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Catalysis Today 53 (1999) 73–80

CATALYSIS TODAY

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Comparison of catalytic processes with other regeneration methods of activated carbon

Moshe Sheintuch *, Yurii I. Matatov-Meytal

Department of Chemical Engineering, Technion-IIT, 32000 Haifa, Israel

Abstract

This article provides an overview of regeneration methods for activated carbon (AC) adsorbents saturated with toxic and biorefractoty organics, with special emphasis on catalytic regeneration methods which were suggested recently. The latter use either separate desorption of the compounds followed by catalytic liquid-phase oxidation, or direct oxidation of the adsorbed species on an AC adsorbent modified with a catalyst. In the former approach, the water is not contacted with the catalyst and metal dissolution is not problem but desorption may not occur at low temperatures. Basic trends, the limitation encountered in these processes and the potential for improvement are assessed. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Activated carbon; Adsorption; Regeneration; Heterogeneous catalysis; Oxidation; Reduction; Water treatment

1. Introduction

One of the major technologies for the abatement of low concentrations of toxic organics in water is based on adsorption by activated carbon (AC), either in the powdered or in granular form [1]. AC adsorption can replace biotreatment methods and it can be effective for capturing a biorefractory organics from water. The saturated AC, however, must be regenerated before reuse. Moreover, the spent AC itself may be considered a hazardous waste and requires a special treatment facility. Thus, successful regeneration is required for a wider application of carbon adsorption processes.

The first significant commercial-scale granular carbon regeneration was the burning of spent AC made from animal bones in sugar refineries around 1828 [2] (after [12]). This procedure have provided burning rather than regeneration in the modern sense that is aimed to restore the adsorptive capacity without much loss of carbon and without altering the surface of the AC. Over the years a variety of regeneration techniques have been suggested, evaluated and applied. These methods are based either on desorption, induced by increasing temperature or by displacement with a solvent, or on decomposition induced by thermal, chemical, electrochemical or microbial processes (Fig. 1). This article provides an overview of regeneration methods for AC adsorbents saturated with toxic organics, with special emphasis on catalytic regeneration methods that were recently developed by our group.

2. AC regeneration methods

Thermal regeneration refers to processes of drying, thermal desorption and high temperature reactive treatment (700–1000°C) in the presence of inert gases or

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* Corresponding author. Tel.: +92-4-8292823; fax: +92-4-8230476
E-mail address: cermsll@techunix.technion.ac.il (M. Sheintuch)

PII: S0920-5861(99)00104-2

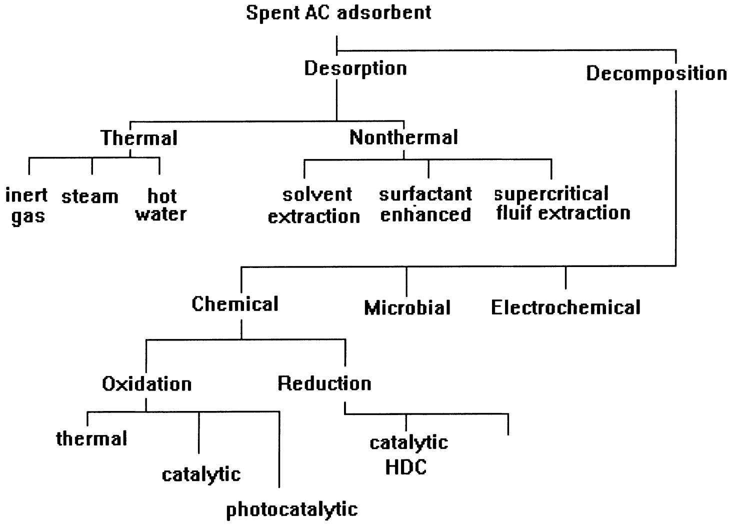

Fig. 1. Overview of available techniques for regeneration of spent AC adsorbents.

of limited quantities of oxidizing gases such as water vapor or flue gas [3]. Due to its high-temperature it is usually not conducted in situ, requiring shipment of the spent AC to special regeneration units such as multiple hearth furnaces or rotary kilns. The high-temperature regeneration typically results in a continuous loss of 5–15% per cycle in adsorption capacity and in surface area. This indicates a weakening of the carbon structure and clogging of the smaller pores at high temperatures. The adsorption capacity may even drop to zero after few cycles. Although high temperature regeneration is applicable to all but the most troublesome spent AC adsorbents, it is economically feasible only for large systems that use more than 500,000 ton of granular AC per year [1].

Thermogravimetric analysis (TGA) and temperature programmed desorption (TPD), combined with gravimetric analysis or mass-spectroscopy, has been used to study the thermal regeneration behavior of the AC loaded with various compounds [4,5]. AC with sorbed organics undergoes the following scenario with increasing temperature: drying and loss of highly volatile compounds occurs at temperatures below 200°C, vaporization and decomposition of unstable compounds takes place at $200 < T < 500°C$ and pyrolysis of nonvolatile adsorbates to form char occurs at $500 < T < 700°C$ followed by oxidation of the residue at higher temperatures. Exposure to temperatures of 750–980°C leads to oxidation of the residual material as well as that of the carbon itself. The latter step includes oxygen attack on the AC itself which may alter the pore structure where small pores (<2 nm) are lost while larger pores are created. The degree of desorption and conversion to char depends on the nature of the adsorbent and the adsorbate and the rate of the process [6].

Extractive regeneration methods that use volatile solvents (*solvent regeneration*) has been reported [7], but current applications of this technology with AC are not known. Supercritical fluid extraction [8,9] exhibits enhanced mass-transfer properties over liquid solvent extraction. However, complete regeneration of AC loaded with organics like phenolic compounds, with supercritical fluid extraction using CO_2, could not be achieved and a large amount of CO_2 would be required. *Surfactant-enhanced regeneration* involves flushing a concentrated surfactant solution through the spent AC. Organic adsorbates desorb and are solubilized into micelles in the regenerant solution; the micelles are surfactant aggregates that typically contain 50–100 molecules. Effective adsorption capacity of over 50% of that on virgin AC were observed on regenerated samples [10]. The practice of these regeneration techniques is becoming increasingly expensive and environmentally unacceptable since it serves only to transfer the contaminant from one location (AC) to another (solvent or surfactant) which must be treated subsequently.

Reactive regeneration methods destroy the adsorbed organics by *chemical* (including acid–base [11] or oxidative transformations [12]), *microbial* [13] or *electrochemical* processes [14]. The chemical methods may involve complete mineralization of the adsorbed species (to carbon dioxide and water), transformation of complex molecules into simple compounds and the conversion of hazardous materials to more desorbable, water-soluble or more biodegradable compounds. Chemical oxidation using various oxidants (chlorine, chlorine dioxide, peroxide, ozone and potassium permanganate) has been tested [12] and at least partial restoration of AC adsorption capacity was demonstrated; these processes, however, have not proven technically feasible for continuous operation, nor have they been shown to be economically viable. An established technology for regeneration of spent AC with organics or oxidizable inorganic compounds is *wet air regeneration* [15,16] but this method is rather expensive because of the required large investments in high pressure equipment and the high cost of running the regeneration at high pressures and temperatures.

3. Catalytic regeneration

3.1. Oxidative treatment

Catalytic regeneration methods may enhance the decomposition rates and enable to carry the regeneration at lower temperatures and lower residence times. Several catalytic regeneration schemes were suggested in recent years. These use either desorption followed by catalytic liquid-phase oxidation, or direct oxidation of the adsorbed species on an AC-adsorbent modified with a catalyst. In the former approach, the water is not contacted with the catalyst and metal dissolution is not a problem. In the latter approach, metal dissolution may occur and should be monitored.

3.1.1. Catalytic oxidation after desorption

In a process with pre-desorption, the adsorbed organics may be removed by temperature swing method, in which hot water at high temperatures (up to 200°C) and elevated pressures is routed through the adsorber. A recovery of 95% of initial adsorption capacity for phenol was reported [17]. The desorbed organics can be subsequently abated by catalytic liquid-phase oxidation [18].

Common problems of catalytic abatement of dissolved water pollutants have been recently reviewed by the authors [19]. Catalytic wet air oxidation (WAO) [16] is an established technology and catalytic supercritical water oxidation (SCWO) is under development [20] for decomposition of dissolved oxidizable species, high efficiency in these methods, however, concur with high-cost of the high-temperatures and high-pressures of supercritical units.

3.1.2. Photocatalytic regeneration

Photocatalytic oxidation can be used to regenerate spent AC adsorbents and destroy organic adsorbates simultaneously [21]. This method employs photocatalysts (TiO_2, SnO_2, and ZrO_2), organized in layers within the same bed or impregnated on AC, and illuminated with UV or solar light to generate highly reactive radicals which can mineralize organic compounds.

Photooxidation of trichlorethene (TCE) and *p*-dichlorobenzene (DCB) on the Pt–TiO_2 impregnated AC (Filtrasorb-400) carried out in a plate photoreactor was studied by Crittenden and coworkers [22]. The amount of photocatalyst loaded onto external surface of adsorbent has no significant impact on the adsorption capacity of the AC/catalyst adsorbent. The working capacity for an influent TCE of 1 mg/l is about 70% of virgin capacity of Filtrasorb-400. For the strongly adsorbing compound, DCB, no stable working capacity was found and only less than 40% of the loaded adsorbate was mineralized (Fig. 2). Based on this study the photocatalytic regeneration process was found to be limited by the reaction rate at the beginning of the regeneration cycle and then by desorption of adsorbates from the interior of the AC. The photocatalytic regeneration was a very long process which makes it still unsuitable for practical application. A possible way to maximize the photocatalysis efficiency is to increase the desorption rate through heating and match the photocatalytic oxidation rate to the desorption rate.

3.1.3. Direct oxidation on AC/catalyst

In situ catalytic treatment of spent AC, although not currently used for AC regeneration, has been claimed

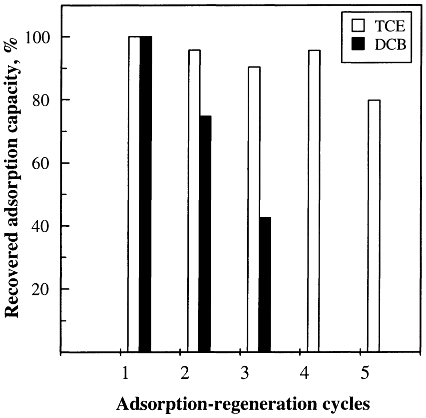

Fig. 2. The recovered adsorption capacity of 1% Pt–TiO_2/AC (Filtrasorb-400) loaded with trichlorethene (TCE) and *p*-dichlorobenzene (DCB) vs regeneration cycle number [22].

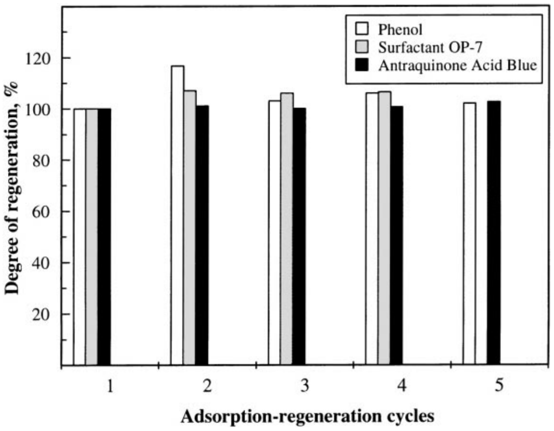

Fig. 3. The degree of regeneration of 7,1 wt.% Fe_2O_3/AC (AG-3) vs. regeneration cycle number. Regeneration applied with 5% oxygen in nitrogen at 350°C, [25].

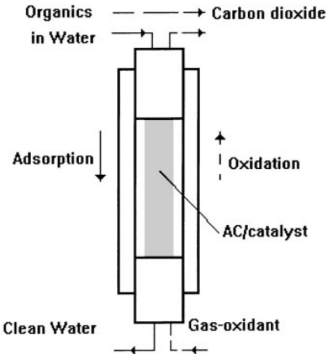

Fig. 4. Generalized scheme of periodic adsorption and catalytic oxidation using AC/catalyst.

to be promising as an alternative to thermal regeneration [23–26,28]. The advantages of the integration of adsorption and catalytic processes on AC/catalyst adsorbents are that the process will be accelerated by the high concentrations of pollutants eluted from the adsorbent and that the low-temperature regeneration will be conducted in situ, even in small units, thus improving the economy of the process. Moreover, the catalytic process can be operated at ambient conditions using the low potential heat energy. Catalysts may be deposited on the adsorbents so that they would act both as an adsorbent for capturing the dissolved contaminants and as a catalyst for destroying the adsorbed compounds. This provides intimate contact in a single unit, reduces diffusion paths and accelerates desorption rate, but it may diminish the adsorption capacity and may lead to metal elution.

Catalytic regeneration for ACs impregnated with metal oxides like Cr_2O_3, CuO, Co_3O_4, V_2O_5, MoO_3, WO_3 and metals like Pt and Pd has been first applied by Nwankwo and Turk [23]. Complete oxidation of styrene and benzene, adsorbed from gas-phase, was achieved at low temperatures (150–240°C over WO_3 and 120–210°C over BaO/Cr_2O_3). AC ignition occurred at temperature higher by about 150°C. Iron oxide was found to reduce the working adsorption capacity of AC for small molecules (phenol) and the surface area by 20–30% without affecting the adsorption of large molecules [27]. Koganovskii and coworkers have demonstrated that AC containing manganese oxides [24], or mixture of Fe_2O_3, CuO and Al_2O_3 [25], were able to regenerate the spent AC, after liquid-phase adsorption directly in the same adsorption column at 280–350°C, rather than the high-temperature of thermal regeneration (Fig. 3). The mean losses of carbon due to burn-off amounted to 2.35–2.86% per operation and depended on the adsorbate and regeneration temperature.

Periodic process of liquid-phase adsorption followed by heterogeneous catalytic oxidation of adsorbates in the gas-phase, of AC impregnated with mixture of metal oxides, was recently applied in our group for purification of phenol solution [30] (see schematic drawing in Fig. 4).

The phenol adsorption isotherms were determined for untreated AC, and for several fresh and regenerated AC/catalysts. The isotherms correlate well with

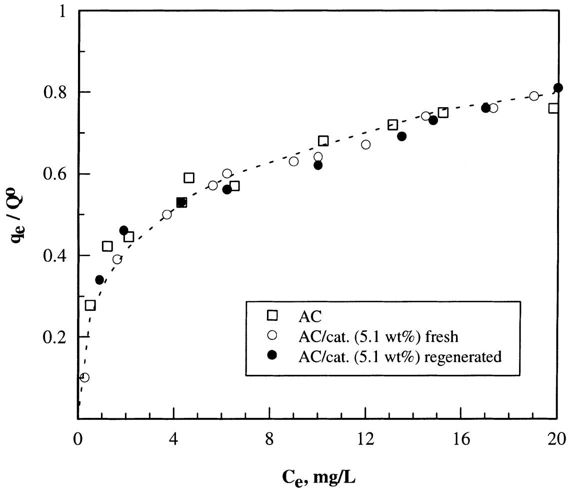

Fig. 5. Effect of impregnation by catalyst and of regeneration procedure on adsorption isotherms of phenol on the AC/catalyst (5.1 wt.% $Fe_2O_3 : CuO : Cr_2O_3$). The isotherms (25°C), shown for the AC, fresh and regenerated AC/catalyst were rescaled with respect to the respective saturation value Qo. Regeneration was carried out at 250°C with air [28].

the Langmuir adsorption isotherm. The incorporation of about 5–10 wt.% of metal oxides into AC led to a loss of about 12–18% and 23–25% in adsorption capacity and in surface area, respectively, as compared with the virgin AC. The presence of metal oxides in the AC pores did not affect the shape of equilibrium adsorption isotherms, as evident by the equal shape of the three AC/catalysts. The isotherms for the AC and of one AC/catalyst are plotted in Fig. 5, after rescaling the amount of adsorbed phenol (qe) with respect to the saturation adsorption capacity of that sample (Qo), showing that the three lines overlap. Adsorption on the regenerated AC/catalyst exhibits the same features.

To characterize the regeneration process, we determine the temperature ranges of catalytic oxidation (T_p), of carbon ignition (T_c) and its burn-off by thermogravimetric and differential thermal analysis (TGA/DTA) in oxidizing and inert atmospheres [31]. These show that the catalyst impregnation alters the behavior of the carbon-phenol system (Fig. 6). The impregnated catalyst facilitated phenol oxidation but also lowered the T_c of the AC. Catalytic regeneration can be conducted between T_p (220–240°C) and T_c (320–370°C).

The results obtained from the polythermic studies correlate well with those from the isothermal regeneration of AC/catalyst samples. Regeneration of AC impregnated with mixture of $Fe_2O_3 : CuO : Cr_2O_3$ in flowing gas containing oxygen (5–20%) at 240–290°C, of spent AC saturated with phenol, has restored almost all of its original adsorption capacity even after 10 cycles of regeneration (Fig. 7). Regeneration of the AC without catalyst under the same conditions resulted in a 13–18% recovery of adsorption capacity. Adsorption breakthrough curves of phenol from fresh and regenerated beds of modified AC/catalyst are presented in Fig. 8. The general trend in declining of the recovered phenol adsorption capacity seems to be more pronounced in data for column adsorption experiments (dynamic conditions, Fig. 8) than in data for batch adsorption experiments (static conditions, Fig. 7). It is evident from the early breakthrough in a bed of regenerated AC/catalyst after 7–10 adsorption-regeneration cycles when compared with a freshly adsorbed AC/catalyst, indicating complex nature of adsorption-reaction processes in the regenerated bed of AC/catalyst.

While the results for regeneration in phenol-AC/catalyst system are promising, poor regeneration was achieved with p-chlorophenol (CP) and p-bromophenol (BP) which amounted to a loss of almost 50% per regeneration cycle (Fig. 7). Under such conditions, HCl, which besides CO_2 was the major product during CP oxidation, is rejected into the gas-phase and the activity of AC/catalyst is depressed and complete regeneration is practically impossible. Metal oxide catalyst deactivation by HCl and Cl_2 had already been observed and documented [30,31].

3.2. Reductive treatment

Reductive methods for regeneration purposes may offer an alternative solution that will avoid catalyst deactivation problem and are currently receiving a growing attention. For example, catalytic hydrodechlorination (HDC) may be used for converting chlorinated hydrocarbons [32–35] and chlorinated phenols [36] into the dechlorinated ones, using various reductants such as H_2 and $NaBH_4$ [32] or H_2 and N_2H_4 [33–36] over Pd/AC. These processes are still in the developing stage and the long-term performance of the catalyst is yet to be studied.

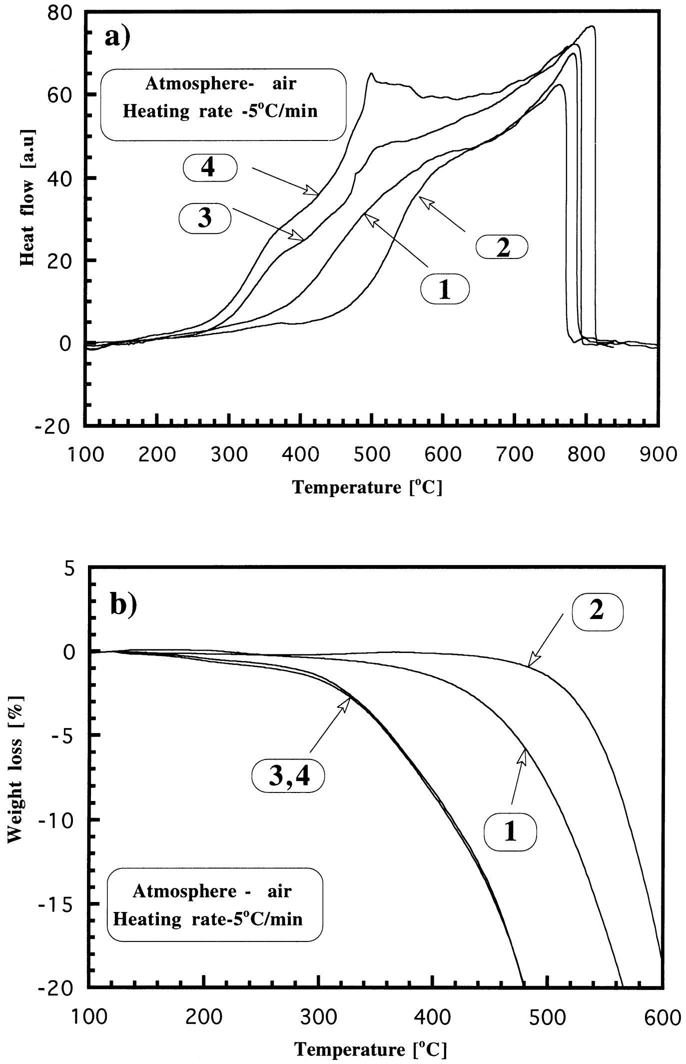

Fig. 6. Effect of the catalyst on the thermal behavior of the AC(Filtrasorb-400)/catalyst during TGA/DTA study: (1)-phenol on AC, (2)-virgin AC, (3)-phenol-on AC/catalyst (5.1 wt.% $Fe_2O_3 : CuO : Cr_2O_3$) and (4)-phenol on AC/catalyst (5.1 wt.% $Fe_2O_3 : CuO : SiO_2$) [29].

4. Summary

Catalytic regeneration methods may enhance the decomposition rates and enable to carry the regeneration at temperatures and residence times that are much lower than those of thermal regeneration. These use either separate desorption of the compounds followed by catalytic liquid-phase oxidation, and direct photooxidation or oxidation of the adsorbed species on AC adsorbent modified with a catalyst. In the former approach, the water is not contacted with the catalyst and metal dissolution is not problem but desorption may not occur at low temperatures. These processes are still in the developing stage and the long-term performance of AC/catalyst is yet to be studied. Better understanding of mechanism of regeneration and large scale demonstrations of new catalytic techniques are needed.

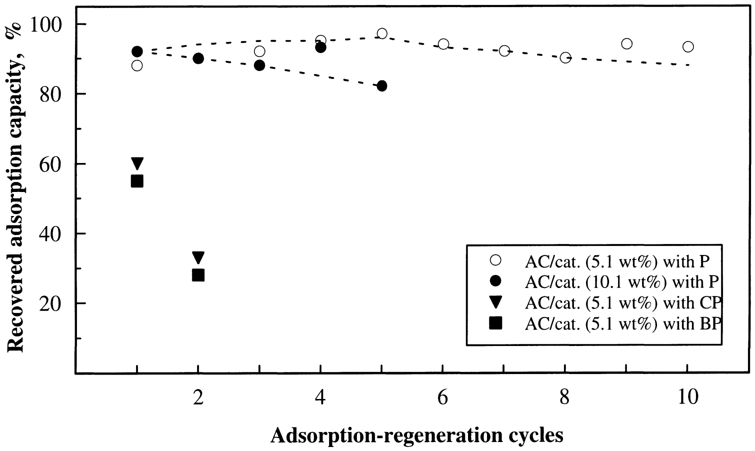

Fig. 7. The recovered adsorption capacity of the AC(Filtrasorb-400)/catalyst vs. regeneration cycle number. Regeneration of AC/catalysts saturated with phenol was applied at 250°C with 5% oxygen in nitrogen (open symbols) or with air (full symbols). Regeneration of spent AC/catalysts saturated with halogenated phenols was applied at 270°C with air [28].

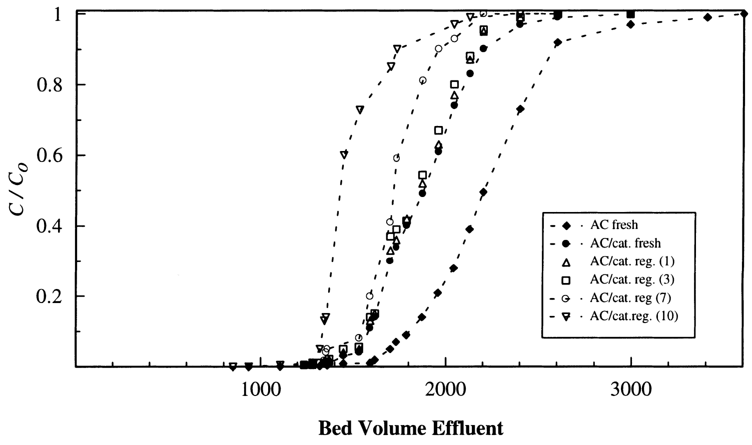

Fig. 8. Phenol breakthrough curves from virgin AC or from fresh and regenerated AC(Filtrasorb-400)/catalyst (5.1 wt.% $Fe_2O_3:CuO:Cr_2O_3$) beds. Regeneration was applied at 250°C with 5% oxygen; *C*o and *C*-denote feed and effluent concentrations [28].

Acknowledgements

This research was supported by The Water Research Institute, The Center for Absorption in Science, (Ministry of Immigrant Absorption), and the Ministry of the Environment, State of Israel. The CRE group is supported by the DuPont Educational Aid Fund.

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