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Comparison of the advanced oxidation processes and adsorption with chitosan-zeolite composite in reducing the amount of airport wastes containing glycol pollution

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Today, the increasing growth of industrial activities has led to the entry of many pollutants into water resources. Due to the toxicity of these pollutants, their removal from water resources is essential. Also, as a result of the dehydration crisis, providing highly efficient and economical solutions for the purification and reuse of water has been considered alongside the removal of pollutants from these wastewaters.

In recent years, several methods have been considered, which include the use of adsorbents, and photo catalytic materials and carbon materials, and the most common methods for the removal of water pollutants and wastewater is the use of adsorption process by adsorbents.

A group of environmental pollutants which are cationic pollutants such as ethylene glycol can be absorbed by biological material from contaminated industrial wastewaters and can also be absorbed by a variety of adsorbents. These methods are cheap and also useful. In this study, zeolite adsorbents, chitosan powder and synthesized chitosan-zeolite composite were used, and their application was studied to remove the cationic contaminants, ethylene glycol, from aqueous environments of airport's contaminated wastewaters in different conditions in a discontinuous manner.

Non-continuous adsorption experiments were conducted to examine the effect of the factors on the removal process, including the effect of contact time of absorbent with contaminant, pH, initial concentration of the pollutant and the amount of consumed adsorbent.

Keywords: Advanced Oxidation; Lead oxide nanostructure; Waste Reduction, Glycol Pollution.

INTRODUCTION

To avoid pollution of the environment and water resources, industrial wastewaters purification is one of the needs of today's world. For this purpose, the removal of hazardous compounds in these sewages is one of the main problems, as many biological methods have been widely used.

Ethylene glycol (EG) is one of these hazardous substances. EG is a clear, colorless and odorless liquid that is soluble in water. It is obtained from the reaction of ethylene oxide and water. According to the global estimate, about 9.4 million tons of EG was produced in 1993, which is used as intermediate in the production of polyester, polymer production, bottles and packaging containers, etc.

Ethylene glycol has many commercial applications and is used in many industries such as synthetic fibers, film, antifreeze, resin, explosives, fibers, paper, leather, protective coatings, printing ink and textile industries. It is also a common antifreeze composition. Although, it is relatively non-toxic, it produces oxidizing metabolism in vivo, glycolic acid and oxalic among other products.

The first use of EG for engine cooling occurred in 1925. This usage was initially low, but gradually increased because of the benefits, and currently the largest consumption of EG is in cooling engine production. Absorption through skin contact, brain damage, damage to the central nervous system (CNS) and joints, eye injury, toxicity, etc., are major problems that sewages containing ethylene glycol can cause [1-5].

Ethylene glycol and water are the main components of ethylene glycol-based liquids which are used at airports to protect flights against accidents caused by heavy rainfall, to eliminate snow and ice and prevent frost and as antifreeze in the aircraft and runway.

After using these materials, when the aircraft is raised, these fluids are removed from the aircraft and mixed with rain and other fluids on the ground. The wastewaters are either collected or discharged from the airport as wastes. The fluids collected may be transported to a public purification facility or recycled for other uses. The wastewater containing diluted ethylene glycol (WEG) is shed to surrounding soil and the environment, where ethylene glycol is biodegraded. [6]

The use of ethylene glycol leads to the formation of sewages containing EG in admixture with mineral salts. There are several methods for treating these wastewaters, which include the destruction of toxic organic substances. These methods include ozonation and filtration with electric current.

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There are two main methods for EG physical and chemical removal from water and sewage:

1- Demolition processes such as ozonation [7, 8], ozonation / UV or oxidation of H_2O_2 / UV [9]

2. Absorption process, such as adsorption by activated carbon [10, 11]

Since the purpose of this study is to eliminate ethylene glycol from water resources, the researches done in recent years on this pollutant were first reviewed:

Typically, airplane sewage is mixed with sewage generated from airport buildings and the method of purification is through biological processes [12].

In 1898, Geo et al. conducted adsorption of polyethylene glycol (PEG) with various molecular weights in aqueous solutions by activated carbon; the results of which indicated that high PEG adsorption capacity was obtained by activated carbon with high molecular weight [13].

Chang et al. [11] investigated the PEG absorbance equilibrium with molecular weight (in average of 6000) of electroplating solutions on activated carbon at 338-288 K and examined the possibility of its removal.

In 2001, Zitomer and colleagues [14] using COD test in the winter season, reported on the amount of WEG in the wastewater of the airport, which was associated with high COD concentrations.

Orecki et al. have extensively studied the recycling of WEG and its usage as raw materials in various chemical industries [15].

In recent years, given the scarcity of energy and greenhouse gases emissions, more effort on renewable energies, even from sewage, is needed.

The anaerobic process which can produce methane gas and reduce nutrient contents with high loading rates, has been assessed [16-18].

Kennedy in 2005 used an anaerobic sludge reactor (UASB) to purify WEG, and the efficiency of removal rate was reported to be 93%. [19]

The performance rate of the anaerobic reactor depends on the time of the sludge storage (SRT), and the formation of the granule is a recommended step [20 -22].

Zhang et al. (2009) used PVA-gel beads in an anaerobic compact reactor (AFB) and the removal efficiency obtained was 91% in OLR = 27.5 g COD l-1 d-1 [23].

The biological air process for WEG purification is preferred because of simple set-up operation and good removal function with a range of chemical oxygen (COD) ranging from 1,000 to 3,000 mg/l [24,25].

The formation of microbial granules is a key factor for the successful functioning of an anaerobic reactor. However, if the formation of granule does not occur during EG filtration, the purification process is usually performed by reducing the amount of organic matter loading (OLR) [26].

But in this study, the authors aimed to investigate the efficiency of the adsorption phenomenon to remove ethylene glycol from industrial effluents, which was done by low-cost and biodegradable absorbents such as chitosan, zeolite and synthesized chitosan-zeolite composites, so that this method can be used as an effective, low-cost and harmless method for the environment in the removal of cationic contaminants such as ethylene glycol in the case of removal suitable efficiency.

MATERIALS AND METHODS

Materials

The materials used in this research include: ethylene glycol (molecular formula $C_2H_6O_2$) with molecular mass 62.07 $g.mol^{-1}$, density 1.11 $g.cm^{-3}$ and 99% purity which was selected because it is a pollutant which is soluble in water at any rate, and purchased from Merck Company. Also, industrial zeolite of Kilino and chitosan and synthesized chitosan-zeolite composites were used as adsorbents. Standard solutions of HCl 0.1 M and NaOH 0.1 M were used to adjust the pH of the solution.

Devices

In this research, after the necessary steps to absorb contaminant by adsorbents used to measure the rate of removal of pollutant from aqueous solution, the GC-Ms version 2200/3800 (AUS) made by Varian Company (AUS) was used. But due to the lack of desired results with this device, after the change of device, to get better results, the Japan made TOC version 31 A was used to carry out the experiments.

A stirrer device version L-81 manufactured by the German company, Hudolth, was used to mix the solution to increase the contact surface of the adsorbents with a contaminated solution. Also, to isolate suspended solid absorbent particles from the solution after the desired time, 108 H-N centrifuge of the Kokusan Corporation of Japan was used. Digital pH meter was used to adjust the solution pH.

METHODS

Preparation of chitosan absorbent

The general steps of synthesis of this adsorbent are as follows:

In the first step, the extraction of chitin from shrimp's shell and chitosan production, to determine the characteristics of produced chitosan in terms of harvesting percentage, protein rate, ash rate and percentage of acetylation, were done.

In this study, fresh tiger shrimps' shells were used. The shells were obtained from shrimp wholesalers. In the next step, the shells were thoroughly washed with water and soaked in a 0.5% caustic soda for 4 h to remove shrimp residues from the skin. The shells were then washed again with water and dried for 2 h in an oven at 60ºC and then turned into powder with milling machine. Then, the extraction of chitin from the shells was carried out following the steps based on the method proposed by Chang et al. (1997). This operation was performed using a normal caustic soda solution at 90ºC for 2 h. The weight ratio of shrimp shell powder was 1 to 20. The residue was then soaked and the remaining material washed on a filter with distilled water until it reached neutral pH. The residues from the prior steps were placed in a 1/4 normal chloric acid solution for 1 h.

The weight ratio of shell to acid was 1:10. The shell debris was then filtered and the remaining material washed to obtain neutral pH. The resulting chitin was yellow and colorless. To produce chitin free of carotenoid pigments, chitin was rinsed with acetone to make it clear and white. In this stage, the chitosan was produced by chitin de acetylation. De acetylation was carried out at 100ºC for 6 h in a 50% soda solution. Then, suspended materials were filtered and the aforementioned substances (chitosan) which remained on the filter were washed using distilled water to obtain neutral pH. The chitosan was then dried in an oven at 60°C for 1 h.

Synthesis of chitosan-zeolite composite

Composite is a substance composed of two phases of matrix and amplifier, and the second phase used is at least 5%. The combination of matrix with fibers (or amplifier) less than 5% is called composite. Composite consists of two main parts of the matrix and amplifier. The matrix keeps the amplifier in its relative location. The amplifier improves the mechanical properties of the structure. In general, the amplifier can be either short or long and continuous fibers.

4 g of chitosan and 4 g of zeolite (1: 1 ratio) were mixed with 160 ml of acetic acid 0.5 M. Suspension was vigorously stirred for 2 h, then 100 ml of acetic acid 0.5 M was added to it; the suspension was stirred again vigorously for 1 h. Then, the produced suspension was added drop by drop to a bath containing 500 ml 0.5 M NaOH. The resulting mixture was put on a stirrer for 3 h at a speed of 100 rpm. The sediments were filtered with smooth paper and washed with distilled water to obtain neutral pH, and eliminate the excess soda. Finally, the sediments were dried in the environment and used as adsorbent.

Preparation of standard solutions

The mother solution containing ethylene glycol at a concentration of 1000 ppm was made in distilled water using standard methods. Standard ethylene glycol solutions with different concentrations in distilled water were made by dilution of mother solution in a concentration range of 400-1000 ppm.

Absorption studies

The study of adsorption of ethylene glycol by zeolite, chitosan and synthesized composite of chitosan-zeolite was performed taking into account the influence of different parameters such as adsorbent amount, contact time, initial concentration of ethylene glycol solution, pH rate and adsorption rate.

For this purpose, in each test with a calibrated cylinder, 50CC of a solution of ethylene glycol with a predetermined concentration of contaminant was poured into a series of Arlenes, and then different amounts of adsorbent were added in the range of 0.1 to 2 g. The solution was rapidly mixed at the speed of 200 rpm and the absorbance rate was measured at different time intervals. At the end of the designated time, a portion of the solution was isolated, centrifuged and examined for absorption studies.

In order to investigate the effect of the above factors on absorption, each of these factors were investigated with different limits.

The contact time between 30 and 120 min, adsorbent amount of 0.1-2 g, pH range from 2-8, initial concentration of ethylene glycol between 400 and 1000 ppm for all experiments were investigated for this purpose.

The residual ethylene glycol absorption in the solution was then measured by TOC and the percentage of removal was calculated by the formula below:

Percentage of removal of ethylene glycol from the sample solution =

$$\frac{\text{Initial concentration} - \text{final concentration}}{\text{Initial concentration}} \times 100$$

DISCUSSION AND CONCLUSION

Standard effluent with zeolite absorbent

The test design diagram is related to zeolite and as shown, this design has two parts. The first part of this design is the main effects plot for means. In this section, the best point in each parameter is given and as shown, these parameters include: time, amount of adsorbent and solution. In this design, the best absorbent value was 2 g, which had the best absorption of the pollutant. Also, increase in concentration of the solution increased the absorption rate.

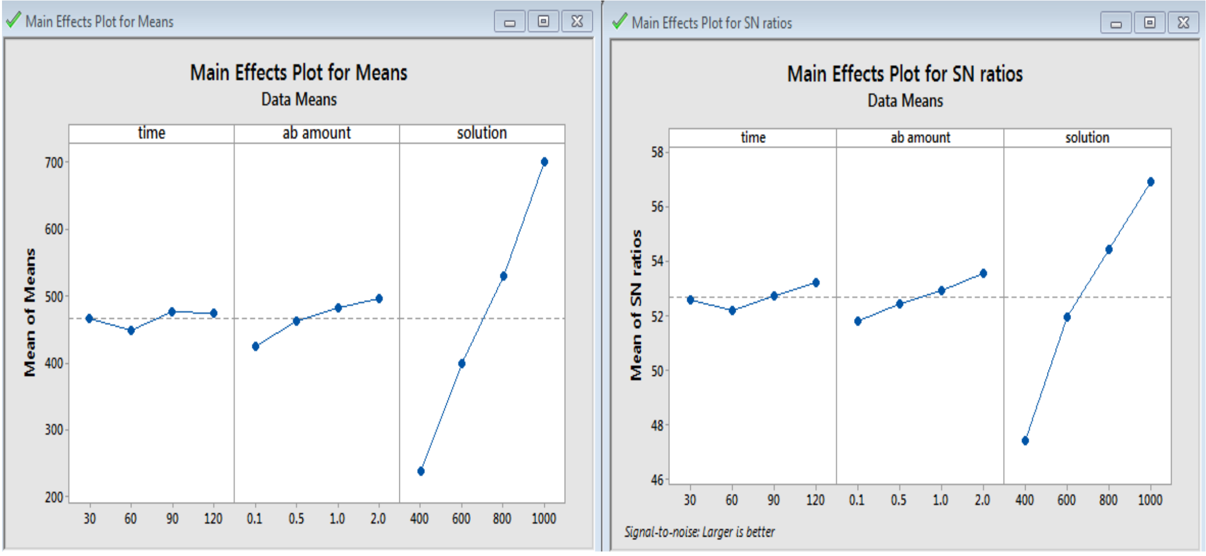

Fig. 1. Main effects for mean plot of Zeolite

In the second part, the main effects plot for SN ratio and the effect of each parameter are given. As indicated in the design, the concentration of the solution in the absorption of the pollutant had the greatest impact.

Considering the proper interaction between zeolite adsorbent in this design and the pollutant, ethylene glycol, present in the wastewater with increasing concentration, there were also sites for absorbing pollutants, and therefore, the rate of pollutant adsorption on the adsorbent was increased.

In another parameter, which is the amount of adsorbent, as expected, adsorption increased with increase in adsorbent, but after increase to a certain amount, the increase in adsorption was not high, and it was observed that as the adsorbent increased, the graph ascended. As shown in the diagram, an increase in contact time did not affect the parameter, and since the adsorbent is not a good absorbent with high effect, the absorption occurred at the first few minutes and before the first 30 min, and absorption of ethylene glycol from the solution took place

Table 1 Pollutant absorption rate with zeolite 0.1 g adsorbent and neutral pH with 250 rpm stirring round

The amount of solution in ppm	400 ppm	600 ppm	800 ppm	1000 ppm
Standard	279.9	419.4	553.3	685.5
Zeolite adsorbent	231.1	372.1	504.5	612.1

Table 2 Pollutant absorption rate with zeolite 0.5 g adsorbent and neutral pH with 250 rpm stirring round

The amount of solution in ppm	400 ppm	600 ppm	800 ppm	1000 ppm
Standard	279.9	419.4	553.3	685.5
Zeolite adsorbent	171.5	304.9	447.5	553.6

Table 3 Pollutant absorption rate with zeolite 1 g adsorbent and neutral pH with 250 rpm stirring round

The amount of solution in ppm	400 ppm	600 ppm	800 ppm	000 ppm
Standard	279.9	419.4	553.3	685.5
Zeolite adsorbent	131.8	232.8	385.4	486.2

Table 4 Pollutant absorption rate with zeolite 2 g adsorbent and neutral pH with 250 rpm stirring round

The amount of solution in ppm	400 ppm	600 ppm	800 ppm	1000 ppm
Standard	279.9	419.4	553.3	685.5
Zeolite adsorbent	105.8	193.9	282.2	413.5

Standard effluent with chitosan absorbent

The test design diagram is related to chitosan, as shown, this design has two parts. The first part of this design is the Main Effects plot for Means. In this section, the best point in each parameter is given and these parameters include: time, amount of adsorbent and solution. In this design, the best absorbent value was 2 g, which had the best absorption of the pollutant. Also, increase in the concentration of the solution increased the absorption rate.

In the second part, "the main effects plot for SN ratio", the effect of each parameter was shown. As indicated in the design, the concentration of the solution in the absorption of the pollutant had the greatest impact.

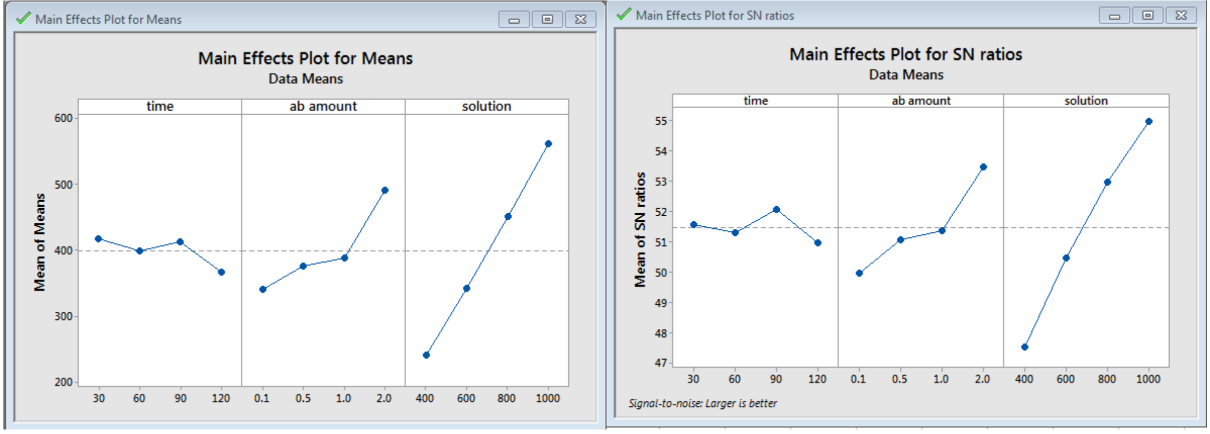

Fig. 2. Main effects for mean plot of Chitosan

Due to the proper interaction between the chitosan adsorbent in this design and the ethylene glycol pollutant present in the wastewater, with increase in concentration, there were still sites to absorb the pollutant, and therefore, the adsorption rate of the adsorbent increased. In another parameter which is the amount of adsorbent, as expected, adsorption increased with increase in the amount of adsorbent, but after increasing the amount of adsorbent to a certain amount, adsorption did not increase anymore. As shown in the graph, the increase in adsorption had an ascending graph. As shown in the diagram, increase in the contact time was not a significant parameter, and because the adsorbent was suitable with high efficiency, absorption took place at the first and before the first 30 min, and ethylene glycol absorption from the solution occurred.

Table 5 Pollutant absorption rate with 0.1 g chitosan adsorbent and neutral pH with 250 rpm stirring round

The amount of solution in ppm	400 ppm	600 ppm	800 ppm	1000 ppm
Standard	223.4	327.2	440.8	541.2
Chitosan adsorbent	201.1	286.1	390.2	480.8

Table 6 Pollutant absorption rate with 0.5 g chitosan adsorbent and neutral pH with 250 rpm stirring round

The amount of solution in ppm	400 ppm	600 ppm	800 ppm	1000 ppm
Standard	223.4	327.2	440.8	541.2
Chitosan adsorbent	170.4	204.7	287.2	390.5

Table 7 Pollutant absorption rate with 1 g chitosan adsorbent and neutral pH with 250 rpm stirring round

The amount of solution in ppm	400 ppm	600 ppm	800 ppm	1000 ppm
Standard	223.4	327.2	440.8	541.2
Chitosan adsorbent	142.4	147.2	204.2	275.1

Table 8 Pollutant absorption rate with 2 g chitosan adsorbent and neutral pH with 250 rpm stirring round

The amount of solution in ppm	400 ppm	600 ppm	800 ppm	1000 ppm
Standard	223.4	327.2	440.8	541.2
Chitosan adsorbent	83.4	102.5	145.3	163.1

Standard effluent with composite absorbent

The test design diagram is related to composite, as shown, this design has two parts. The first part of this design is the Main Effects plot for Means. In this section, the best point in each parameter is given and these parameters include: time, amount of adsorbent and solution. In this design, the best absorbent value was 2 g, which had the best absorption of the pollutant. Also, increase in the concentration of the solution increased the absorption rate.

In the second part (the main effects plot for SN ratio), the effect of each parameter was given. As indicated in the design, the concentration of the solution in the absorption of the pollutant had the greatest impact.

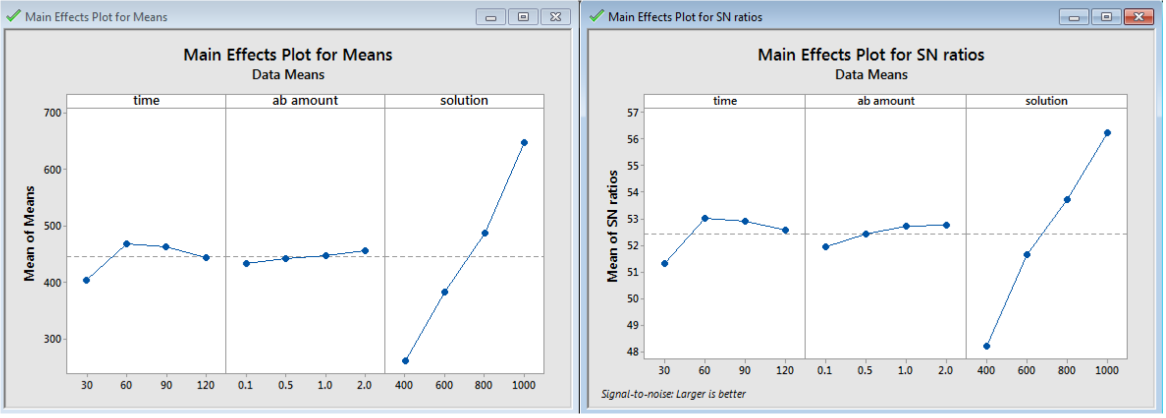

Fig. 3. Main effects for mean plot of composite

Due to the proper interaction between the synthesized composite absorbent chitosan-zeolite produced in this design and the ethylene glycol pollutant in the wastewater, with increase in the concentration, there were still sites for absorption of pollutants and thus the percentage of adsorption on the adsorbent increased. In another parameter which is the amount of adsorbent, as expected, increase in the amount of adsorbent increased the amount of adsorption, but after increasing the amount of adsorbent to a certain amount, the level of adsorption did not increase anymore. As shown in the graph, increase in absorption has an ascending graph. As shown in the diagram, increase in contact time is not an effective parameter, and since adsorbent has a good effect and efficiency, absorption occurred at the first few min and before the first 30 min, and absorption of ethylene glycol from the solution took place.

Table 9 Pollutant absorption rate with 0.1 g composite adsorbent and neutral pH with 250 rpm stirring round

The amount of solution in ppm	400 ppm	600 ppm	800 ppm	1000 ppm
Standard	240.4	385.5	530.8	645.2
Composite adsorbent	145.2	290.5	415.5	512.5

Table 10 Pollutant absorption rate with 0.5 g composite adsorbent and neutral pH with 250 rpm stirring round

The amount of solution in ppm	400 ppm	600 ppm	800 ppm	1000 ppm
Standard	240.4	385.5	530.8	645.2
Composite adsorbent	107.5	205.8	327.2	340.3

Table 11 Pollutant absorption rate with 1 g composite adsorbent and neutral pH with 250 rpm stirring round

The amount of solution in ppm	400 ppm	600 ppm	800 ppm	1000 ppm
Standard	240.4	385.5	530.8	645.2
Chitosan adsorbent	65.5	112.8	160.1	201.3

Table 12 Pollutant absorption rate with 2 g composite adsorbent and neutral pH with 250 rpm stirring round

The amount of solution in ppm	400 ppm	600 ppm	800 ppm	1000 ppm
Standard	240.4	385.5	530.8	645.2
Composite adsorbent	35.7	57.8	59.7	105.5

CONCLUSION

According to the design of the experiment, it was observed in the graphs and tables above that the highest amount of ethylene glycol absorbed among the adsorbents used in this study was by chitosan-zeolite synthesized composite adsorbent. This adsorbent has a high potential for removal of ethylene glycol from aqueous solution. It can be said that this adsorbent, due to the combination of two effective adsorbents: zeolite and chitosan, provided a more suitable substrate for absorbing the pollutant as compared to other adsorbents, and thus, resulted in the best removal of this contaminant from aqueous solutions. In this research, it was shown that the greatest absorption occurred when the equilibrium time was reached (88%), which is an acceptable value when this adsorbent is used for the purification of industrial wastewaters.

Appendix A. List of acronyms

EG - ethylene glycol
WEG - wastewater containing diluted ethylene glycol
PEG - polyethylene glycol
COD - chemical oxygen demand
TOC - total organic carbon

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