Bull. Environ. Contam. Toxicol. (2004) 73:1017–1024

DOI: 10.1007/s00128-004-0527-5

Bulletin of Environmental Contamination and Toxicology

Photocatalytic Regeneration of Exhausted Activated Carbon Saturated with Phenol

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Received: 5 March 2003/Accepted: 9 September 2004

Activated carbon either in powder or in granular form can offer an efficient technology to remove organic contaminants from industrial and municipal wastewater (Yuan QZ, Ravikrishna R 2001). Activated carbon adsorption can replace bio-treatment methods and it is effective to capture the bio-refractory organics from water. The exhausted activated carbon, however, must be regenerated before reuse for environmental and economical consideration. A variety of regeneration techniques for exhausted activated carbon saturated with organic pollutants such as phenol, have been suggested, e.g. thermal regeneration and chemical regeneration. Thermal regeneration of spent granular activated carbon at 850-1000 ℃ is economically feasible only for large system that uses more than 500000 lb granular carbon per year (Moshe S, Yurii MM 1997). When regenerated through chemical methods, the exhausted activated carbon doesn't need to be returned to the manufacturer to regenerate and carbon loss could be neglected. The regeneration efficiency by chemical methods depends on the types of organic pollutants. Since it is a very important process to treat tap water and wastewater contaminated with phenol by activated carbon, the research regarding how to regenerate this kind of exhausted activated carbon is very attractive. The granular activated carbon saturated with phenol is usually regenerated by chemical methods such as using Lewis base desorption and electrochemical oxidation (Zhang HP 2002). It is, however, relatively difficult to make the regeneration efficiency of activated carbon over 70%. Another alternative method is catalytic regeneration in which catalyst was impregnated onto activated carbon to remove carbon-adsorbed species through the catalytic decomposition reaction. The advantages of catalytic regeneration are as follows: (1) the low temperature regeneration can be conducted in situ, even in small units, thus to improve the economy of the process; (2) a large number of adsorption-regeneration cycles are expected to proceed without loss in capacity. Heterogeneous photocatalytic process using anatase TiO_2 as catalyst is one of the most promising advanced oxidation processes. This process is based on the generation of very reactive species, such as hydroxyl radicals (•OH) that can oxide a broad range of organic pollutants quickly and non-selectively (Martra G 2000). Most organics can be mineralized to water, carbon dioxide and mineral acids by successive hydroxyl radical attack and fragmentation. Considering the economical and environmental viewpoint, its fully destructive characteristics and potential of using solar

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radiation makes this process one of the most attractive environmental decontamination methods (Blake D M 1999).

The objective of this study is to investigate the technical feasibility of the regeneration of exhausted activated carbon saturated with phenol by photocatalytic oxidation and develops a newly practical in-situ activated carbon regeneration method. The photocatalyst-impregnated carbon was regenerated in organic-free water. Control experiment was conducted in dark and without photocatalyst, respectively. In addition, a possible controlling mechanism responsible for the photocatalytic regeneration of exhausted carbon was discussed.

MATERIALS AND METHODS

The granular activated carbon used in this work was made from coal for industrial use, which was specifically for water treatment and friendly supplied by Xinhua Chemical Factory (Shanxi, China). Prior to use, all carbon samples were washed with boiling water and oven-dried at 120 ℃ for 24 hr. All chemicals were purchased and used as chemical purity grade. Aldrich TiO_2 was used as photocatalysts. Ag-TiO_2 was synthesized by photochemical deposition method (Liu SX, Wang Y, Zhang SR 2001). Photocatalyst was used to impregnate onto carbon surface through impregnation-desiccation method. The amount of loading catalyst was determined by ash analysis. The twice-distilled water was used for preparing all the solutions.

A 722 spectrometer was used to analyze the phenol with 4-amino-antipyrine-ferricynaide photometric method (Environmental Protection General Bureau of China 1989). The saturated adsorption values of activated carbon were denoted by the equilibrium adsorption values of phenol on activated carbon under a 2.0 g/L concentration. Regeneration experiments were carried out in a batch-type plate photoreactor; an 8 W UV lamp (253.7 nm) was used as irradiation source (Liu SX, Wang Y, Zhang SR 2001). The regeneration efficiency was evaluated through comparing the saturated adsorption value of the regenerated carbon with that of the fresh carbon under the same equilibriums adsorption condition.

Scanning electron microscope (SEM) was used to observe any structural changes and analyze distribution of catalyst on the activated carbon. Adsorption and desorption isotherms of N_2 were measured at 77 K.

RESULTS AND DISCUSSION

Photocatalytic regeneration of activated carbon was attributed to desorption and photocatalytic degradation of adsorbates. Therefore, the desorption and degradation rate of adsorbate may affect the regeneration efficiency. Photocatalyst modification, regeneration temperature, regeneration cycles, pH value, oxidant additive, and inorganic ions additive are the most possible variables affecting regeneration efficiency. These variables were investigated in this paper to assess the photocatalytic regeneration process so as to improve the operation

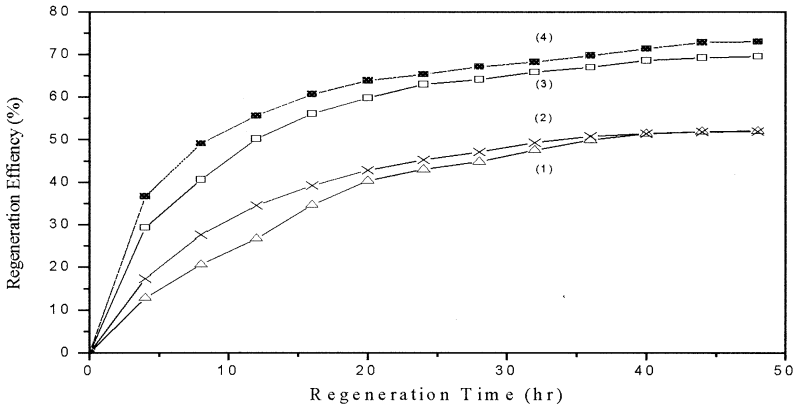

Figure.1 Effect of photocatalyst modification on regeneration efficiency. (1) TiO_2 0.6 wt%; (2) TiO_2 1.9 wt%; (3) Ag-TiO_2 0.6 wt%; (4) Ag-TiO_2 1.9 wt%

performance and understand the regeneration mechanism.

Activated carbon was impregnated with TiO_2 and Ag-TiO_2 respectively. Small clusters of silver on the photocatalyst lead to a decrease of the recombination of the photogenerated charge carriers by accelerating the formation of the superoxide radical anion (O_2•$^-$). Hence, sliver can increase the formation rate of the hydroxyl radicals (•OH). The Ag-TiO_2 used in this study was prepared by the method described in the literature, and its photocatalytic activity was much higher than TiO_2 (Liu SX, Wang Y, Zhang SR 2001).

The experimental data were present in Figure.1. The result shows that regeneration efficiency was higher than untreated TiO_2 when Ag-TiO_2 was used. Photocatalytic regeneration of activated carbon consist of two processes: desorption and photocatalytic degradation of adsorbates. Due to the high activity of Ag-TiO_2, the desorbed adsorbate drived by concentration difference between interior and exterior of activated carbon was degraded quickly, especially at the beginning of regeneration process, resulting in the higher regeneration efficiency when Ag-TiO_2 was used as catalyst. It also can be seen from Figure.1, with the regeneration reaction proceeds, the regeneration rate decreases gradually due to the low rate of adsorbate desorption.

Because of the photonic activation, the photocatalytic systems do not require heating and can be operated at room temperature. The true activation energy Et is nil, whereas the apparent activation energy Ea is often very small (a few kJ/mol) in the medium temperature range (20 ℃$\leq \theta \leq$80 ℃) (Crittenden JC, Liu J, Hand DW, Perram DL. 1997). Since adsorption is an exothermal process, the adsorptive capacity of the carbon decrease considerably as temperature increased. High temperature is, therefore, beneficial to the desorption of most adsorbate (F.Salvador, C. Sānchez Jimēnez 1999).

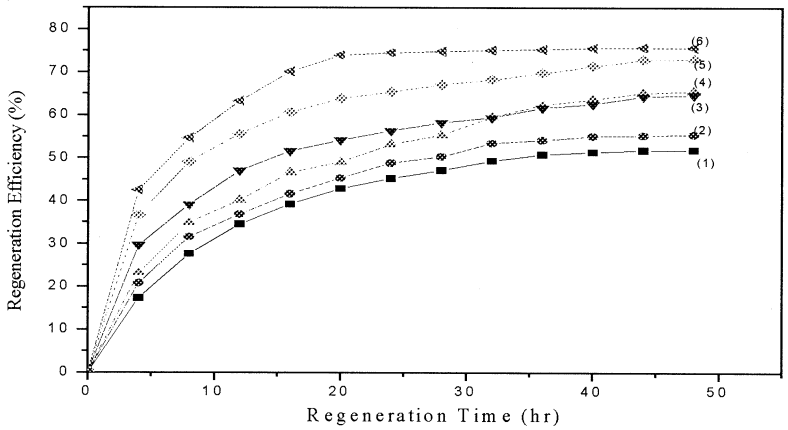

Figure 2. Regeneration efficiency at different temperature.
(1)Room temperature TiO_2; (2) 50℃ TiO_2; (3) 70℃ TiO_2;
(4) room temperature Ag-TiO_2; (5) 50℃ Ag-TiO_2; (6) 70℃ Ag-TiO_2.

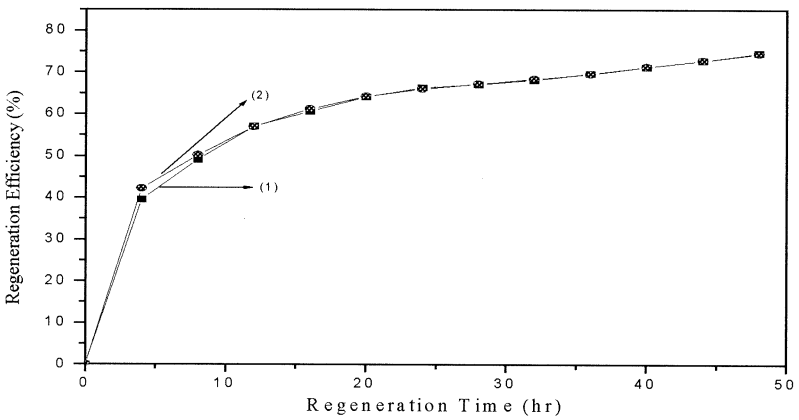

Figure.3 Effect of H_2O_2 on the regeneration efficiency.
(1) No H_2O_2; (2) add H_2O_2.

In order to evaluate the effect of temperature on the photocatalytic regeneration efficiency, the regeneration experiments were carried out under different temperature. The results were shown in Figure 2. It can be seen that high temperature can significantly increase initial regeneration rate for Ag-TiO_2 system, but has only a little effect on final regeneration result. Similar result was obtained when TiO_2 as photocatalyst.

One practical problem when using TiO_2 as photocatalyst is electron-hole recombination which, in the absence of proper electron acceptors, is extremely

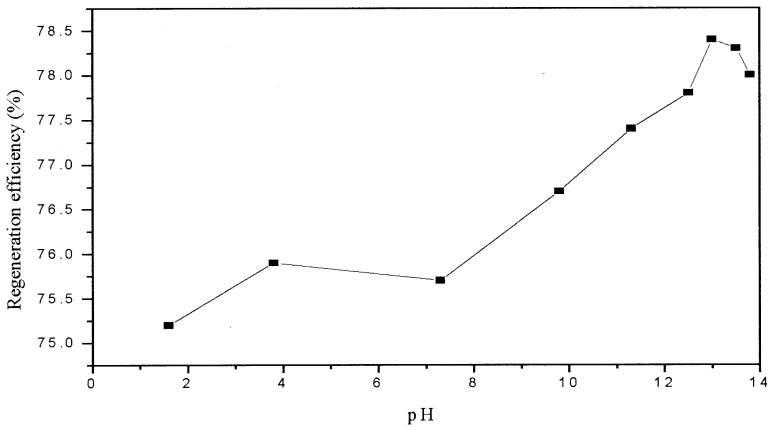

Figure 4. Regeneration efficiency (12hr) at different pH conditions.

efficient and thus represents a major energy-wasting step and limitation to achieve high quantum yield (Matos J, Laine J, Herrman JM 1999). One strategy for inhibiting electron-hole recombination is to add other electron acceptors to the reaction. The use of inorganic peroxides such as hydrogen peroxide, ozone and peroxydisulphate has been demonstrated to remarkably enhance the rate of degradation rate of different organic contaminants (Mario S. 1993). The effect of H_2O_2 on the regeneration efficiency was depicted in Figure. 3. It shows that the H_2O_2 only has a little effect on initial regeneration rate, and no effect on finally regeneration efficiency.

The surface charge of TiO_2 is pH-dependant. The pH of the aqueous phenol solution affects its uptake on activated carbon. In general, the uptake decreases at either lower or higher pH value (Serrano B, Lasa H. 1999; Tomkiewicz M. 2000). At lower pH value the uptake of phenol is less due to the presence of H^+ ions suppressing the ionization of phenol and its reduced uptake on polar adsorbent. In the higher pH range phenol can form salts, which is readily ionized to leave negative charge on the phenolic group. At the same time, the presence of OH^- ions on the adsorbent hinders the uptake of phenolate ions.

In order to find out the optimum pH for maximum regeneration efficiency, experiments were conducted at different pH and the results are shows in Figure.4. It is evident that the regeneration efficiency decreases when pH value is above 13.0. When optimal pH value was determined, an activated carbon loaded with 1.9% of Ag-TiO2 was regenerated at 50 ℃, pH of 13 for 72 hours. The absorbing capacity was recovered to 78.4%.

The activated carbon loaded with 1.9% Ag-TiO_2 was used to absorb phenol and regenerated repeatedly under the ambient temperature at neutral pH for 48 h. The

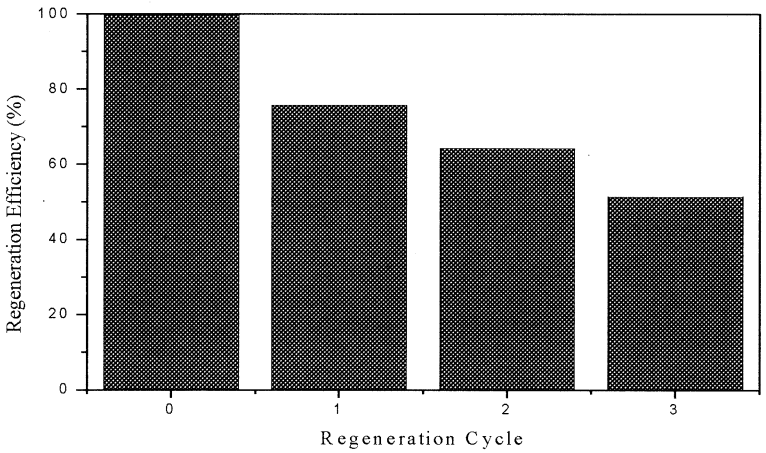

Figure.5 Effect of regeneration cycles on regeneration efficiency.

regeneration efficiency of activated carbon was calculated and the result is shown in Figure. 5. The regeneration efficiency decreases gradually in successive adsorption-regeneration cycles. This may be due to the formation of strongly absorbed intermediate product and loss of photocatalyst.

From the SEM images of activated carbon, it was clear that the photocatalyst was mainly adsorbed on the macro-pore and hollow site and distributed unevenly. The adsorbed photocatalyst jammed only a part of adsorption pathway. No obvious structure change was observed for regenerated carbon. Table 1 shows the value of the main textural characteristics of the original and treated carbons of different regeneration stage. Surface area was determined using the BET method. Micropore volume and the mean pore size were determined using the method of t-plot method (Salvador F, Jimēnez CS. 1993). It can be seen that the specific area of saturated carbon was recovered gradually as the photocatalytic regeneration proceeded.

Table 1. Textural characteristics of original and treated activated carbons.

Sample No.	*1#*	*2#*	*3#*	*4#*	*5#*
BET (m^2/g)	724.6254	708.3864	332.4038	656.3848	679.2010
Microspore volume (mL/g)	0.174674	0.18260	0.019718	0.171331	0.147369
Mean pore size(A°)	18.4812	18.2223	30.7805	18.0457	19.1456

Note: 1# raw carbon material, 2# 1.9% Ag-TiO_2 loaded carbon, 3# was 2# exhausted with phenol, and 4# was 3# regenerated for 48h, 5# was 3# regenerated for 72h.

Photocatalytic regeneration of activated carbon was attributed to desorption and

photocatalytic degradation of adsorbate. Photocatalytic regeneration process consisted of four steps: adsorbate diffusion from the inner to the exterior of activated carbon; adsorbate adsorption; and oxidation on photocatalyst surface; oxidized product desorption from the photocatalyst surface into the liquid-phase. Photocatalytic oxidation reaction of organic adsorbates occurred on the interface of activated carbon and TiO_2. During the early stage of regeneration, photocatalytic oxidation of organic adsorbate was the controlling step in the regeneration process. Afterwards, desorption of organic adsorbate from inner to exterior surface of activated carbon was the controlling step. Low desorption rate of adsorbate determined the low rate of photocatalytic regeneration.

The results show that it is possible to regenerate exhausted carbon saturated with phenol using photocatalytic oxidation method. The absorbing capacity of activated carbons loaded with suitable of Ag-TiO_2 loading was recovered by 78.4% in this work. Based on this, the photocatalytic regeneration process was found to be a very long process, although it is limited by the photocatalytic oxidation rate and then by the desorption rate of adsorbate. In order to develop this method to be suitable for practical use, a possible way to maximize the photocatalytic regeneration efficiency is to increase the desorption rate and match it to photocatalytic oxidation rate when modified high activity photocatalyst was used.

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