diagonal line. A relatively high $R^2$ confirms the model integrity.

3.2. Investigation of factors and their interactions

To observe how the factors affect the response, they were studied in pairs in three different levels of initial feed concentration of ethylene glycol (160, 185 and 210 mg/L). As shown in Fig. 3 (a & b), in low concentrations of EG in high levels of granular activated carbon and retention time, response surface becomes horizontal. In early stages of the adsorption (low retention times), adsorption occurs mainly on the outer surface of the adsorbent. The observed concentration gradient in Fig. 3 (a & b) is due to this happening. The flattening of concentration surface in higher retention times shows that in order to exploit inner porous areas of the adsorbent, a higher level of driving force is required for happening of the diffusion. Driving force can be altered by changes in concentration levels of ethylene glycol which is affected by the adsorption; hence, decrease in ethylene glycol concentration lowers the driving force needed to utilize inner porous areas of the adsorbent needed to further decrease the concentration of the EG. In Fig. 3 (c, d, e, f), as it is expected, increment in levels of activated carbon and retention time have positive effects on the adsorption process. It is obvious that by increasing of GAC amount and adsorption time, the removal efficiency improves.

![Fig. 1. Normal plot of residual for remained concentration of EG.](image1)

![Fig. 2. Plot of predicted response vs. actual value for remained concentration of EG.](image2)
However, by considering of economical and feasibility aspect, it is not reasonable to use higher concentration, higher temperature and higher retention time. The used area in RSM design is usual concentration, temperature and time of adsorbent in the industrial application. In all cases, the efficiency of activated carbon with 20-30 mesh was higher than the GAC with 10-20 mesh. By decreasing of the adsorbent size, the surface area of the material improves and the adsorption sites reachability increases. The falling slopes of the diagrams shown in Fig. 3 indicate saturation of the adsorbent and reach to equilibrium.
Fig. 3. Effects of activated carbon amount and retention time on the remained concentration of ethylene glycol in different levels of feed concentration and two different meshes.

Interactions of granular activated carbon and temperature were investigated for all three concentrations (160, 185 and 210 mg/L) and the results are presented in Fig. 4 (a-f). In all three concentrations, increment of activated carbon’s amount and decrease in temperature result in higher ethylene glycol removal. It is probably due to the exothermic nature of the adsorption process (Vatanpour et al. 2018).

As it is expected, longer retention times and low temperatures improve the adsorption. In this case, the lower temperatures elevate the driving force needed to render inner porous areas available by improving diffusion phenomenon. Fig. 5 (a-f) shows how the outlet concentration responded to variations in retention time and temperature.
Fig. 4. Effects of activated carbon amount and temperature on the outlet concentration of ethylene glycol in different levels of feed concentration and two different meshes.

Interactions of granular activated carbon and temperature were investigated for all three concentrations (160, 185 and 210 mg/L) and the results are presented in Fig. 4 (a-f). In all three concentrations, increment of activated carbon’s amount and decrease in temperature result in higher ethylene glycol removal. It is probably due to the exothermic nature of the adsorption process (Vatanpour et al. 2018). As it is expected, longer retention times and low temperatures improve the adsorption. In this case, the lower temperatures elevate the driving force needed to render inner porous areas available by improving diffusion phenomenon. Fig. 5 (a-f) shows how the outlet concentration responded to variations in retention time and temperature.
3.3. Optimization and validation

3.3.1. Optimization

Design-Expert 8.0.1 is equipped with an optimization toolbox was employed for optimizing the adsorption process of ethylene glycol. Each possible solution was evaluated and marked by a “Desirability” criteria ranging between 0 and 1. If a solution satisfies all conditions its “Desirability” would be 1 and 0 for the least desired situation when none of the conditions, any other case would be between these two values. In this investigation, the main goal was to minimize ethylene glycol outlet concentration and limiting factors were not needed. Therefore, the optimization criteria for all factors were defined as “within range” and “minimize” was selected for remained concentration of ethylene glycol.

3.3.2. Validation

Fig. 5. Effects of retention time and temperature on the outlet concentration of ethylene glycol in different levels of feed concentration and two different meshes.

After optimization, the most desirable solution was selected which had a “Desirability” value of 0.995. At these conditions, the predicted response had a value of 31.20. In order to verify the cubic model assigned to the adsorption process, a validation experiment was carried out. Table 4 shows the acceptable agreement between the experimental data and the predicted values for remained concentration of ethylene glycol.

### Table 4. Predicted optimized conditions and corresponding experimental validation.

<table>
<thead>
<tr>
<th>Optimum condition</th>
<th>Parameters</th>
</tr>
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<tbody>
<tr>
<td>Temperature (°C)</td>
<td>Feed conc. (mg/L)</td>
</tr>
<tr>
<td>27.7</td>
<td>135</td>
</tr>
</tbody>
</table>

### Table 5. Freundlich and Langmuir isotherm parameters for adsorption of EG.

<table>
<thead>
<tr>
<th>Isoterm</th>
<th>Parameters</th>
</tr>
</thead>
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<tr>
<td>Langmuir</td>
<td>$Q_m$</td>
</tr>
<tr>
<td></td>
<td>$K_f$</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$N$</td>
</tr>
<tr>
<td></td>
<td>$K_F$</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
</tbody>
</table>

#### 3.4. Equilibrium isotherms

Conventional batch method was used to measure the equilibrium adsorption of ethylene glycol onto the GAC. Two adsorption isotherms, Langmuir and Freundlich models, were employed to explain the EG adsorption equilibrium. In this section, the investigation of ethylene glycol removal was carried out using 0.4 g of the adsorbent in the concentration range of 50-300 mg/L. Samples were kept in 25 °C for 2 h. To further investigate the case, equilibrium data obtained from the experiments were compared with Freundlich and Langmuir models.

The Langmuir isotherm is a theoretical model derived base on the assumptions that adsorption is monolayer, homogeneous and without lateral interactions between adsorbing species (Salehi et al. 2012). Considering linear form of Langmuir model and data at hand, correlation coefficients can be determined using these equations:

$$
\frac{C_e}{q_e} = \frac{1}{K_fQ_m} + \frac{C_e}{Q_m}
$$

where $C_e$ (mg/L) is equilibrium EG concentration and $q_e$ is the equilibrium adsorption capacity of the adsorbent. By determining the slope and the intercept of Langmuir isotherm ($Q_m$ and $K_f$), the constants were calculated. In order to fit the experimental data, linear Freundlich equation was used:

$$
\log(q_e) = \log(K_f) + \frac{1}{n_f} \log(C_e)
$$

where $n_f$ and $K_f$ are Freundlich constants, which depend on adsorbate and adsorbent and on the temperature which adsorption is taking place. Plotting $\log(q_e)$ versus $\log(C_e)$ will result in a linear equation. The slope can be used to calculate $n_f$ and the intercept reveals $K_f$. Both Freundlich and Langmuir isotherm models exhibited acceptable correlation with the experimental data. Figs. 6 and 7 show linear approximations used to estimate contains for Langmuir and Freundlich isotherms. The calculated isotherm parameters for adsorption of EG were depicted in Table 5. The Langmuir isotherm provided much better fit to the equilibrium data compared with the Freundlich isotherm based on the higher $R^2$ values.

4. Conclusions

In this research, efficiency of granular activated carbon for removal of EG was investigated, which it presented outstanding characteristics as a cheap adsorbent. Amount of activated carbon, temperature, retention time and feed concentration of ethylene glycol along side of different meshes of granular activated carbon were chosen as the factors influencing the adsorption process. Using these factors, a statistical modeling approach was taken to estimate the remained concentration of ethylene glycol. A series of central composite design based experiments were conducted using RSM. Observations showed that increment of retention time and amount of the adsorbent had positive effects on adsorption phenomenon while an increase in temperature resulted in remaining higher levels of ethylene glycol in the feed solution, i.e. decreasing EG removal. Maximum adsorption was achieved at 27.7 °C with 0.8 g of 20-30 mesh activated carbons for a feed concentration of 135 mg/L ethylene glycol at 210 minutes. Also, the kinetics of the adsorption process was studied and experimental data had a good agreement with Langmuir isotherm.
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