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Preparation of sludge-based activated carbon and its application in dye wastewater treatment

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Abstract

A novel activation process was adopted to produce highly porous activated carbon from cyclic activated sludge in secondary precipitator in municipal wastewater treatment plant for dye removal from colored wastewater. The physical properties of activated carbon produced with the activation of 3 M KOH solution in the atmosphere of steam were investigated. Adsorption removal of a dye, Acid Brilliant Scarlet GR, from aqueous solution onto the sludge-based activated carbon was studied under varying conditions of adsorption time, initial concentration, carbon dosage and pH. Adsorption equilibrium was obtained in 15 min for the dye initial concentration of 300 mg/L. Initial pH of solution had an insignificant impact on the dye removal. Results indicated that 99.7% coloration and 99.6% total organic carbon (TOC) were removed after 15 min adsorption in the synthetic solution of Acid Brilliant Scarlet GR with initial concentration of 300 mg/L of the dye and 20 g/L activated carbon. The Langmuir and Freundlich equilibrium isotherm models fitted the adsorption data well with $R^2 = 0.996$ and 0.912, respectively. Accordingly, it is concluded that the procedure of developing activated carbon used in this study could be effective and practical for utilizing in dye wastewater treatment.

Keywords: Activated carbon; Activated sludge; Adsorption; Acid Brilliant Scarlet GR

1. Introduction

Activated sludge has been employed to treat a wide variety of wastewaters, and over 90% of the municipal wastewater treatment plants use it as the core part of the treatment process [1]. Due to the rapid urbanization and implementation of higher standards for effluent in many countries in recent decades, the activated sludge, unavoidable by-product generated in typical secondary municipal sewage treatment, is being produced in an ever increasing amount. The sludge production is too high to be disregarded, and handling, treatment and disposal of this solid waste account for 25–65% of the total operating cost of a secondary treatment plant [2]. Traditional disposal routes include landfill, incineration, reutilization as construction materials [3] and application to farm and forest lands as manure. All these disposal methods have some limitations such as occupying valuable landfill sites or having some degrees of environmental impact. Therefore, there is a need to seek a cost-effective, environmentally sound and innovative alternative to sludge disposal.

Activated carbon is widely used in decontamination of air and wastewater. Its effectiveness in removing pollutants has been found to be superior to many other methods because of the high quality of the effluent achieved, simplicity of design, ease of operation and insensitivity to toxic substances [4]. Despite the prolific use of this adsorbent, it continues to be an expensive treatment process for large-scale application. Therefore, many efforts have been made to produce activated carbons from a range of residues, such as waste newspaper [5], waste tires [6] and a vast number of agricultural by-products [7,8]. There are basically two methods for manufacturing activated carbons, i.e. physical and chemical activation [9]. Physical activation consists of two steps, the carbonization of a carbonaceous precursor below 1073 K under an inert atmosphere and thereafter the activation of the resulting product at upper temperature with activating agent such as CO_2, steam or air [10]. The most widely

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used activating gas is steam because for a given temperature, the activated carbon produced with steam has larger adsorptive capacity and wider pore size distribution than that produced with CO_2 [11]. In the chemical activation process, however, these two steps proceed simultaneously by carrying out thermal decomposition of the raw material impregnated with certain chemical agent such as phosphoric acid [12,13], sulfuric acid [10,14], potassium hydroxide [9,15,16] or zinc chloride [4,17] in an inert atmosphere. These impregnants are used as dehydrating agents and oxidants that influence pyrolytic decomposition and inhibit formation of tar, thus enhancing the yield of carbon [9]. Some authors have studied the combination of these two methods [18,19] to obtain activated carbon with specific surface properties.

Because of carbonaceous structure and richness in organic materials, activated sludge is potentially suitable for the production of activated carbon. Tay et al. [17] tested different source materials and showed that by $ZnCl_2$-chemical activation at heating temperature of 650 °C for 2 h, the activated carbon made from undigested sewage sludge had higher BET surface area (541.7 m^2/g) and a better adsorption performance in phenol removal than that made from anaerobically digested sewage sludge. Martin et al. [14] showed that the activated carbon produced from surplus sewage sludge pyrolyzed at 700 °C under nitrogen atmosphere in the presence of H_2SO_4 was mainly mesoporous in nature, with a surface area of 253 m^2/g and an average pore diameter of 2.3 nm. It was superior in the adsorption of anionic-type dyes in solution, but poor in the removal of Basic Red 46 compared with a commercial activated carbon. For sewage sludge, zinc chloride and sulfuric acid are generally used as activating agents in chemical activation [20].

There are few reports relating to the production of activated carbon from sewage sludge by KOH activation. Moreover, almost all sludge-based activated carbons produced by chemical activation were pyrolyzed under nitrogen atmosphere. However, this purge gas is expensive and merely shields the product from air. The technique of pyrolyzing KOH-impregnated sludge in steam in a single step has the potential to reduce the cost of the process and further improve the adsorptive properties of the activated carbon.

In this work, potassium hydroxide has been chosen as activating agent. The difference from the normal chemical activation process is the replacement of flow gas N_2 by steam during the pyrolysis stage. The merit of this modification is that steam acting as an oxidant in high temperature can assist KOH to produce and/or widen micropores and mesopores in the activation process. The adsorption performance of the activated carbon generated by a novel activation process for dye adsorption was assessed. Isothermal adsorption equilibrium data for the adsorption of Acid Brilliant Scarlet GR by the produced activated carbon were determined and modeled. The influences of adsorption time, initial concentration, carbon dosage and solution pH on dye adsorption were also investigated to seek an optimum condition to improve the adsorption effectiveness of activated carbon produced.

2. Experimental

2.1. Production of activated carbon

The activated sludge used as raw material for the production of activated carbon was obtained from the secondary precipitator in the wastewater treatment plant of Minhang district, Shanghai. The characteristics of the sludge are presented in Table 1. The volatile suspended solids (VSS) content is 11.4 g/L in the sludge, and the ratio of VSS to total suspended solids (TSS) is 71.6% by weight. It can thus be deduced that the activated sludge would mainly contain organic materials if dried, which would have potential to produce the activated carbon with good adsorption properties.

The raw sludge was first dewatered by centrifugation. Then it was dried in a vacuum oven at 105 °C to constant weight and subsequently crushed and sieved into a uniform size of less than 1 mm. The resulted granular particles were then impregnated with a 3 M KOH solution (M/V = 1:2.5) for 24 h at room temperature. After the supernatant liquid was removed, the sample was subjected to heating at 105 °C to a constant weight. The sludge was subsequently crushed again into a fine powder, which is designated as sludge powder (SP).

Fifteen grams of SP was pyrolyzed in a heating tube furnace (SK2-2-10, Changcheng Industrial Furnace Plant in Shen Yang Province) with steam as purge gas. The heating temperature increased at 40 °C/min and the final heating temperature was 600 °C. The dwell time at the final temperature was 1 h and the steam flow was maintained at 300 cm^3/min. Following pyrolysis, the product was rinsed 10 times with 50 mL deionized water to remove residual potassium hydroxide and inorganic matters in it and subsequently dried to a constant weight for use. Fig. 1 shows a schematic diagram of the experimental apparatus used in the activation process. The final product yield, determined gravimetrically, was about 41.8%.

2.2. Characterization of activated carbon

The iodine number for the produced activated carbon was determined according to the procedure established by the American Society for Testing Materials (ASTM) [21] to evaluate its adsorption capacity. The surface area and pore structure of the activated carbon were determined using a surface area analyser (ASAP2010 M + C, Micromeritics Instrument Corp., USA). The surface physical morphology of the activated carbon was observed by a scanning electron microscopy (S-2150, Hitachi High-Technologies Corp., Japan).

Table 1
Properties of the activated sludge used for this study

Property	Value
pH	5.65
Solid content (wt.%)	1.59
VSS/TSS (wt.%)	71.6
VSS (g L^{-1})	11.4

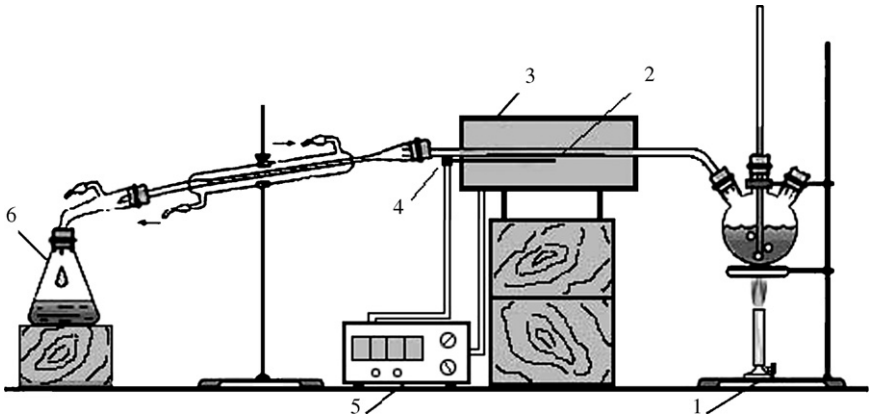

Fig. 1. Schematic diagram of the experimental apparatus for activation. (1) Steam generator, (2) activated sludge sample, (3) heating tube furnace, (4) thermocouple, (5) temperature controller and (6) gas collection trap.

2.3. Adsorption study

To estimate the applicability of produced activated carbon as an adsorbent for dye wastewater treatment, Acid Brilliant Scarlet GR was used as the adsorbate in this study. Solutions with different initial concentrations of the adsorbate ranging from 50 to 500 mg/L were prepared. Known amounts of activated carbon produced were placed in a 500 mL sealed flask and 100 mL of the synthetic dye solution was added. After shaking the flasks in a mechanical shaker (QYC 211, Shanghai Fuma Laboratory Instrument Co. Ltd.) at a rolling speed of 150 rpm at a constant temperature of $25 \pm 2\,^{\circ}C$, the activated carbon was separated from solution by filtration and the concentration of Acid Brilliant Scarlet GR remaining in solution was measured using VIS adsorption (Shimadzu UV-2450PC UV/VIS Spectrophotometer) at 510 nm. Total organic carbon (TOC) content of the solution was analysed in a TOC/TN Analyser (Analytik Jena AG multi N/C 3000). The pH of the initial dye solution was not adjusted with HCl or NaOH except for the study on the effect of pH on the dye removal.

3. Results and discussion

3.1. Characteristics of the sludge-based activated carbon

The characteristics of the activated carbon resulting from the pyrolysis of activated sludge with 3 M KOH solution in the presence of steam are shown in Table 2.

Table 2 shows that the total pore volume and micropore volume of the activated carbon are 0.25 and 0.11 cm^3/g, respectively. The specific surface area of dried sludge is generally about 3 m^2/g [10,14]. The corresponding value reported in Table 2 for sludge-based activated carbon shows that the evolution of organic matter during pyrolysis results in a clear improvement in the surface area of the adsorbent, from about 3 m^2/g for the raw sludge to a value of around 382 m^2/g for the product. However, the activated carbon produced has a lower specific surface area than most commercially available activated carbons, which typically have specific surface area of about 400–1500 m^2/g [22]. The lower specific surface area of the produced activated carbon is related to the little microporosity present, which is primarily attributed to the properties of the precursor. The average pore diameter (d) of the produced activated carbon is 5.62 nm, indicating that the activation process mainly developed mesopores ($2\,nm < d < 50\,nm$) in the activated carbon [18].

The iodine number of the sludge-based activated carbon was 563.10 mg/g, which is similar to the iodine number of activated carbon prepared by Martin et al. [14]. Iodine number is an alternative indication of the porosity of activated carbon. The adsorption of aqueous I_2 is considered a simple and quick test for evaluating the surface area of activated carbon associated with pores with $d > 1$ nm [23]. Multiplication of the iodine number shown in Table 2 by the liquid molar volume of I_2, 68 cm^3/mol, would give the maximum volume accessible for the adsorption of I_2 from the liquid phase [24]. This value was calculated to be 0.15 cm^3/g, which is smaller than the total pore volume, indicating that in the produced activated carbon part of the micropores that make up the structure are not accessible to the iodine molecule in aqueous solution.

The surface of the dried sludge and activated carbon obtained was observed using scanning electron microscopy (SEM) as shown in Fig. 2. The structure of the raw sludge is very dense and there are almost no micropores in it (Fig. 2a). After the activation process, the structure becomes different; it is less dense and pores of different size and shapes appear as shown in Fig. 2b. The process of oxidation and gasification of organic matter in

Table 2
Characteristics of the porous structure of the sludge-based activated carbon

Pore volume (cm^3/g)	Micropore volume (cm^3/g)	Average pore diameter (nm)	Specific surface area (m^2/g)	Iodine number (mg/g)
0.25	0.11	5.62	381.62	563.10

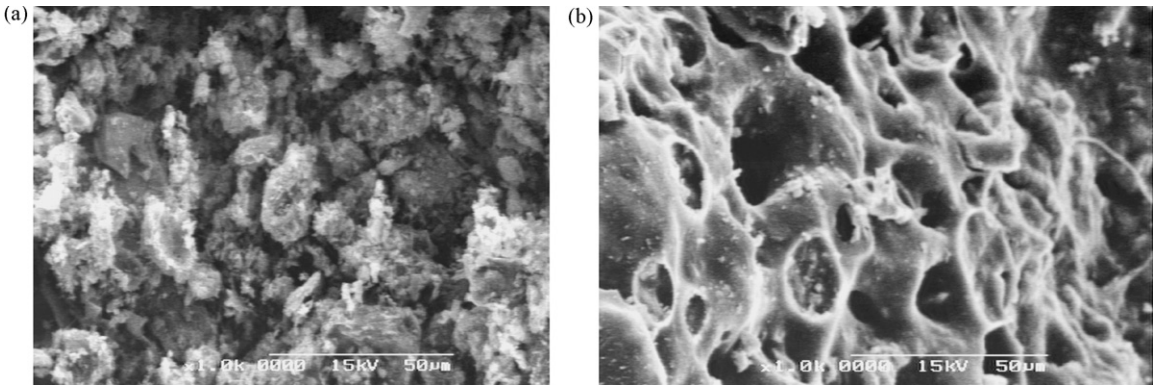

Fig. 2. SEM micrographs of raw sludge (a) and produced activated carbon (b).

the course of thermal treatment results in the development of porosity, and the subsequent washing and rinsing remove residual inorganic matter which could possibly block the pores to some extent.

3.2. Aqueous adsorption test

3.2.1. Effect of adsorption time on the dye removal efficiency

The effect of adsorption time on Acid Brilliant Scarlet GR adsorption, shown in Fig. 3, was studied with an initial dye concentration of 300 mg/L in the solution, a pH value of 6.4 and the additive dosage of produced activated carbon of 20 g/L.

Fig. 3 shows that the degree of coloration and total organic carbon of the dye solution decreased significantly with an increase in the contact time until equilibrium was attained in 15 min. About 98.2% color and 97.3% TOC were removed at 5 min contact time from the adsorbate with initial concentration of 300 mg/L. At the equilibrium time of 15 min, the removal efficiency of color increased to 99.7% and that of TOC increased to 99.6%. This indicates that the produced activated carbon can efficiently adsorb the dye. The contact time required for the dye removal is very short, which is important for practical wastewater treatment applications.

3.2.2. Effect of initial concentration on the dye removal efficiency

The effect of initial concentrations of Acid Brilliant Scarlet GR in solution ranging from 50 to 500 mg/L were investigated to study dye removal efficiency. The initial pH of the solution was 6.4, without any adjustment. The adsorption process was conducted with 20 g/L carbon dose and 15 min contact time. As shown in Fig. 4, the removal efficiency of color and TOC in the dye solutions decreased with the increase in the initial concentration. About 100.0% color and 99.9% TOC were removed from solution for the initial concentration of 50 mg/L, while 98.0% color and 97.9% TOC were removed for 500 mg/L. It appears that the removal efficiencies of color and TOC merely decline about 2% with the initial concentration rising 10 times from 50 to 500 mg/L, indicating that the activated carbon made from activated sludge has high adsorption capacity for Acid Brilliant Scarlet GR.

3.2.3. Effect of carbon dosage on the dye removal efficiency

The effect of carbon dosage on the adsorption performance was studied with carbon doses varying from 5 to 30 g/L at a 15-min adsorption time, 300 mg/L initial dye concentration and pH 6.4 value in solution. As shown in Fig. 5, above 86% color and TOC were removed at the carbon dosage of 5 g/L. The color degree and TOC removals of the dye in solution increased

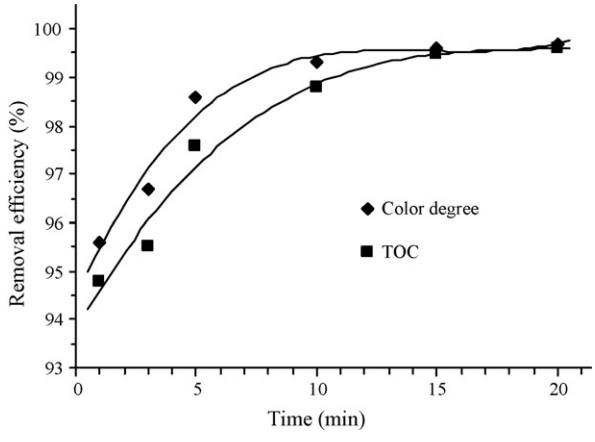

Fig. 3. Effect of adsorption time on the removal of Acid Brilliant Scarlet GR.

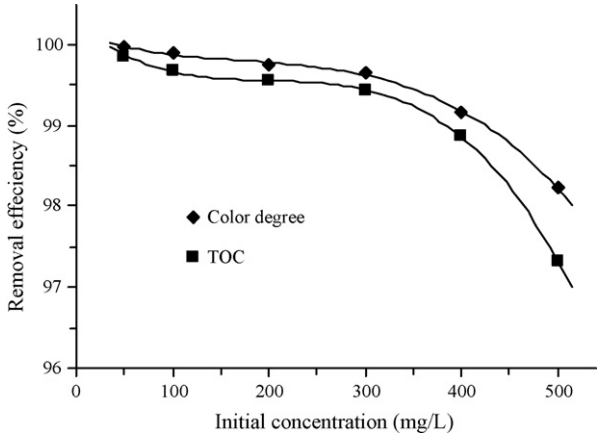

Fig. 4. Effect of initial concentration on the removal of Acid Brilliant Scarlet GR.

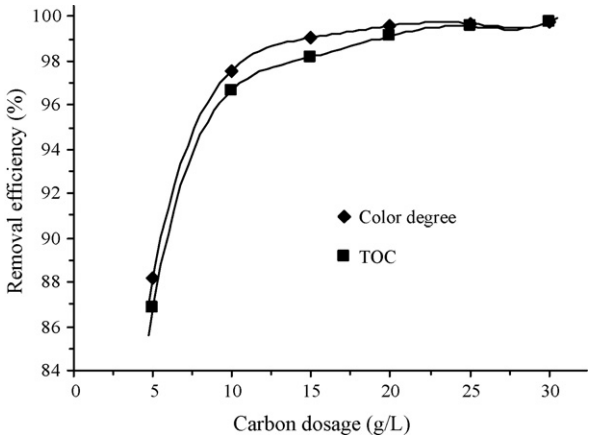

Fig. 5. Effect of carbon dosage on the removal of Acid Brilliant Scarlet GR.

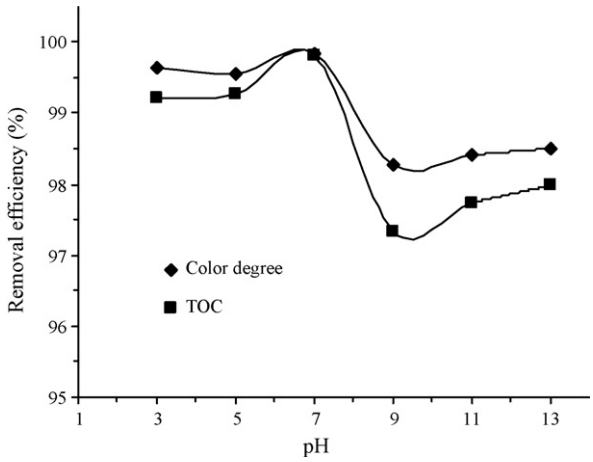

Fig. 6. Effect of initial pH on the removal of Acid Brilliant Scarlet GR.

sharply with increasing carbon dosage from 5 to 10 g/L. However, at the dosage above 10 g/L, the removal efficiencies did not increase much, with complete removal being attained at 20 g/L. This is due to the availability of more surface area at higher carbon dosages.

3.2.4. Effect of pH on the dye removal efficiency

The adsorption capacity of activated carbon depends not only on its physical properties, such as surface area, pore size distribution, etc., but also on the chemical nature of its surface. Change of pH value in adsorption system could lead to the transformation of chemical characteristics on the surface of activated carbon and the form of the adsorbate, thus it plays an important role in the adsorption performance. The experiment was carried out by varying the initial pH from 3 to 13, under a constant initial dye concentration of 300 mg/L, adsorption time of 15 min and a carbon dosage of 20 g/L. The dependence of the equilibrium adsorption capacity of produced carbon for Acid Brilliant Scarlet GR on initial pH is illustrated in Fig. 6.

The adsorbed amounts of Acid Brilliant Scarlet GR, an anionic-type dye, are more in acidic condition than in alkaline condition. Over the range of initial pH 7–9, the removal efficiency of TOC and color degree decreased sharply. This may be explained as follows: when the pH value in solution is below 7, activated carbon is negatively charged due to the adsorption of hydrated hydroxyl ions, and there is electrostatic repulsion between the activated carbon and Acid Brilliant Scarlet GR, which is also negatively charged in alkaline solution. Besides, the higher concentration of OH^- ions present in the reaction mixture competes with the negatively charged dye ions for the adsorbing surface sites, resulting in a decrease in the removal of Acid Brilliant Scarlet GR. At a pH value of 7 maximum removal was observed. But in this study, initial solution pH within the range of 3–13 had little effect on the adsorption of Acid Brilliant Scarlet GR onto the produced activated carbon.

3.2.5. Adsorption isotherm of sludge-based activated carbon for the dye

The produced activated carbon was tested for its adsorption efficiency for the dye of Acid Brilliant Scarlet GR. To determine the adsorption isotherm, the initial dye concentration ranged from 50 to 500 mg/L. The adsorption process was studied without any control over the pH of the aqueous phase. The isotherm

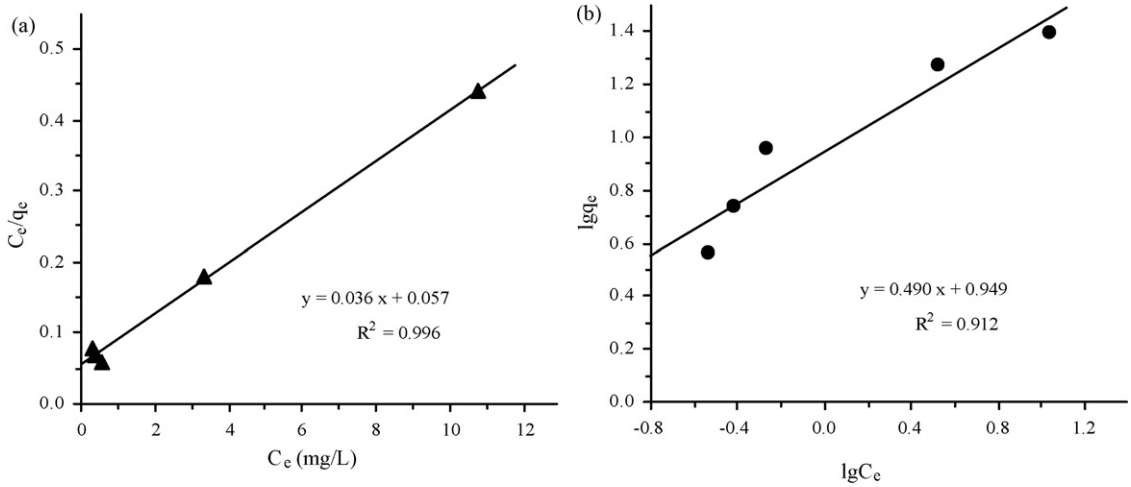

Fig. 7. Langmuir isotherm (a) and Freundlich isotherm (b) of Acid Brilliant Scarlet GR adsorption onto produced activated carbon. C_e: equilibrium concentration; q_e: amount of dye adsorbed at equilibrium time.

data were fitted o Langmuir and Freundlich equations and the results are shown in Fig. 7. It appears that both the Langmuir and Freundlich equations fit the data fairly well. Accordingly, it can be deduced that there is mainly monolayer adsorption, involving chemical and physical adsorption, of Acid Brilliant Scarlet GR onto the produced carbon. That means once a dye molecule occupies a site, no further adsorption can take place at that site and a saturation value, i.e. Q_0, is reached which corresponds to the completion of a monolayer.

4. Conclusions

The conversion of activated sludge to activated carbon can not only significantly eliminate the need for further treatment of sludge, reduce the cost of hauling, landfilling and transporting the sludge, but can also produce a valuable adsorbent with lower cost than commercial activated carbons. In this work, a novel method of pyrolyzing surplus activated sludge from wastewater treatment operations impregnated with potassium hydroxide in steam atmosphere was developed. The results obtained showed that under the preparation conditions of 600 °C heating temperature and 1 h heating time, the activated carbon produced was mainly microporous and mesoporous in character with specific surface area of 381.62 m^2/g, and the total pore volume and the micropore volume of 0.25 and 0.11 cm^3/g, respectively.

In the adsorption studies, the amount of Acid Brilliant Scarlet GR adsorbed onto the sludge-based activated carbon was most dependent on adsorption time and carbon dosage. The time to attain equilibrium for the adsorption of the dye was 15 min. Twenty grams per liter of carbon dosage was sufficient for the removal of the dye in the solution with initial concentration of 300 mg/L. Over the range of initial concentration investigated, the dye removal efficiency remained above 97%, indicating that the produced carbon had large adsorption capacity. A change in the initial pH in solution from 3 to 13 had little effect on the adsorption of Acid Brilliant Scarlet GR; however, a relatively higher removal efficiency was obtained at acidic and neutral conditions, which could be attributed to the electrostatic repulsion between the negatively charged activated carbon and the dye ions, as well as the competition for the surface adsorbing sites between OH^- ions and the dye ions in the alkaline condition. The data on adsorption of the dye on the produced activated carbon fit the Langmuir and Freundlich equilibrium isotherm models well.

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