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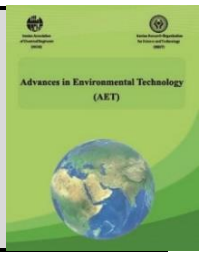

Optimization of chemical regeneration procedures of spent activated carbon

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ABSTRACT

The chemical regeneration of granular activated carbon exhausted in a petrochemical wastewater unit was investigated. Gas chromatography and energy-dispersive X-ray spectroscopy demonstrated that spent activated carbon carries large types of organic and inorganic materials. Diverse chemical solvents were adopted in comparison with traditional chemical solvents and regeneration efficiency was investigated for each approach. The optimum procedure and optimum condition including temperature, concentration of solvent, and time were determined. The regenerated activated carbon was used in the adsorption of methylene blue (MB) in order to find its regeneration efficiency. The regeneration efficiency can be identified by comparing of amount of MB absorbed by the fresh and regenerated activated carbon. The best acidic regenerator was hydrofluoric acid. The higher the temperature causes the faster desorption rate and consequently, the higher regeneration efficiency. The regeneration efficiency increased by means of an increase in the time of regeneration and solvent concentration, but there was an optimum time and solvent concentration for regeneration. The optimum temperature, solvent concentration and regeneration time obtained was 80 ^{o}C, 3 molar and 3 hours, respectively.

1. Introduction

Adsorption is one of the popular methods for removal and recovery of water organic pollutants. There has been an increasingly large amount of literature dedicated to the study of adsorption for the removal of aqueous pollutant species using activated carbon in past decades [1-7]. Due to their large surface area, high-speed adsorption kinetics and well-developed pore structure, activated carbon has been widely used in a variety of industrial applications such as separation, purification, catalysis, as electrodes in batteries, and the removal of pollutants in water and wastewater treatment [8,9]. It is axiomatic that adsorbents encounter demanding conditions in industrial applications which result in the production of secondary pollution and exhausted adsorbent. In the past, when activated carbon (AC) reached its saturation level, it was considered useless and usually taken to a landfill for disposal; however, for economic, environmental and energy saving reasons, the spent granular activated carbon (GAC) should undergo several cycles of regeneration-adsorption rather than being discarded. Therefore, the regeneration of spent activated carbon has increasingly been studied [10]. In turn, the selection of an appropriate regeneration technique depends on the adsorbates, types of adsorption, cost, and processing conditions. Various regeneration techniques such as bioregeneration, thermal regeneration, chemical regeneration and regeneration via ultrasound have been attempted. Bioregeneration is known as an inexpensive but slow method which sometimes takes months to reach the specified regeneration efficiency (RE) [11]. However, the ultrasonic method is a high speed regeneration method, but it decreases RE and adsorption capacity due to the high energy waves which hurts the adsorbent's structure [12].

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Thermal regeneration is a simple regeneration method but is an energy and time consuming method and causes a considerable amount of carbon loss [13]. An alternative approach to the thermal regeneration method is the chemical regeneration method in which chemical reagents are applied to the spent carbon. Traditionally, acid and alkali solutions (with oxidizing capacity) and organic solvents (solubilizing capacity) have been used to dissolve the adsorbates, so that the ability of adsorption of the activated carbon will be recovered. This regeneration method becomes valuable, particularly when adsorbates have strong bonds with the adsorbent's surface [14]. Some solvents that have been used in previous researches are shown in Table 1. The main advantages of the chemical regeneration method include high regeneration efficiency, high speed regeneration and low carbon loss (nearly to zero). In this study, the chemical regeneration of activated carbon which was exhausted in a petrochemical wastewater unit was investigated. Six approaches with diverse materials were applied to the spent AC. The regenerated AC's were used for the adsorption of MB in order to determine their adsorption capacity and for the evaluation of RE.

Table 1. Previous researches of chemical regeneration of activated carbons

Adsorbate	Solvent	Reference
Color	NaOH Hot water Oxidant Surfactant	[14]
Methylene Blue	NaOH H_2O_2 $KMnO_4$ $FeSO_4$ H_2SO_4	[15]
octamethylcyclotetrasiloxane	H_2O_2 O_3	[16]
Coking wastewater contents	C_5H_{12} CH_2Cl_2 $(C_2H_5)_2O$ $C_{18}H_{29}NaO_3S$	[17]
Toluene	$C_2H_2O_4$ H_2SO_4	[18]
Color	Ethanol	[19]
Copper Ions	NaOH	[20]

2. Experimental

2.1. Materials

A commercial granular activated carbon was obtained from Active Char (AC) products Pvt. Ltd.; the characteristics of the GAC according to the manufacturer are presented in Table 2. The granular activated carbon was used in the Tabriz Petrochemical Co. wastewater plant (Tabriz- Iran) and collected after exhaustion. The spent AC sample was washed with distillated water and oven-dried at 105 °C for 24 hours. Ethanol, NaOH, HCl, HF, CS_2 and methylene blue ($C_{16}H_{18}N_3SCl$; MW: 319.85) were purchased from the Merck Company, Germany. The MB's concentration was determined at 665 nm using a UV–Vis spectrophotometer (model SP 3000 plus) according to the calibration curve obtained at the same conditions.

2.2. Characterization

Several characterizations by means of scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDAX), thermogravimetric analysis and ultraviolet-visible spectrophotometer (UV-Vis) were performed on the fresh, used and regenerated AC in order to obtain adsorbent surface morphologies, elemental composition of the adsorbates, thermal stability/decomposition and adsorption capacity, respectively.

2.3. Regeneration method

The spent granular activated carbon (EGAC) which had inappreciable adsorption capacity was filtered, washed by distillated water and oven-dried in the first step. The following steps were employed for the first procedure of regeneration tests:

I. Measuring the known amount of EGAC (which were same in all other procedures).
II. Mixing the measured EGAC with 50 ml of HCl in a shaker which was in a water bath at a constant temperature for 2 hours.

III. After 2 hours, the granular activated carbon was filtered and washed with hot distillated water to access the constant pH.

IV. Mixing the sample with 50 ml of NaOH in a shaker which was in a water bath at a constant temperature for 2 hours.

V. Samples were filtered and washed with hot distillated water till reaching the constant pH and then oven-dried at 105 °C for 24 hours.

Due to the variation of adsorbates, diverse solvents were selected as the regenerator. Table 3 shows six different approaches for the regeneration of EGAC. It should be noted that each sub-step of every procedure was done in 2 hours and between each sub-step, the samples were washed with hot distillated water and prepared for the next step.

Table 2. Characteristics of fresh granular activated carbon

Sample	Ash	Iodine Value	Surface Area	Moisture
Activated Carbon	4% Max	1050-1100 mg/g.Min	1050-1100 m^2/g	4% Max

Table 3. Diverse procedures for regeneration of EGAC

SAMPLE	STEP 1	STEP 2	STEP 3	STEP 4
#1	Acid treatment by HCl	Alkali treatment by NaOH		
#2	Washing with ethanol	Acid treatment by HCl	Alkali treatment by NaOH	
#3	Desulfurization by CS_2	Acid treatment by HCl	Alkali treatment by NaOH	
#4	Desulfurization by CS_2	Washing with ethanol	Acid treatment by HCl	Alkali treatment by NaOH
#5	Desulfurization by CS_2	Washing with ethanol	Acid treatment by HF	Alkali treatment by NaOH
#6	Alkali treatment by NaOH	Acid treatment by HCl		

Samples #2, #4 and #5 were washed with ethanol in order to eliminate organic adsorbates. Many organic solvents such as methanol, ethanol, toluene, acetic acid and isopropanol were tested to eliminate the organic pollutants; since ethanol had the best effect on the desorption of organic materials, it was selected as the organic solvent. For the desulfurization step of samples #3, #4 and #5, CS_2 was selected as the effective solvent. In the end, all samples underwent adsorption of MB to find the more effective approach and the maximum adsorption capacity among the samples.

2.4. Adsorption experiments

The effect of temperature and pH on the adsorption of MB by fresh AC was investigated. MB's adsorption increased with increasing temperature, but at higher temperatures, the change was subtler. Also, pH had a direct effect on the MB's adsorption. At a higher pH, higher adsorption occurred. This meant that the higher adsorption of methylene blue occurred in ambient conditions. Because the number of negative adsorption sites increased in comparison with the positive adsorption sites, it caused a higher amount of cationic dye adsorption on the activated carbon absorbents. The optimum pH and temperature for the adsorption of MB were found as pH= 9 and T= 50 ^oC. These conditions were exerted on the adsorption of methylene blue by regenerated AC.

2.5. Calculation of regeneration efficiency

The regeneration efficiency (RE) was defined as the proportion of adsorption capacity of the regenerated activated carbon to the adsorption capacity in the fresh activated carbon:

$$RE = (A_{\text{regenerated AC}} / A_{\text{fresh AC}}) \times 100$$

The adsorption capacities were calculated by a UV-vis spectrophotometer.

3. Results and discussion

3.1. Characterization of adsorbates

The characterization analysis of EGAC showed that it included a high range of organic and inorganic materials. The quantitative results of the EDAX analysis are shown in Figure 1. The results presented that inorganic materials

such as Al, Fe, Si, Ca and S had been adsorbed by activated carbon during wastewater filtration. On the other hand, investigation of the GC analysis results demonstrated that EGAC also included a low range of organic materials.

3.2. Optimum approach

Six approaches were applied to EGAC; the regeneration efficiency (RE) of each procedure was calculated and is shown in Table 4. Sample #1 underwent only acid and base treatment which have been commonly used in older researches in the regeneration of activated carbon and resulted in 75% RE. Sample #1 and its RE were set as the criterion for the subsequent samples. Sample #2 had one more step than sample #1 which included an organic solvent treatment; the effect of the organic solvent on the regeneration of EGAC can be found by comparing the RE of both samples. As shown in Figure 2, ethanol did not have much effect on the regeneration process due to the low amount of organic adsorbates. In the same way, by comparing sample #1 and sample #3, it can be found that the desulfurization step improved the RE to 80%.

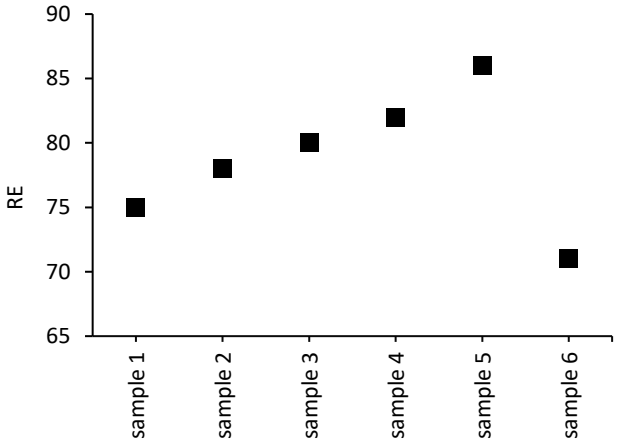

Fig 1. Regeneration efficiency of diverse regeneration methods of activated carbon

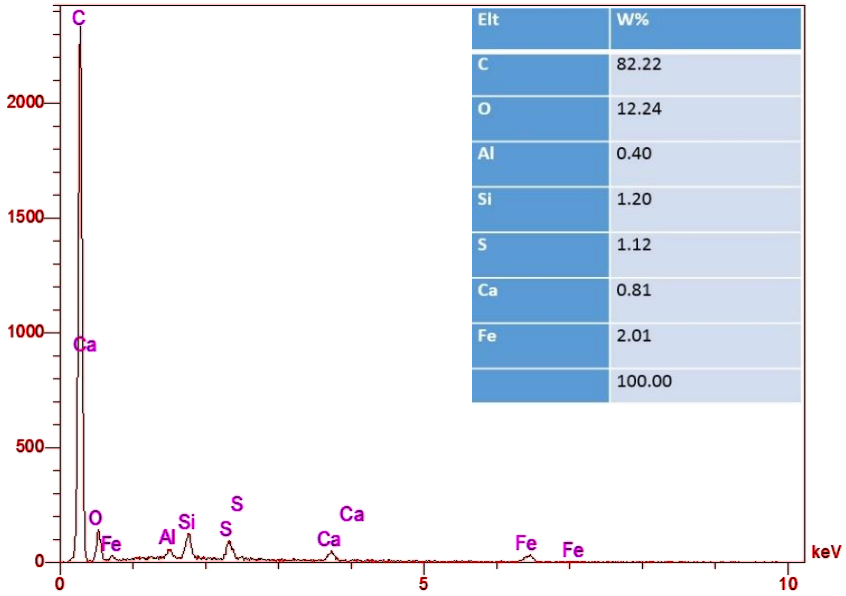

Fig 2. EDAX spectrum of EGAC

Table 4. Results of adsorption of methylene blue, adsorption coefficients and regeneration efficiency

SAMPLE	ADSORPTION COEFFICIENT	AMOUNT OF ADSORBED METHYLENE BLUE (PPM)	RE (%)
FRESH AC	0.074	23.4	100
SAMPLE #1	1.22	17.55	75
SAMPLE #2	1.09	18.25	78
SAMPLE #3	1	1.72	80
SAMPLE #4	0.91	19.18	82
SAMPLE #5	0.72	20.12	86
SAMPLE #6	1.44	16.61	71

Both desulfurization and organic treatment were applied on sample #4, but the same results of previous procedures were obtained. However, by applying desulfurization and organic solvent steps to the acid-base regeneration of AC, the regeneration efficiency was improved by 7%; but by selecting an appropriate acidic, sample #5 was more effective than procedure #4. Sample #5, which used HF for

regeneration, had the highest RE. 86% regeneration efficiency was achieved when HF was used as the acidic regenerator. HF had a better effect than HCl on the desorption and removal of Si compounds which decomposed the silica to form silicon fluoride SiF_4 that was adsorbed by the spent activated carbon. Finally, sample #6 first underwent alkali treatment and then acid treatments were employed. According to Figure 2, it is clear that the relocation of acid and alkali treatments decreased the RE. El-Naas et al. reported 70% regeneration efficiency for chemical regeneration of activated carbon exhausted in petroleum refinery wastewater. They used ethanol, sodium hydroxide and hydrogen peroxide for desorption of only one substrate such as phenol from activated carbon surfaces [21]. Do et al. reported 65% efficiency for regeneration by hydrogen peroxide of the activated carbon exhausted with methyl orange [22]. It should be noted that in the present research, the regeneration of activated carbon exhausted with diverse pollutants was investigated whereas El-Naas et al. and Do et al. just applied chemical regeneration on activated carbon exhausted with a single pollutant.

3.3. Effect of temperature on regeneration process

The regeneration experiments were performed in five temperatures that included ambient temperature, 50 °C, 60 °C, 70 °C and 80 °C. All experiments were done in a water bath while other factors were fixed. Figure 3 shows the effect of temperature on RE. It can be seen from Figure 2 that temperature had a direct effect on the regeneration process. This meant that at higher temperatures, higher desorption occurred. Admittedly, temperature was an indicative for the assignment of physical characteristics of desorption in terms of ambulation of the solvent molecules and viscosity of the solvent. When temperature increased, the ambulation of the solvent molecules also increased and while the viscosity of the solvent decreased, the rate of diffusion of the solvent molecules toward the external boundary layer and subsequent internal pores diffusion was enhanced. Obviously, increasing the temperature more than 80 °C would cause solvent vaporization and therefore, it has been disregarded.

3.4. Effect of solvent's concentration and time on the regeneration process

Figure 4 clearly shows the effect of HF's concentration on the regeneration of EGAC. It can be gathered from Figure 4 that a higher concentration of acid caused a higher RE and while there was an optimum concentration for HF as 3M, a concentration higher than 3M did not influence the regeneration process significantly. However, a higher concentration also decreased RE a bit. The regeneration time had the same effect on RE. This meant that by increasing regeneration time, a higher efficiency was obtained while there was an optimum time for the regeneration process, and holding the regeneration process more than the optimum time caused time, cost and energy consumption. The optimum was signed as 3 hours. Figure 5 shows the effect of time on RE.

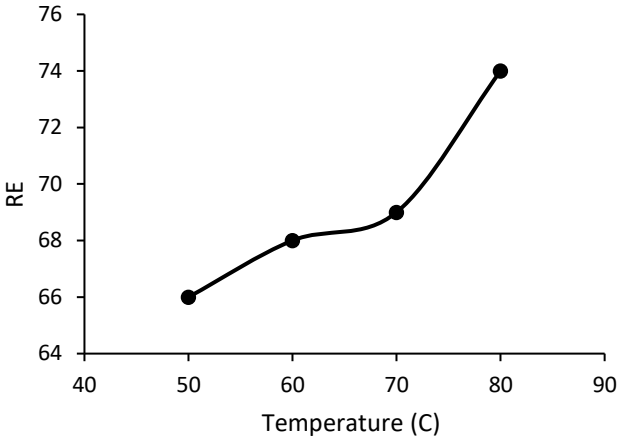

Fig.3. Effect of temperature on regeneration efficiency

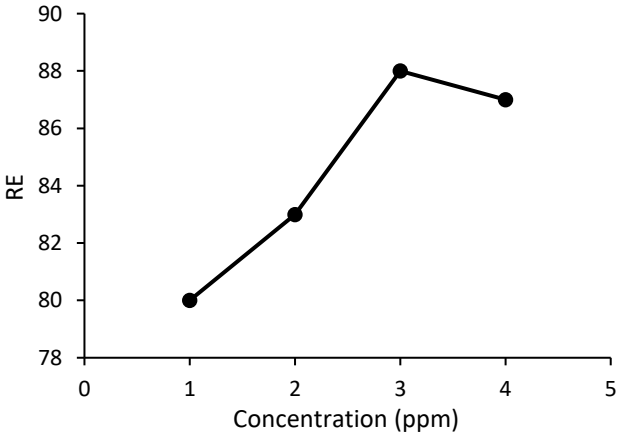

Fig 3. Effect of concentration on regeneration efficiency

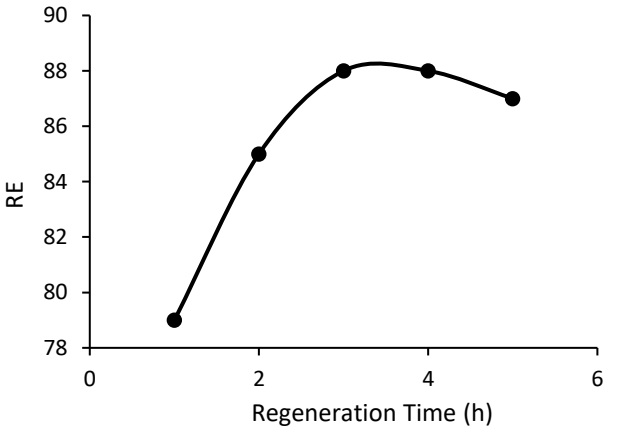

Fig 4. Effect of regeneration time on regeneration efficiency

3.5. Microscopic structure analysis of the activated carbon

The SEM of the spent and the regenerated activated carbon is shown in Figure 6a and 6b. It was taken to observe the surface characters of GAC before and after regeneration. It was clear that the surface of the AC was covered by

pollutants so the pore structure of the AC cannot be clearly seen. After regeneration, impurities were removed from the surface and the pore structure of the AC was visible, as understood from Figure 6b.

3.6. Thermal analysis of activated carbon

Thermal analysis was exerted for the spent activated carbon to investigate the thermal stability of the adsorbates. The thermos gravimetric result of the spent activated carbon is shown in Figure 7.

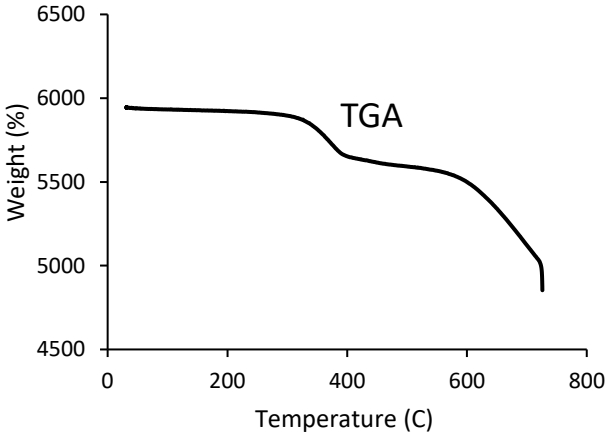

Fig 5. Thermal analysis of spent activated carbon

TGA analysis shows two weight losses within temperatures range of 300–400 °C and 600–700 °C. The first one most probably indicated the desorption of volatile and semi-volatile compounds including organic adsorbates. The second descending shift which occurred between 600 °C and 700 °C could be the result of the decomposition of low volatile compounds. However, metallic salts required a higher temperature including gasification with steam and CO_2. Hence, by comparing the experimental temperatures that were applied in this study and the TGA results, chemical regeneration was more effective than thermal regeneration, as thermal regeneration caused high energy consumption which led to high costs as well as carbon loss.

4. Conclusions

Diverse approaches and solvents were applied to spent activated carbon which was exhausted in a petrochemical waste water unit. The acid-base regeneration method was employed as the regeneration method. However, desulfurization and organic solvent washing procedures were applied to EGAC and it did not significantly affect regeneration efficiency. Hydrofluoric acid was found as the best solvent for regeneration which resulted in 86% regeneration efficiency. The effect of temperature, solvent concentration and regeneration time were investigated. A higher temperature resulted in a higher RE. Solvent concentration and regeneration time had a direct effect on regeneration efficiency. The optimum concentration and time were assigned as 3M and 3 hours, respectively. The SEM results of the regenerated activated carbon indicated that impurities were removed from the activated carbon surface after regeneration. The regenerated activated carbon was used for the adsorption of MB and demonstrated a high adsorption capacity.

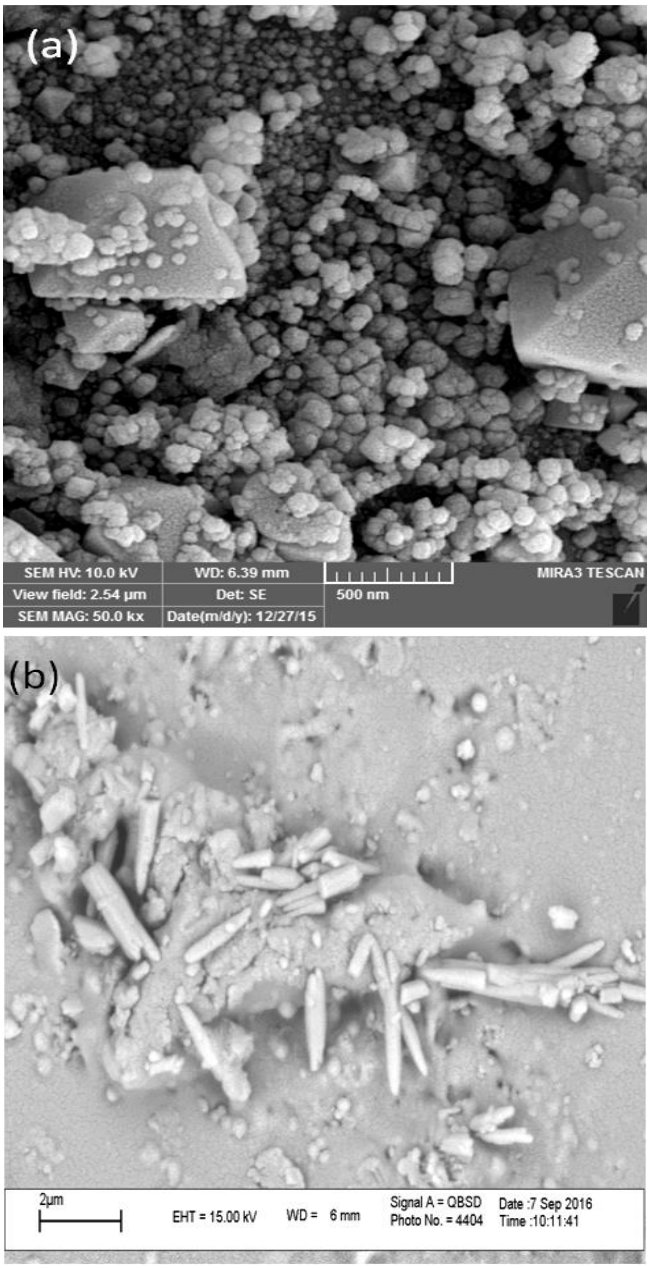

Fig 6. SEM pictures of (a) exhausted and (b) regenerated activated carbon

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