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## **TREATMENT OF BLEACHING EFFLUENT BY GUANIDINE PHOSPHATE-ACTIVATED PAPER MILL SLUDGE ACTIVATED CARBON**


*The influence of the addition of guanidine phosphate (MGP, BGP, TGP) on adsorption toward AOX from bleaching effluent was studied for the preparation of paper mill sludge activated carbon. The preparation was performed with the addition of guanidine phosphate (0 wt%-14 wt%) at temperatures which ranged from 500°C to 800°C for 30 min. – 90 min. of roasting, 2 h-14 h of CO<sub>2</sub> activation. The influence of the porous structure of the activated carbons on AOX removal from bleaching effluent was discussed. The improvement depended on the conditions used in the preparation of the activated carbon. In comparison, the activated carbon prepared with the addition of TGP showed enhanced removal of AOX, which was explained by the number of guanidine by the FTIR characterization on the activated carbon. Optimal conditions of the preparation of the paper mill sludge activated carbon were obtained.*

**Keywords:** paper mill sludge, activated carbon, guanidine phosphate, AOX, bleaching effluent

### **Introduction**

At present, chlorine-containing chemicals including chlorine, chlorine dioxide and hypochlorite are used as bleaching agents in the pulping process in the pulp and paper industry. Meanwhile, some organochlorides including chlorate, chloroform, phenols, acid resins, chlorinated hydrocarbons, furans, catechols, guaiacols, vanillins and dioxins are formed during the pulp bleaching. These chlorinated compounds easily and naturally accumulate due to their stable chemical properties, which can bring great harm to the environment [Odabasi 2008; Malhotra et al. 2013]. Therefore, it is necessary to deal with these compounds in bleaching effluent using membrane separation, catalysis, UV, biological degradation and adsorption [Ashrafi et al. 2015]. Among the alternatives, activated carbon has been increasingly used in the pulp and paper

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industry for this goal due to its simple operation and high adsorptivity [Bazrafshan et al. 2016; Yadav and Garg 2016].

Some commercially activated carbons prepared from coal and polymer, however, were sparingly used due to their very high cost, it is therefore desirable to find low cost wastes to prepare activated carbon with excellent adsorption performance. Some researchers used unconventional raw materials such as palm seeds, coconut shell, coffee, corn core and nut shell to prepare activated carbon for the removal of pollutants [Ioannidou and Zabaniotou 2007; Prauchner et al. 2016; Tsubota et al. 2016]. Sewage sludge is a carbonaceous material, which is produced in wastewater treatment. Tian et al. [2017] found that the phosphorous removal was enhanced by sludge activated carbon prepared during biological treatment. Rashed et al. [2016] obtained a new activated carbon by chemical technology and physical activation using drinking water treatment sludge as raw material for the removal of MB dye.

Paper mill sludge is generated in the process of pulping and papermaking. It is mainly composed of organic (cellulose, hemicellulose and lignin) and inorganic (bauxite,  $\text{CaCO}_3$ , kaolin and other inorganic salts) matters. Paper mill sludge has the main characteristics of complex composition, high water content and difficulty in treatment. At present, paper mill sludge is generally treated using landfill, air exposur or burning, however, there are some disadvantages such as environmental pollution, space occupation and low utilization [Kamali et al. 2016]. The functional products are accordingly often developed in the field of utilization of paper mill sludge, including brick, ceramic, cement, artificial zeolite, building board, filler and coating material [Kuokkanen et al. 2008]. In addition, it can be used as raw material for the preparation of activated carbon because the sludge contains a lot of carbon. Pirzadeh and Ghoreyshi [2013] reported the synthesis of activated carbon using paper mill sludge as a low cost waste material to remove phenols from aqueous solutions.

Although there are some studies on activated carbon using paper mill sludge as raw material, the sorption capacity still needs to be improved. Hence, some amino group-containing compounds were used to enhance sorption capacity of activated carbon [Machida et al. 2012; Liu et al. 2013]. Guanidine phosphate provided nitrogen atoms and phosphorus atoms in its chemical structure, which influenced the pyrolysis characteristics of lignocellulosic materials [Gao et al. 2005]. Therefore, this paper studied the preparation of activated carbon with a high specific surface area using paper mill sludge with the addition of guanidine phosphate, and it was used for the treatment of bleaching effluent from pulp mills.

## Materials and methods

### Synthesis of activated carbon

The sludge was obtained from the wastewater treatment plant in a paper mill in the Yunnan province. The sample was dewatered and then dried at 105°C. The dried sample was added with deionized water, mixed with guanidine phosphate (Sinopharm Chemical Reagent Co., Ltd., 98%), and then dried at 105°C. The dried sample was placed in a tube furnace, heated to 600°C at the heating rate of 15°C/min. under flowing N<sub>2</sub>. The temperature was maintained for 60 min. and then the flowing gas was changed from N<sub>2</sub> to CO<sub>2</sub>. The temperature continued to be maintained for 6 h under flowing CO<sub>2</sub>, then the flowing gas was changed from CO<sub>2</sub> to N<sub>2</sub> for taking the activated carbon from the tube furnace. The treated sample was washed with hot deionized water, dried at 105°C and then ground through a 100 mesh sieve for the next stage.

### Bleaching effluent

The bleaching effluent used in this work was obtained from a pulp mill in the Yunnan province and its characteristics are shown in table 1.

**Table 1. Characteristics of bleaching effluent**

pH	COD <sub>Cr</sub> [mg/L]	BOD <sub>5</sub> [mg/L]	SS [mg/L]	Chromaticity [times]	Residual active chlorine [mg/L]	AOX [mg/L]
8.02	2326	826	258	2206	309.8	76.6

### Treatment of bleaching effluent

A flask was placed in a water bath. The bleaching effluent was placed in the flask, then the activated carbon was added. Each mixture was subjected to shaking under a magnetic stirring in the water bath. Afterwards, each mixture was filtered, to separate activated carbon and the effluent (filtrate) was analysed.

### Characterization and analysis

The specific surface area of the activated carbon was determined by an OMNISORP100CX adsorption instrument. FTIR spectra of activated carbon were recorded from 400 to 4000 cm<sup>-1</sup> using a Fourier-380FT-IR spectrometer (USA).

AOX content in bleaching effluent was analysed with a TE XPLORER AOX analyzer.

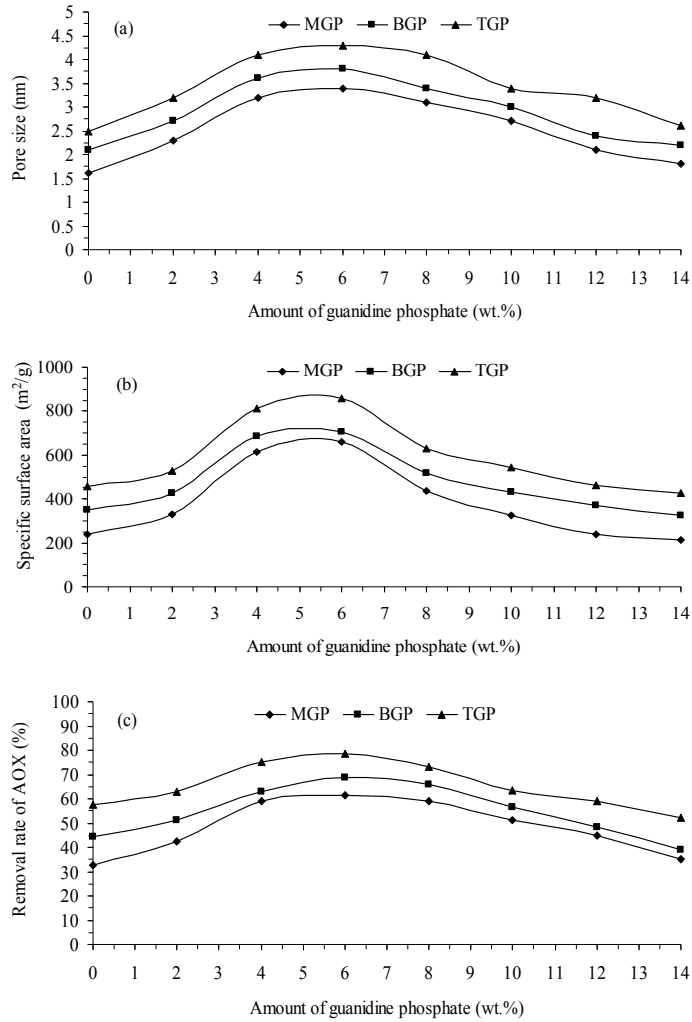
## Results and discussion

Effect of amount of guanidine phosphate on property of activated carbon  
Guanidine phosphate as a flame retardant for cellulosic materials, improved the microstructure of biomass activated carbon [Wang et al. 2015]. Because paper mill sludge contained cellulose, hemicellulose and lignin, it was mixed with guanidine phosphate, the activation was investigated in detail for the estimation of the performance of the activated carbon.

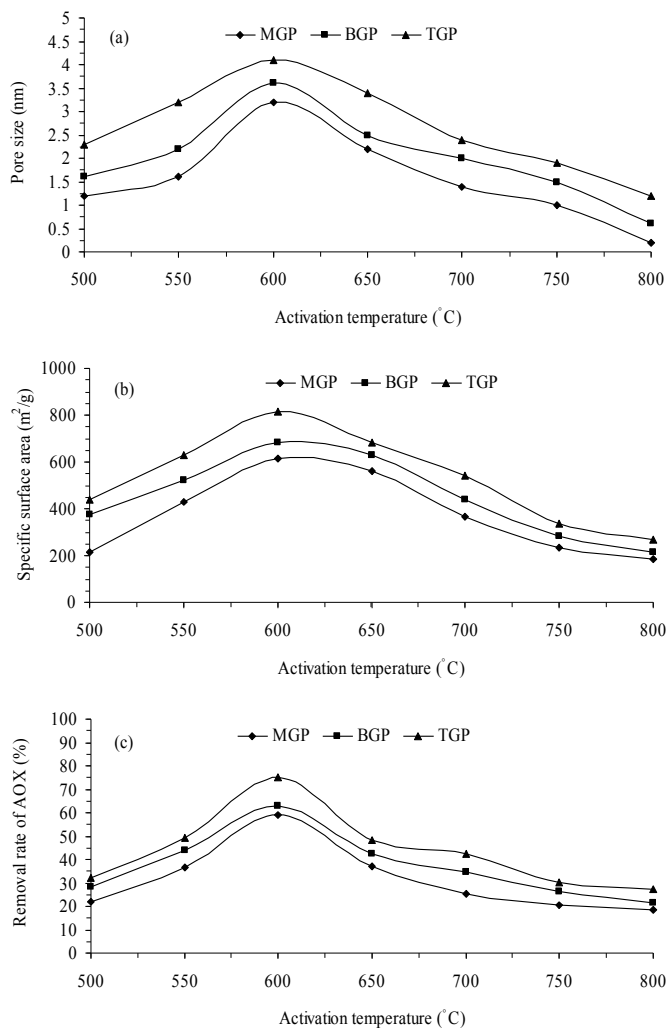
The AOX removal of bleaching effluent was significantly improved after the paper mill sludge was added with guanidine phosphate (fig. 1c). The guanidine phosphate was believed to suppress the pyrolysis temperature, which affected the chemical structure of the activated carbon with the increase in the amount of guanidine phosphate, resulting in the increase of activated carbon pore size (fig. 1a) and specific surface area (fig. 1b) [Granzow 1978]. Moreover, the N content affected the microstructure of the activated carbon (fig. 1a, b) due to the inhibition on the pyrolysis when different guanidine phosphate (MGP, BGP, TGP) was added [Ren et al. 2008], thus influencing the AOX removal of the bleaching effluent (fig. 1c).

### Effect of activation temperature on property of activated carbon

When the activation temperature was set at 600°C, AOX in the bleaching effluent was removed most effectively, which showed the activation temperature was relatively low for the synthesis of the paper mill sludge activated carbon. Jeyaseelan and Lu [1996] prepared an activated carbon with municipal sludge and they found that the best performance of activated carbon was obtained at the activation temperature of 850°C. At the same time, it was found in this study that the specific surface area of the activated carbon prepared by the addition of TGP (814 m<sup>2</sup>/g) was comparatively high. dos Reis et al. [2016] used a sewage sludge to prepare an activated carbon with a specific surface area of 679.3 m<sup>2</sup>/g. When the activation temperature was lower than 600°C, the pore size (fig. 2a) and the specific surface area of the activated carbon (fig. 2b) was low, resulting in the low removal of AOX of the bleaching effluent (fig. 2c), which was caused by the difficulty in forming void structures in the activated carbon due to the insufficient activation at low temperature. However, the case was just the opposite due to the excessive activation-induced shrinkage of microcrystalline structure at the activation temperature higher than 600°C [Inguanzo et al. 2001; Kalpana and Lee 2016].



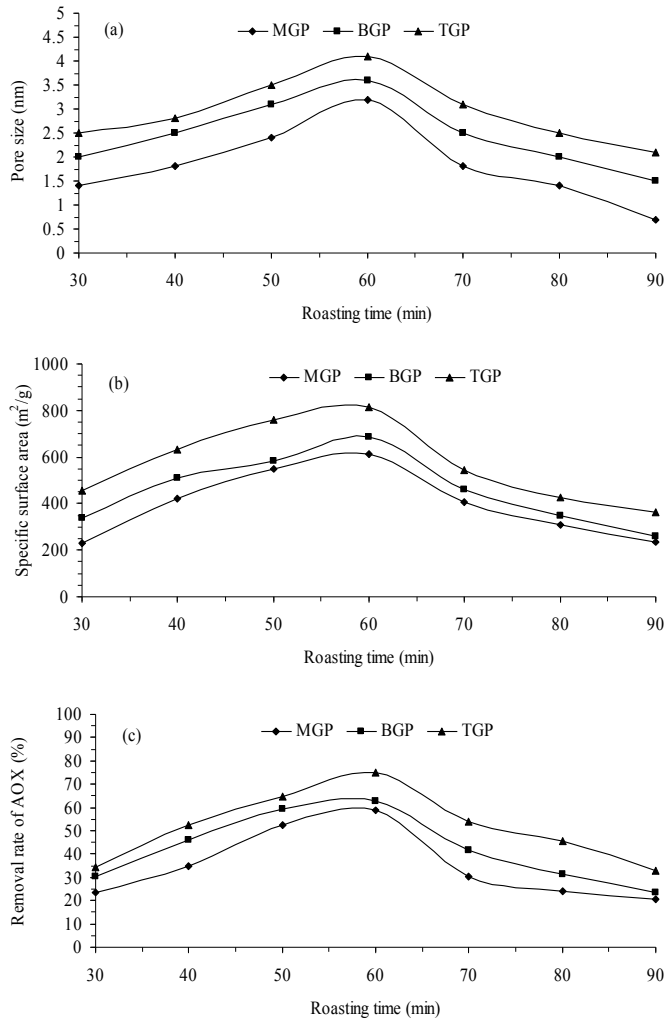
**Fig. 1.** Amount of guanidine phosphate vs pore size (a), specific surface area (b) of activated carbon, and AOX removal of bleaching effluent (c). Preparation of activated carbon: temperature 600°C, roasting time 60 min., activation time 6 h; Treatment of bleaching effluent: 2 g activated carbon/L, 30°C, 1 h. MGP: monoguanidine phosphate; BGP: biguanidine phosphate; TGP: triguanidine phosphate



**Fig. 2.** Activation temperature vs pore size (a), specific surface area (b) of activated carbon, and AOX removal of bleaching effluent (c). Preparation of activated carbon: 4 wt.% amount of guanidine phosphate, roasting time 60 min., activation time 6 h; Treatment of bleaching effluent: 2 g activated carbon/L, 30°C, 1 h

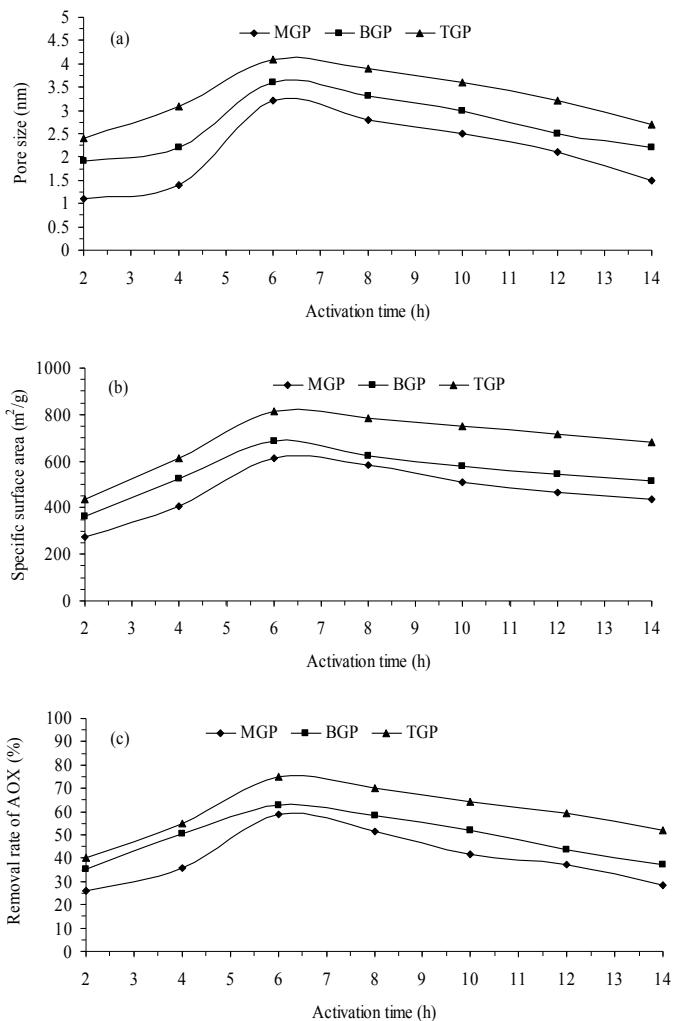
### Effect of activation time on property of activated carbon

It can be seen from figure 3, when the roasting time was not enough for pyrolysis, a fluffy textured activated carbon could not be formed due to the incomplete activation, so that its pore size (fig. 3a) and specific surface area (fig. 3b) decreased. When the roasting time exceeded 60 min., excessive pyrolysis caused carbon loss and sintering [Bandosz 2006]. When the roasting



**Fig. 3.** Roasting time vs pore size (a), specific surface area (b) of activated carbon, and AOX removal of bleaching effluent (c). Preparation of activated carbon: 4 wt.% amount of guanidine phosphate, activation temperature 600°C, activation time 6 h; Treatment of bleaching effluent: 2 g activated carbon/L, 30°C, 1 h

time was set at 60 min., the best effect was obtained according to the AOX removal of the bleaching effluent (fig. 3c). Moreover, the pore size (fig. 4a) and specific surface area (fig. 4b) of the activated carbon increased with the increasing CO<sub>2</sub> activation time up to 6 h, resulting in the maximum AOX removal of the bleaching effluent at 6 h (fig. 4c). Tsubota et al. [2014; 2016] found a similar phenomenon on the CO<sub>2</sub> activation of guanidine phosphate-added cellulose.



**Fig. 4. CO<sub>2</sub> activation time vs pore size (a), specific surface area (b) of activated carbon, and AOX removal of bleaching effluent (c). Preparation of activated carbon: 4 wt.% amount of guanidine phosphate, activation temperature 600°C, roasting time 60 min.; Treatment of bleaching effluent: 2 g activated carbon/L, 30°C, 1 h**

The activated carbon obtained under optimal conditions was characterized with FTIR. As shown in figure 5, it was observed that the N content in activated carbon increased with the number of guanidine from MGP to BGP to TGP, which explained the enhanced AOX removal of the bleaching effluent by activated carbon.



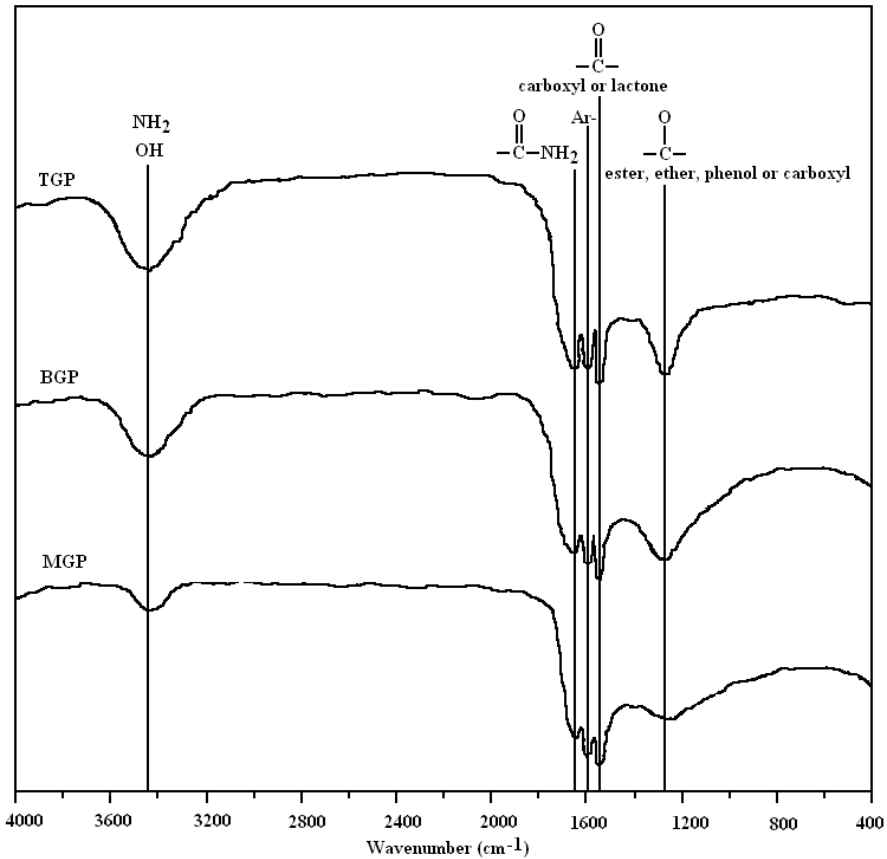


Fig. 5. FTIR spectra of the activated carbon

## Conclusions

The improvement in the AOX removal of bleaching effluent on paper mill sludge activated carbon was related to the addition of guanidine phosphate (MGP, BGP, TGP) and an optimal condition used in the preparation of activated carbon was obtained that influences the treatment of the bleaching effluent. Moreover, the type of guanidine phosphate had significant impact on the porous structure of activated carbons. The TGP-activated carbon exhibited larger volumes of micropores and showed a higher ability to remove AOX from the bleaching effluent.

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