

Chemical Regeneration of Exhausted Granular Activated Carbon Used in Citric Acid Fermentation Solution Decoloration

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ABSTRACT: *An improved chemical regeneration of the granular activated carbon (GAC) exhausted by the color (pigments and pollutants) from citric acid fermentation solution (CAF) was investigated. In the experiments, improved means were adopted to advance the traditional chemical regenerating method and the adsorption capacity of the first time renewed GAC is 103 % of original GAC. Using oxidant and surfactant in addition to just using NaOH solution can recover 10 % more adsorption capacity of renewed GAC. The adding dosage of oxidant is good at 3 % of exhausted GAC weight; that of surfactant is good at 0.1 %. Hot water as cheap reagent was found to be much helpful to the regeneration efficiency. Comparing with steam regeneration high regeneration yield (>95 %) of this method was an attractive economic factor. The result of this investigation can offer an advanced chemical regeneration method to regenerate exhausted GAC from citric acid refine industry.*

KEY WORDS: *Chemical regeneration, Granular activated carbon, Decoloration, Citric acid fermentation.*

INTRODUCTION

Activated Carbon has been broadly used in all kinds of industries such as: Food, Medical, Chemical, Metallurgy, Electronic and Water Treatment etc. because of its special pore structure and superficial surface activated function [1-7]. The powder activated carbon (PAC) has been used in liquid decoloring and refining for decades.

The PAC has some shortcomings, such as: the huge dust, the difficulty of its filtration and regeneration, the whole operation process can deteriorate the environment. While the granular activated carbon (GAC) can overcome those shortcomings still it has well decoloration

capability and can be reused for many times. The dosage used is small and the operation is simple, which make it possible for continuous and automatic production process [8].

Along with the expanding of GAC manufacture and its wide use in many fields, it is necessary to regenerate and reuse the exhausted GAC. It can not only economize the natural resources, reduce the secondary pollution, but also bring along considerable economic profit [9]. In recent years, many scientists have focused on the research of the mechanism and technology of activated carbon regeneration [10]. The most common technique

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Table 1: Characteristics of granule activated carbon supplied by NSTD Co.

| Sample | I ₂ value (mg·g ⁻¹) | MB value (mg·g ⁻¹) | Hardness (%) | Bulk density (g·mL ⁻¹) | Moisture (%) | Ash (%) | S _{BET} (m ² /g) | V(cm ³ /g) | Average pore diameter (nm) |
|--------|--------------------------------------------|--------------------------------|--------------|------------------------------------|--------------|---------|--------------------------------------|-----------------------|----------------------------|
| GAC | 1281 | 255 | 95 | 0.45 | 7 | 2 | 1048.4 | 0.588 | 2.481 |

practiced in regeneration is the thermal volatilization in which adsorbed substances are desorbed by volatilization and oxidation at high temperature [11]. This thermal regeneration technique is characterized by the loss of carbon (10-15 %) due to oxidation and attrition, and by the cost of energy in treating the carbon to around 800-900 °C [12]. An alternative technique is that of chemical regeneration in which chemical reagents are applied to the exhausted carbon. Traditionally, acid and alkali solutions are used to dissolve the adsorbate, so that recover the ability of adsorption of activated carbon.

In the present study, GAC exhausted with pigments and pollutants of citric acid fermentation was used as tested material. The influences of regenerating reagents on the efficiency of regeneration were discussed. NaOH solution, hot water, oxidant and surfactant were selected as regeneration reagents during the procedure.

EXPERIMENTAL

Materials

Wooden GAC supplied by NSTD Co. (China) was used for all the experiments. The carbon was sieved (ASTM Mesh No.30×40) and washed before it was used. Its characteristics according to the manufacturer are shown in table 1.

CAF supplied by BBKA Group (China) was selected as tested solution. All of the reagents used were of analytical grade and all the solutions were prepared with distilled water.

Color of original CAF liquor and filtrate liquor were measured using a 722 UV/Vis spectrophotometer. The UV wavelength is fixed at 426 nm according to previous research.

Method

The exhaustion of the GAC was carried out by mixing CAF liquor and GAC together for 72 h on a shaker. Preliminary study [13] showed that this period of time was more than sufficient to ensure adsorption equilibrium. After exhaustion, the GAC was filtrated and

washed with distilled water subsequently dried at 105 °C for 2 h, then stored in desiccator.

The regeneration procedure of the exhausted GAC was as follows. Measuring one unit of exhausted GAC mixed with NaOH solution in a 250 mL glass conical flask, kept the flask and its contents in water bath at constant temperature, termly agitating. After equilibrium, the solution was decanted leaving the wet GAC which was washed by 150 mL hot water, and then immersed in oxidant or surfactant solution at room temperature. Using dilute hydrochloric acid to adjust the pH of GAC to neutral before drying at 105 °C to acquire renewed adsorbent. Compare the adsorptive capacity of regenerated GAC with original GAC by decoloring CAF liquor and calculating the regeneration efficiency.

Calculation of regeneration efficiency

The regeneration efficiency is judged on the extent that it recover the adsorption capacity of the GAC. The following method of calculation was employed to quantify the recovery rate [11].

The regeneration efficiency is signed as RE %. The original adsorption capacity (A₀) of the GAC for a particular adsorbate was deemed to be that the quantity of adsorbates adsorbed from solution by per unit weight of GAC at the end of contact. The adsorption capacity of the regenerated GAC (A_r) was deemed to be that quantity of the same adsorbates adsorbed from solution per unit weight of regenerated GAC at the end of contact.

$$\text{Eq. A RE \%} = (A_r / A_0) \times 100 \%$$

RESULTS AND DISCUSSION

Influence of NaOH solution concentration

The main purpose of using activated carbon to refine CAF liquor is to remove the color (pigments and organic pollutants) such as: protein, colloid, bacterial metabolized substance which must be eluted during the regeneration process. NaOH can weaken the van der Waals force between the adsorbate and micropore surface, undermine the chemical bond between adsorbate and surface

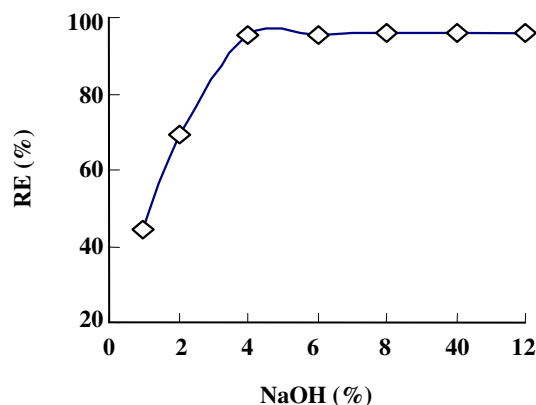


Fig. 1: Influence of NaOH on regeneration efficiency.

functional groups, so that pigments and organic pollutions can be eluted. In addition, NaOH can make most organic pollutants into soluble salt which is easily ionized in water so that the micropore surface of exhausted GAC was cleaned [11]. First 7 units of 1g exhausted GAC were placed into 100ml glass conical flasks separately, subsequently measured volume (25 mL) of NaOH solution with concentration of 1 %, 2 %, 4 %, 6 %, 8 %, 10 % and 12 % were added. The flasks were bathed in 90 °C water for 4 h, while solution-carbon mixture were stirred in the flasks. Then the fluid was filtered to remove any particles. The absorption (ABS) value of filtrate solution was measured with UV/Vis spectrophotometer. The bigger of the ABS value of filtrate solution, the more color were washed out, which means regeneration efficiency is higher. NaOH solution can affect the characteristics of the activated carbon surface significantly, big alkaline solution concentration can give higher regeneration efficiency for these color. It would therefore be seen from Fig. 1 that the 4 % NaOH solution is sufficient in the experiments, more NaOH can not contribute to get higher regeneration efficiency. The results would suggest that 4 % alkaline solution contained enough NaOH to regenerate the carbon at a reasonable efficiency and that interference from the water phase was sufficient to prevent greater efficiency.

Influence of temperature and time

Adsorbate desorption is a process of decalescence. Higher the temperature is, faster desorption rate will be. High temperature can fasten the pervasion rate of regeneration reagents in the micropore so that desorption

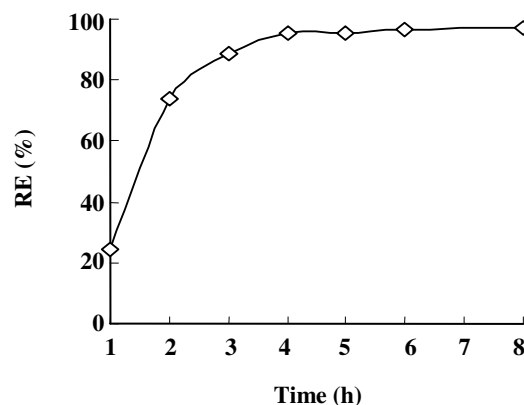


Fig. 2: Influence of time on regeneration efficiency.

efficiency will be enlarged [14]. According to the energy cost and previously work [13], the testing temperature was as 90 °C. 7 units of 1 g exhausted GAC were placed into seven 100 mL glass conical flasks separately, subsequently measured volume (25 mL) of 4 % NaOH solution were added and worked under temperature of 90 °C for 1, 2, 3, 4, 5, 6 and 8 h separately, while solution-carbon mixture were stirred in the flasks. Then the fluid was filtered to remove any particles. ABS value of filtrate solution was measured with UV/Vis spectrophotometer. Results see Fig. 2. The bigger of the ABS value of filtrate solution, the more color were washed out, which means regeneration efficiency is higher. It was observed that 4 h is the optimal time, little would be gained, in terms of regeneration efficiency by further increasing time. Since the interphase mass-transfer coefficient is a hydrodynamic property, the regeneration may be influenced by the transfer rate at fixed temperature. But more time over 4 hours can not get higher regeneration efficiency.

Influence of oxidant and its dosage

After NaOH regenerating, there are still some adsorbates left on the inside surface of micropore and hardly departed. Normally, the first time regeneration efficiency is around 90 %. The selected oxidant as a reactive reagent can modify adsorbate surface polarity and increase its solubility in the aqueous solution, so regeneration efficiency was raised. Measuring 7 units 1 gram of exhausted GAC mixed with 25 mL 4 % NaOH solution in 7 flasks separately, bathing in 90 °C water for 4 h, agitating. Adding 0.01, 0.02, 0.03, 0.04, 0.05, 0.06 gram oxidant separately into the above flasks, boiling for

Table 2: Compare of different methods on regenerating saturated GAC.

| Sample | Regeneration methods | Regeneration efficiency (%) | Yield (%) |
|-------------------|-------------------------------------------------------|-----------------------------|-----------|
| GAC1 [#] | alkali treatment | 90.3 | 95.6 |
| GAC2 [#] | washing+ alkali treatment | 93.2 | 95 |
| GAC3 [#] | washing+ alkali treatment+ oxidant+ surfactant | 103.2 | 95 |
| GAC4 [#] | washing + alkali treatment + oxidant +surfactant+ HCl | 103.2 | 94 |
| GAC5 [#] | steam regeneration (900 °C) | 95 | 78 |

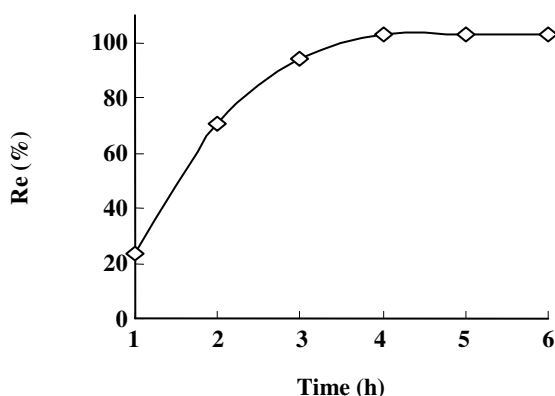


Fig. 3: Influence of oxidant dosage on regeneration efficiency.

10 mins followed by filtrating and measuring the ABS value of the filtrate liquids. Results see Fig. 3. Oxidant acted as regeneration assistant reagent to clean some adsorbates which adhered hardly to the surface of activated carbon. The results can be seen from Fig. 3 that 0.03 g (3 % of GAC weight) is optimal oxidant dosage. Addition of more oxidant can not get higher efficiency

Dosage of surfactant determine

Surfactant has power of surface activation, emulsification, and decentralization etc. which can mostly reduce the attaching force between the color (pigments and organic pollutions) and the surface of micropore. With mechanical stirring, color can easily enter into the aqueous solution, so regeneration efficiency increase. Surfactant is selected as regeneration assistant reagent, but it can also tend to adsorb on the activated carbon, leading to pore blockage that hinders desorption, so the oxidant dosage just need 0.1 % of the weight of exhausted GAC to get sufficient regeneration efficiency.

Comparing different regeneration procedure and efficiency

Measure 4 units weight of 2 gram of exhausted GAC,

which are signed GAC1#, GAC2#, GAC3# and GAC4# as starting material for regenerating process. GAC1#1 was regenerated with 4 % NaOH solution; GAC#2 was regenerated with 4 % NaOH solution followed by hot water washing; GAC3# was regenerated by adding oxidant and surfactant base on the process of GAC2#; GAC4# was regenerated with acid washing process based on process for GAC3#. Results of regeneration process are shown in table 2. It can be seen from the data, regeneration efficiency of GAC3# is perfect good, and the step of acid washing can not raise the efficiency further.

Regeneration efficiency is 90 % only use NaOH solution, but add oxidant and surfactant agents, the efficiency of first regeneration cycle can reach to 90-103 %. Because oxidant has oxidization power to open the block micropores and remove the surface function groups of GAC, which may block the adsorption to color, so value of first regeneration cycle can even exceed 100 %. After regeneration with NaOH solution, hot water, oxidant and surfactant, the regeneration result is much good, so acid washing is only for adjusting pH to neutral

Comparing regeneration yield with steam regeneration

Regeneration yield is an important economic factor of regeneration process. Thermal (steam) regeneration is a common use method but the disadvantage is the low yield. The method in this paper can get 95 % yield which is much higher than that of steam regeneration (78 %).

CONCLUSIONS

The results of above research showed that during the chemical regeneration process of GAC exhausted by CAF liquid, hot water washing, oxidant and surfactant working can raise the regeneration efficiency on the base of conventional acid-alkali regenerating. And this method can get 95 % regeneration yield which is much higher

than that of steam regeneration (78 %), so the method is worthy for exhausted GAC regenerating industry.

Exhausted GAC being washed with hot water before directly chemical regeneration is good for raising regeneration efficiency and even getting 3 per cents more than just using NaOH solution.

Oxidant can oxidate and remove the color remained in the micropores, thus increasing the efficiency. In addition, oxidant can get rid of surface function groups of GAC that can explain the renewed GAC get higher adsorption ability than original GAC.

Selected surfactant can enhance solubility of pigment and organic pollution in water, but the dosage used is limited below 0.1 % of the weight of exhausted GAC because the over surfactant also tend to adsorb on the surface outside the GAC, leading to pore blockage that hinders desorption.

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