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DECOLORIZATION AND CHEMICAL REGENERATION OF GRANULAR ACTIVATED CARBON USED IN CITRIC ACID REFINING

Kang Sun*, Jian-chun Jiang and Jun-ming Xu

Institute of Chemical Industry of Forest Products, CAF, Nanjing 210042, China

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ABSTRACT. Citric acid fermentation (CAF) liquor decolorization by granular activated carbon (GAC) was studied and an improved chemical regeneration method of the exhausted GAC by the color of CAF liquor was investigated. The effects of the GAC dosage, time and temperature on the decoloring efficiency (DE %) were studied. The DE % of the original GAC was 91 %. The regeneration efficiency (RE %) using chemical regents was 104 % of the original GAC. Hot water as cheap reagent was found to be much helpful to the regeneration efficiency. 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 %. Comparing with steam regeneration method, high regeneration yield (> 95 %) of chemical method was an attractive economic factor. The results of this investigation can be as helpful reference for citric acid manufacturer expanding profits.

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

INTRODUCTION

Citric acid is an important chemical product which wildly used in the food and pharmaceutical industries. Today, essentially all of the commercial citric acid is produced by fermentation using a variety of substrates including sucrose, molasses, corn syrup, and enzyme-treated starch. Color as a key quality parameter of citric acid makes it necessary for producer to control the color of the product.

Activated carbon has been used in liquid decoloring and refining for decades because of its special pore structure and superficial surface activated function [1-7]. The powder activated carbon (PAC) decoloring process is batch operation and has to be filtered to remove exhausted carbon. The decoloring process with PAC uses as much as 10-20 g/L of liquid, which increases production costs.

Granular activated carbon (GAC) has been used in continuous and automatic decoloring process. The advantage of GAC is that it can be regenerated, thus decreasing the amount of solid residue, and they allow the process to be carried out in a continuous mode [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 [9-10]. The most common technique 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 ^{o}C. 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 to recover the ability of adsorption of activated carbon.

In the present study, GAC is used to adsorb pigments and pollutants of CAF liquor and the influences of GAC dosage, time and temperature on adsorption efficiency were studied.

*Corresponding author. E-mail: jacky.sunkang@hotmail.com; Fax: +86 25 85482485

The exhausted GAC was renewed by chemical method and the influences of several regenerating reagents on the efficiency of regeneration were discussed. NaOH solution, hot water, oxidant and surfactant were selected as regeneration reagents during the procedure. The results of this investigation can be as helpful reference for citric acid manufacturer expanding profit.

EXPERIMENTAL

Materials

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

Table1. Characteristics of granular activated carbon supplied by NSTD Co.

Sample	I_2 value ($mg \cdot g^{-1}$)	MB value ($mg \cdot g^{-1}$)	Hardness (%)	Bulk density ($g \cdot mL^{-1}$)	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

The CAF liquor supplied by BBCA Group (An hui, China) was selected as test 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 wavelength was fixed at 426 nm according to previous research [12].

Procedures

Adsorption process. Batch operations were done to determine the decoloring capacity of the GAC. The glass flasks containing a volume of CAF liquor and a dose of GAC was placed on a shaker and agitated for a period of time. Preliminary study [12] 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 ^oC for 2 h, then stored in desiccator for regeneration operation.

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 which bathed in water. After equilibrium, the GAC was filtrated and washed by hot water, and then immerged in oxidant or surfactant solution at room temperature. Using dilute hydrochloric acid to adjust the pH of GAC to neutral before drying at 105 ^oC 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 decoloring efficiency. The decoloring efficiency DE (%) is used to determine the decoloring capacity of GAC. Equation (1) was employed to quantify the DE (%). The absorbence of original liquor was taken as A_0 and that of filtrate was taken as A.

$$DE (\%) = (A_0 - A)/A_0 \times 100 \% \quad (1)$$

Calculation of regeneration efficiency. The regeneration efficiency is judged on the extent that it recovers the adsorption capacity of the GAC. The following method of calculation was employed to quantify the recovery efficiency [13].

The regeneration efficiency is expressed as RE % (equation 2). The original adsorption capacity (A_0) 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.

$$RE \% = (A_r / A_0) \times 100 \% \qquad (2)$$

RESULTS AND DISCUSSION

Decoloring efficiency of GAC

Decoloring capacity of GAC. GAC has been used for decolorization of sugarcane juice [14] and distillery wastewater [15]. Hence, its utility as decoloring agent for citric acid fermentation appeared feasible. Color of fermentation (such as CAF) liquor is mainly due to the presence of melanoidins, caramel, alkaline degradation products and polyphenols. The liquor decoloring mechanism of GAC was complex and the effect factors on adsorption process include adsorbent dosage, time and temperature.

Effect of dosage on decoloring. The decoloring efficiency of GAC was increased with dosage increasing. The decoloring efficiency was studied by taking 8 units of 0.015 g, 0.045 g, 0.075 g, 0.09 g, 0.1 g, 0.12 g, 0.135 g, 0.15 g GAC into 8 glass conical flasks separately, subsequently measured volume (50 mL) of CAF liquor in the above flasks. Measured another 50 mL CAF liquor into an empty flask as control sample. The 9 flasks were placed on a shaker for 72 h. Then the slurries were filtered to remove any particles. Absorbance of filtrate solution was measured with UV/Vis spectrophotometer. Effect of dosage on decoloring efficiency is shown in Figure 1.

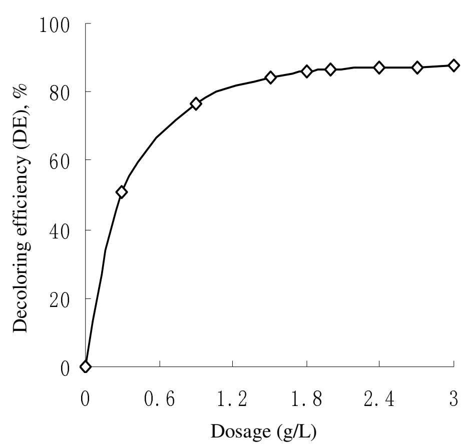

Figure 1. Effect of dosage on decolorization efficiency.

The results in Figure 1 shows that DE % increased with GAC dosage increasing. But when dosage is more than 2 g/L, the DE % does not change further. It was that when sufficient GAC was added, the adsorption behavior will reach equilibrium and concentration of adsorbate is equal in solution and outside surface of GAC. So in this test, 0.1 g GAC is enough for 50 mL CAF liquor decoloring (i.e. 2 g GAC per 1000 mL of CAF liquor).

Influence of temperature on decoloring. It was known that the effect of ambient temperature on adsorption rate is geometric series. High temperature decreased viscosity of liquor, so color molecules can move quickly into pores of adsorbent. On other hand, from the thermodynamics point of view, the high temperature is not good for adsorption because the adsorption behavior is exothermic reaction.

Decoloring test was conducted at different temperature, 25, 40, 60, 80 and 90 ^{o}C for 72 h. The results are shown in Figure 2.

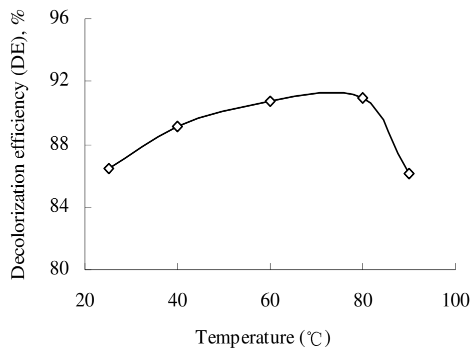

Figure 2. Effect of temperature on decolorization efficiency.

From Figure 2 it can be seen that increasing the temperature increases DE %, but temperature over 80 ^{o}C brings obvious drop of DE %. Because much high temperature can fasten desorption rate, so optimal temperature for CAF liquor decoloration is 60-70 ^{o}C.

Effect of contact time on decoloring. Contact time is a key factor of test, reaction usually increase with increasing time. Experiments were conducted at different time (5, 10, 15, 20, 30, 40 and 60 min) with 0.1 g treating 50 mL CAF liquor. Results are given in Figure 3. When test was conducted for 48 h, color in CAF liquor was adsorbed adequately and DE % reached 91.1 %. Extending test time over 48 h does not bring corresponding increase in DE % but just 0.7 % which means the GAC was saturated. To ensure an adequate adsoprtion time in the test, a period of 72 h was recommended.

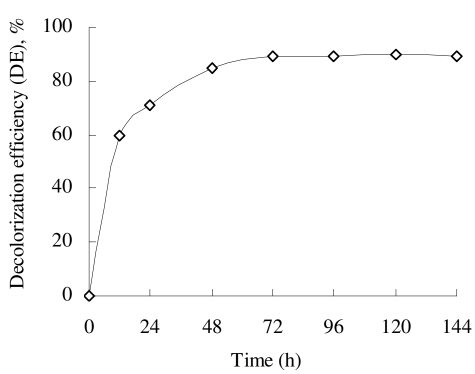

Figure 3. Effect of adsorption time on decolorization efficiency.

Regeneration efficiency of exhausted GAC

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 functional groups, so that pigments and organic pollutions can be eluted. In additional, NaOH can make most organic pollutants into soluble salt which is easily ionized in water so that the micropore surface of exhausted GAC get cleaned [13]. This was done as follows: first 7 units of 1 g exhausted GAC were placed into 100 mL 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 ^{o}C water for 4 h, while solution-carbon mixture were stirred in the flasks. Then the supernatant was filtered to remove any particles. The absorbance of filtrate solution was measured with UV/Vis spectrophotometer. The higher the absorbance of filtrate solution, the more color was washed out, which means regeneration efficiency is better. NaOH solution can affect the characteristics of the activated carbon surface significantly. Higher alkaline solution concentration can give higher regeneration efficiency for the color removal. It can be seen from Figure 4 that 4 % NaOH solution is sufficient for the regeneration. More NaOH can not contribute to get higher regeneration efficiency. The results 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.

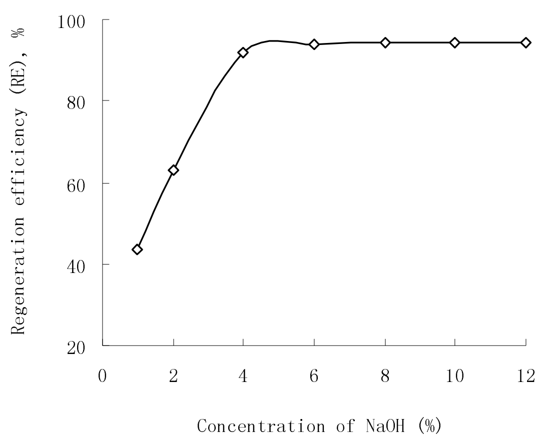

Figure 4. Influence of NaOH on regeneration efficiency.

Influence of temperature and time. Adsorbate desorption is a process of decalescence. Higher the temperature faster the desorption rate will be. High temperature can fasten the pervasion rate of regeneration reagents in the micropore so that desorption efficiency will be increased [16]. According to the energy cost and previous work [12-13], the testing temperature was as 90 ^{o}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 ^{o}C for 1, 2, 3, 4, 5, 6 and 8 h separately, while solution-carbon mixture were stirred in the flasks. Then the supernatant was filtered to remove any particles. The absorbance of filtrate solution was measured with UV/Vis spectrophotometer. Results are shown in Figure 5. The higher the absorbance 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, there was no increased in regeneration efficiency by further increase in time. Since the inter-phase 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.

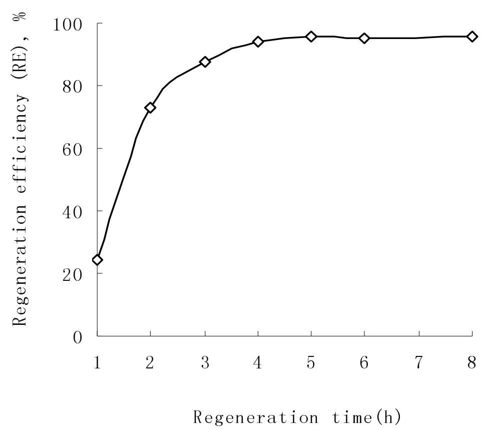

Figure 5. Influence of time on regeneration efficiency.

Influence of oxidant and its dosage. After NaOH regeneration, 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. This was done by measuring 7 units 1 gram of exhausted GAC mixed with 25 mL 4 % NaOH solution in 7 flasks separately, bathing in 90 ^oC water for 4 h, agitating. Adding 0.01, 0.02, 0.03, 0.04, 0.05, 0.06 g oxidant separately into the above flasks, boiling for 10 min followed by filtrating and measuring the absorbance of the filtrate liquids. Results are shown in Figure 6. Oxidant acted as regeneration assistant reagent to clean some adsorbates which adhered hardly to the surface of activated carbon. It can be seen from Figure 6 that 0.03 g (3 % of GAC weight) is optimal oxidant dosage. Addition of more oxidant can not give higher efficiency.

Dosage of surfactant. 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.

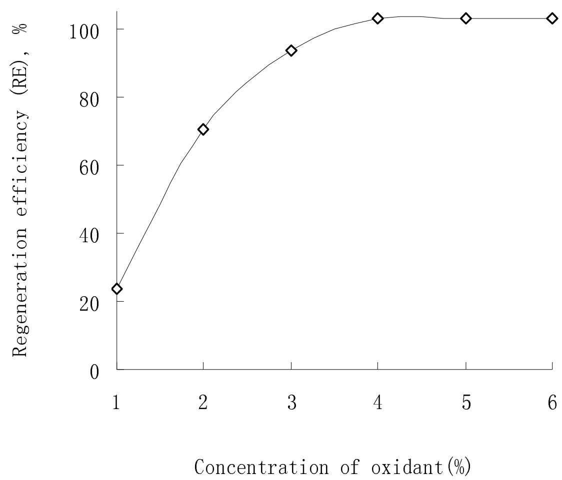

Figure 6. Influence of oxidant dosage on regeneration efficiency.

Comparing different regeneration procedure and efficiency. Four units weight of 2 g of exhausted GAC, which are named as GAC-1, GAC-2, GAC-3 and GAC-4 were used as starting material for regenerating process. GAC-1 was regenerated with 4 % NaOH solution; GAC-2 was regenerated with 4 % NaOH solution followed by hot water washing; GAC-3 was regenerated by adding oxidant and surfactant base on the process of GAC-2; and GAC-4 was regenerated with acid washing process based on process for GAC-3. Results of regeneration process are given in Table 2. It can be seen from the data that regeneration efficiency of GAC-3 is optimum and the step of acid washing can not raise the efficiency further.

Table 2. Comparison of different methods on regenerating saturated GAC.

Sample	Regeneration methods	Regeneration efficiency (%)	Yield (%)
GAC-1	Alkali treatment	90.3	95.6
GAC-2	Washing + alkali treatment	93.2	95
GAC-3	Washing + alkali treatment + oxidant + surfactant	103.2	95
GAC-4	Washing + alkali treatment + oxidant + surfactant + HCl	103.2	94
GAC-5	Steam regeneration (900 ºC)	95	78

Regeneration efficiency is only 90 % when NaOH solution is used, but when oxidant and surfactant agents are added, the regeneration efficiency can reach to 95-103 %. 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 regeneration value can even exceed 100 %. After regeneration with NaOH solution, hot water, oxidant and surfactant, the regeneration result is much better, so the acid washing is only for adjusting the pH to neutral.

Comparing regeneration yield with steam regeneration. Regeneration yield is an important economic factor of regeneration process. Thermal (steam) regeneration is a commonly used 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

(1) The results of above research showed that GAC from NSTD Co. (China) can be a good decoloring agent for CAF liquor. The optimal decoloring efficiency (DE %) can reach up to 91 %. (2) The optimal temperature for CAF liquor decoloration is 60-70 ^{o}C, a period of 72 h was recommended to ensure an adequate adsoprtion time in the decoloring test. (3) Results of the chemical regeneration process of GAC exhausted by CAF liquid, hot water washing, oxidant and surfactant working can raise the regeneration efficiency over the conventional acid-alkali regeneration. The proposed 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. (4) Exhausted GAC being washed with hot water before chemical regeneration is good for raising regeneration efficiency and even getting 3 % more than just using NaOH solution. (5) Oxidant can oxidize 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. (6) 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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