Adsorption of phenol, 3-nitrophenol and dyes from aqueous solutions onto an activated carbon column under semi-batch and continuous operation

I. Moraitopoulos, Z. Ioannou, J. Simitzis

Abstract—The present study examines the adsorption of phenol, 3-nitrophenol and dyes (methylene blue, alizarine yellow), from aqueous solutions onto a commercial activated carbon. Two different operations, semi-batch and continuous with reflux, were applied. The commercial activated carbon exhibits high adsorption abilities for phenol, 3-nitrophenol and dyes (methylene blue and alizarin yellow) from their aqueous solutions. The adsorption of all adsorbates after 1 h is higher by the continuous operation with reflux than by the semi-batch operation. The adsorption of phenol is higher than that of 3-nitrophenol for both operations. Similarly, the adsorption of alizarin yellow is higher than that of methylene blue for both operations. The regenerated commercial activated carbon regains its adsorption ability due to the removal of the adsorbate from its pores during the regeneration.

Keywords—Activated carbon, Adsorption, Phenols, Dyes.

I. INTRODUCTION

MANY industries discharge wastewaters containing hazardous substances such as phenols, dyes and heavy metals. The last decades, however, in EU and US there have been taken district measures for the decline of these dangerous substances in the water. It is well known that the contamination of the water, from the industries provides many problems to human's health including diarrhea, liver damage, anaemia and dark urin [1]. Especially, phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and cause significant taste and odour problems to drinking water [2]. Moreover dyes, such as

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methylene blue cause eye burns, which may be responsible for permanent injury to the eyes of humans and animals. On inhalation, it causes rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [3,4].

Thus, with the increase in the number of chemical industries, a great deal of wastewater is produced in the rivers and the seas. The treatment processes for phenolic wastewater can be classified into two basic categories [5,6], a) destructive process such as destructive oxidation with ozone [7], hydrogen peroxide [8] or manganese oxides [9] and b) recuperative processes such as adsorption into porous solids [10], membrane separation [11] and solvent extraction [12]. Concerning the removal of dyes from wastewaters, several methods are used such as oxidation-ozonation, biological treatment, coagulation-flocculation, membrane processes and adsorption [13]. Some of them are also used for the removal of phenols.

Adsorption is a well established and powerful technique for the removal of organic pollutants from wastewaters. Activated carbon is widely used as adsorbent in gas and liquid phase separation. Precursor materials for the commercial activated carbons are coal, lignite, nutshells, wood and peat, which are transformed in carbonaceous materials by proper carbonization [14]. Typical activated carbons consist of particles with porous structure having a network of interconnected macropores, mesopores and micropores resulting to high surface area and good capacity. The surface chemistry of activated carbons and the chemical characteristics of the adsorbate, such as polarity, ionic nature and functional groups determine the nature of bonding mechanisms and the extent of adsorption [15-23].

The aim of the present study is to examine the adsorption of dyes (methylene blue, alizarine yellow), phenol and 3-nitrophenol from aqueous solutions onto a commercial activated carbon by applying two different operations, semi-batch and continuous with reflux.

I. MATERIALS AND METHODS

A. Materials

Activated charcoal granular 4-8 mm from Fluka AG (number 05110) with cylindrical shape of the particles was

used. The dyes consisted of methylene blue and alizarin yellow R, both from Fluka AG, with the chemical structures of $C_{16}H_{18}N_3ClS$, $C_{13}H_9N_3O_5$ and molecular weights of 319.86 and 287.2 $g \cdot mol^{-1}$, respectively. Phenol and 3-nitrophenol originated from Merck company, had the chemical structures of C_6H_5OH, $C_6H_5NO_3$ and molecular weights of 94.0 and 139.1 $g \cdot mol^{-1}$, respectively.

B. Preparation of aqueous solutions

An aqueous solution containing either phenol or 3-nitrophenol in a concentration of 0.032 $g \cdot l^{-1}$ at 20 ^{o}C under continuous stirring by using a magnetic stirrer was prepared. The amount of remaining adsorbate during the adsorption, after taking proper liquid samples, was determined by the UV-VIS spectroscopic method in an apparatus of a Perkin Elmer Lamba 3 UV-VIS Spectrophotometer. The absorption intensities at the wavenumbers of 210.5 nm for phenol and 228.5 nm for 3-nitrophenol, respectively, were determined and the amount of the corresponding phenols were calculated using the proper calibration curves.

The aqueous solutions of dyes (methylene blue and alizarin yellow) were also prepared in a concentration of 0.032 $g \cdot l^{-1}$ at 20 ^{o}C under continuous stirring by using a magnetic stirrer. The amount of remaining adsorbate during the adsorption, after taking proper liquid samples, was determined by comparing each liquid sample with a chromatometric scale of known concentration of the dye.

The adsorbed amount (b_t) of the adsorbate onto the activated carbon was determined from the difference between the initial amount of adsorbate (b_o) in the solution and the corresponding measured amount of the adsorbate in every sample of solution expressed as %, i.e. $b_t \cdot 100/b_o$.

Two different operations, semi-batch and continuous with reflux were applied for the adsorption of the organic pollutants (adsorbate) from aqueous solutions onto the commercial activated carbon.

C. Semi-batch operation

The semi-batch operation performed in a system shown in Fig. 1.

A standard amount of commercial activated carbon (4.04 g) was added in a glass burette filling 10 cm of height. The aqueous solution containing the adsorbate was passing through the burette with a constant rate of 0.09 $ml \cdot sec^{-1}$ (Case A) or 0.2 $ml \cdot sec^{-1}$ (Case B) by proper regulation of the stopcock in the outlet of the burette. 48 ml of the solution was added in the burette and then 12 ml of the sample were removed from the outlet of the burette. Every 60 sec a new sample of 12 ml of solution was removed. After the 4th sample taking, the procedure was repeated by adding a new volume of 48 ml of the solution. The concentration of the adsorbate in every sample of the solution was determined.
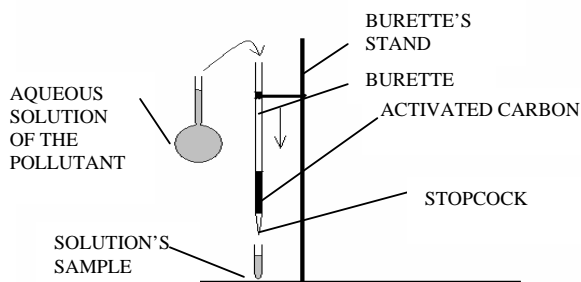

Fig. 1 Semi-batch operation for the adsorption of pollutants onto activated carbon.

The previously used activated carbon was regenerated under vacuum at 200 ^{o}C for 3 h. The above procedure was repeated with new quantities of aqueous solutions of adsorbate in order to re-examine the adsorption ability of commercial activated carbon. The total volume of the solution of the adsorbate after 5th repeating was about 250 ml.

D. Continuous operation with reflux

The continuous operation with reflux performed in a system shown in Fig. 2.

The system of burette containing the activated carbon as previously described was connected with a pump (Grunbeck Wasseraufbereitung GmbH, type GENODOS-Pump GP-2/40) and a tank so that the aqueous solution of the adsorbate was circulated continuously with a constant rate of 0.15 $ml \cdot sec^{-1}$ (Case C). The total volume of the solution was 250 ml. Small quantities of the solution were taken from the tank at different time intervals in order to measure the concentration of the adsorbate and its corresponding amount.
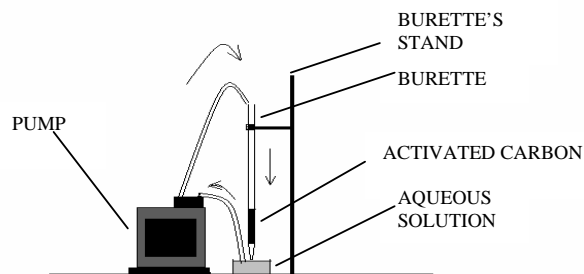

Fig. 2 Continuous operation with reflux for the adsorption of pollutants onto activated carbon.

II. RESULTS AND DISCUSSION

Fig. 3 presents the adsorption of phenol from aqueous solution onto commercial activated carbon with two different operations, the semi-batch operation (Case A and B) and the continuous operation with reflux (Case C). From this figure, the adsorption of phenol by the continuous operation with reflux reaches its maximum (85%) at 65 minutes and the maximum adsorption of phenol by the semi-batch operation reaches almost 50 and 60 % (Case A and B respectively) for times between 5 and 10 minutes. It is remarkable that for the

latter times, the adsorption of phenol operating according to case C is higher (65 %). Concerning the semi-batch operation, the higher rate leads to higher adsorption of phenol. After the first ten minutes, the adsorption ability of the activated carbon is reduced in opposite to the continuous operation with reflux which continues to be increased.
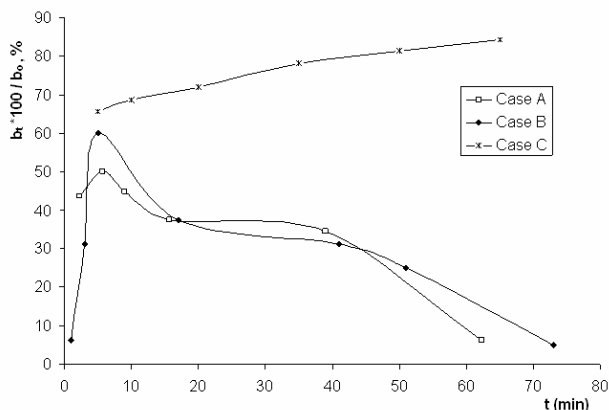

Fig. 3 Adsorption of phenol from aqueous solutions onto commercial activated carbon. b_t: adsorbed amount of phenol, b_o: initial amount of phenol in the solution before the adsorption, case A, B: semi-batch operation with rates 0.09 and 0.2 ml·sec^{-1} respectively, case C: continuous operation with reflux and constant rate 0.15 ml·sec^{-1}.
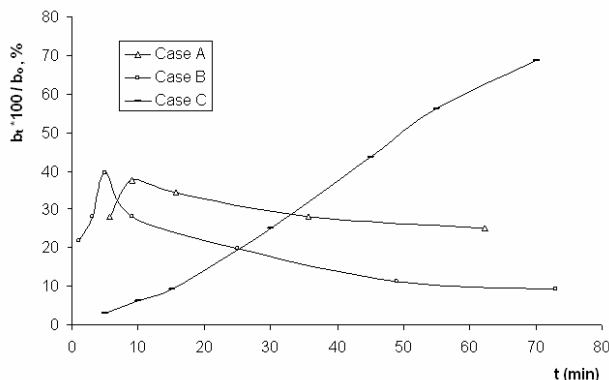

Fig. 4 Adsorption of 3-nitrophenol from aqueous solutions onto commercial activated carbon. b_t: adsorbed amount of phenol, b_o: initial amount of phenol in the solution before the adsorption, case A, B: semi-batch operation with rates 0.09 and 0.2 ml·sec^{-1} respectively, case C: continuous operation with reflux and constant rate 0.15 ml·sec^{-1}.

According to Fig. 4, the adsorption of 3-nitrophenol by the continuous operation with reflux reaches its maximum (70%) at 70 minutes and by the semi-batch operation at almost 37 and 40 % (Case A and B respectively) for times between 5 and 10 minutes. Concerning the continuous operation with reflux, the adsorption of 3-nitrophenol versus time follows a very different course compared to that of phenol (Fig. 3). The adsorption of 3-nitrophenol at the beginning (e.g. 5 min) is only 3 % whereas that of phenol is 65 %. At the final time (e.g. 70 min), the adsorption of 3-nitrophenol is 70 % whereas that of phenol is 85 %.
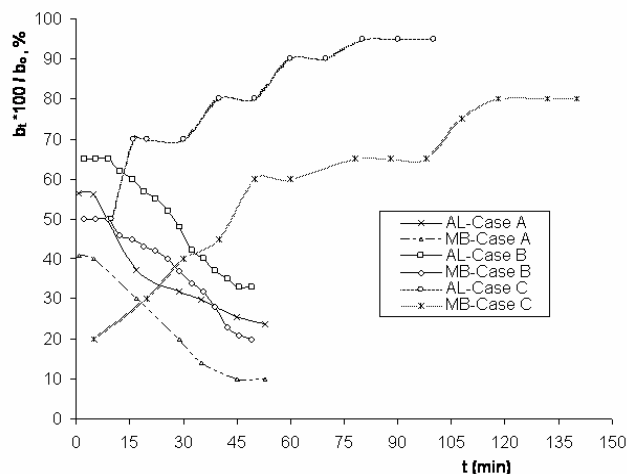

Fig. 5 Adsorption of methylene blue and alizarin from aqueous solutions onto commercial carbonaceous materials. b_t: adsorbed amount of methylene blue and alizarin, b_o: initial amount of methylene blue and alizarin in the solution before the adsorption, amount of carbonaceous material for all cases: 4.04 g, case A, B: semi-batch operation with rates 0.09 and 0.2 ml·sec^{-1} respectively, case C: continuous operation with reflux and constant rate 0.15 ml·sec^{-1}.

According to Fig. 5, the adsorption of dyes by the continuous operation with reflux reaches its maximum (95 % for alizarin and 80 % for methylene blue) at 75 and 110 minutes, respectively. The adsorption of alizarin (65%) and methylene blue (50%) in case B is higher than in case A (58% for alizarin and 40% for methylene blue). Alizarin presents higher adsorption in shorter time than methylene blue in all cases. After the first ten minutes, the adsorption ability of the activated carbon in the semi-batch operation is reduced in opposite to the continuous operation with reflux, which continues to be increased.

The discolouring ability of different adsorbents (e.g. activated carbon, polyacrylonitrile e.t.c.) [24, 25] can be interpreted in terms of the concept of the electron donor – acceptor (EDA). The molecule of methylene blue involves the aromatic rings which includes the functional group of S^+ and $N^+(CH_3)_2$ (electron donors). The molecule of alizarin yellow involves the aromatic ring which includes the functional groups of N=N, COOH, NO_2 (electron acceptors) and OH (electron donor). Moreover, the surface of carbonaceous materials may contain basic or acid groups [26]. The adsorption of methylene blue shows the presence of electron acceptor groups in carbonaceous material and the adsorption of alizarin yellow the presence of electron donor and acceptor groups respectively [24]. The above result indicates that the surface of carbonaceous materials contains both basic and acid groups.

Fig. 6 shows the adsorption of phenol and 3- nitrophenol from aqueous solutions on regenerated commercial activated carbon with the semi-batch operation (Case A and B). The regenerated commercial activated carbon presents similar adsorption abilities with the initial one. Phenol and 3-nitrophenol present higher adsorption (56 % for phenol and

37% for 3-nitrophenol) in case B than in case A (42% for phenol, 35% for 3-nitrophenol). During the regeneration the adsorbate has been almost fully removed from the pores of the activated carbon and the latter regains its adsorption ability.
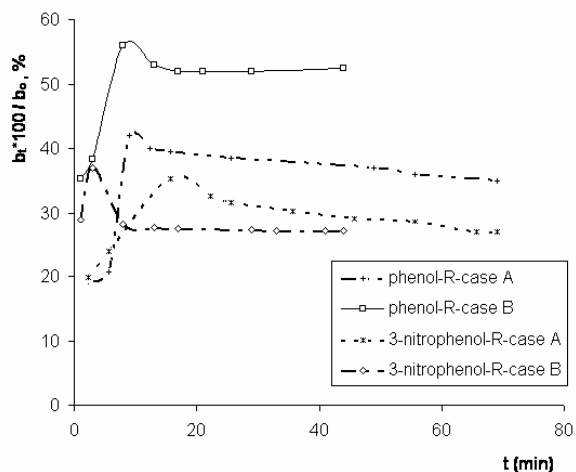

Fig. 6 Adsorption of phenol and 3-nitrophenol from aqueous solutions onto commercial activated carbon. b_t: adsorbed amount of phenol and 3-nitrophenol, b_o: initial amount of phenol and 3-nitrophenol in the solution before the adsorption, case A, B: semi-batch operation with rates 0.09 and 0.2 ml·sec^{-1} respectively.

According to Fig. 7 in comparison with Fig. 5, the regenerated commercial activated carbon presents similar adsorption abilities for methylene blue and alizarin yellow with the initial one. Methylene blue and alizarin yellow present higher adsorption in case B (45% and 60 %, respectively) than in case A (35% and 50%, respectively).
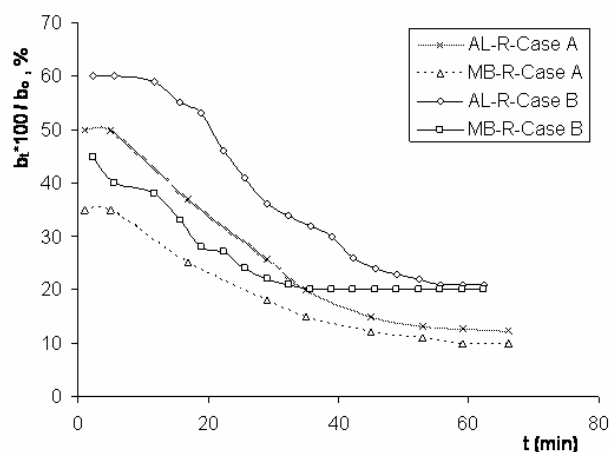

Fig. 7 Adsorption of methylene blue and alizarin from aqueous solutions onto commercial activated carbon. b_t: adsorbed amount of methylene blue and alizarin, b_o: initial amount of methylene blue and alizarin in the solution before the adsorption, case A, B: semi-batch operation with rates 0.09 and 0.2 ml·sec^{-1} respectively.

III. CONCLUSIONS

The commercial activated carbon exhibits high adsorption abilities for phenol, 3-nitrophenol and dyes (methylene blue and alizarin yellow) from their aqueous solutions.

Comparing the two different operations (semi-batch and continuous with reflux), the adsorption of all adsorbates after 1 h is higher by the continuous operation with reflux than by the semi-batch operation.

The adsorption of phenol is higher than that of 3-nitrophenol for both operations. Similarly, the adsorption of alizarin yellow is higher than that of methylene blue for both operations.

The regenerated commercial activated carbon regains its adsorption ability due to the removal of the adsorbate from its pores during the regeneration.

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