

Preparation of Polysulfonamide Porous Paper and Its Adsorption Properties

Sufeng Zhang*, Nan Zhang, Liwei Qian, Min Du

Shaanxi Provincial Key Laboratory of Papermaking Technology and Specialty Paper Development, Key Laboratory of Paper Based Functional Materials of China National Light Industry, National Demonstration Center for Experimental Light Chemistry Engineering Education, Shaanxi University of Science and Technology, Xi'an, Shaanxi Province, 710021, China

Abstract: Three-dimensional porous paper was prepared by using polysulfonamide (PSA) fiber and pulp as the raw materials. The effect of PSA fiber to pulp ratios on the mechanical strength and adsorption properties (using methyl orange and rhodamine B dyes in their aqueous phase) of the paper were studied. The results showed that the tensile strength and elongation characteristics decreased as the PSA fiber to pulp ratio increased, while the tear strength increased. PSA paper showed good adsorption performance for both methyl orange and rhodamine B, with the adsorption process conforming to the pseudo-second-order and Langmuir isotherm models, indicating monolayer chemical adsorption. The study has provided an improved theoretical and scientific basis for the further development and application of PSA paper.

Keywords: polysulfonamide paper; mechanical strength; adsorption property; porous

1 Introduction

Paper is typically a porous material with a three-dimensional network structure, made from short fibers in a water medium by papermaking/forming technology^[1]. Polysulfonamide (PSA) fiber is a high performance synthetic fiber, with a special structure and excellent performance. PSA-based paper is widely used for high temperature flue gas filters, in insulating paper fields, and for honeycomb materials, due to its excellent mechanical strength, heat resistance, and insulation properties^[2-8].

In view of its special structure, PSA contains a large amount of benzene rings and abundant amide groups, so that it not only has excellent mechanical strength, but also has good reaction performance, and the active groups can interact with some water



*Corresponding author:
Sufeng Zhang, professor,
PhD tutor; research interests:
fiber new materials and
papermaking green chemistry;
E-mail: zhangsufeng@sust.edu.
cn; sufengzhang@126.com

Received: 20 May 2019; accepted: 14 June 2019.

pollutants. Combined with the porosity of the paper, PSA paper plays an important role in adsorption and removal of polluting dyes.

In this study, PSA fiber and pulp were used as raw materials to prepare PSA paper by wet forming, and the mechanical strength and adsorption properties of the PSA paper were investigated. Methyl orange (MO) and rhodamine B (RhB) were selected as adsorbates to explore the adsorption effect of PSA paper on dye molecules, as well as the adsorption process and mechanism, in order to better understand the behavior of PSA paper.

2 Experimental

2.1 Materials

PSA short fibers (5~6 mm) and microfibers (pulp) (0.5~1.0 mm) were provided by Shanghai Tanlon Fiber Co., Ltd., while the MO and RhB were purchased from Shanghai Aladdin Biological Technology Co., Ltd.

2.2 Preparation of PSA paper

Firstly, the PSA short fibers and pulp were mixed in different mass ratios and dispersed, and then wet-formed in a paper former; the resultant paper was then vacuum-dried at 105°C. The paper was then hot-pressed at 250°C under 15 MPa for 2 min to obtain PSA paper.

2.3 Characterization of PSA paper surface by scanning electron microscope (SEM)

The surfacial microstructure of PSA paper was observed with a SEM (TESCAN VEGA 3 Easy Probe). The accelerating voltage is 10 kV.

2.4 Mechanical property characterization of PSA paper

The mechanical strength characterization of PSA paper involved testing three important parameters: tensile strength, elongation at break, and tear strength. Tensile strength and elongation were tested according to the national standard GB/T 453—2002, using a tensile strength meter. While tear strength was measured using a tear gauge in compliance with GB/T 455—2002.

2.5 Pore structure of paper analysis

Pore structure of PSA paper was measured by automatic mercury intrusion meter (MIP) tester (USA, Auto Pore IV 9500), the range of pore diameters are 5.0 nm~1000 μm .

2.6 Standard working curves for two dye solutions

The maximum absorption wavelengths of RhB and MO (of 554 nm and 467 nm, respectively) were measured by UV-visible spectrophotometer. Dye concentration (C) was plotted on the abscissa and the absorbance (A) on the ordinate. The standard working curve equations of RhB and MO were fitted to $A=0.0379C-0.0982$, and $A=0.0672C+0.0168$, respectively, and the linear correlation coefficients were $R^2=0.9992$ and 0.9995 , which meant that the relationship was in accordance with the Lambert-Beer law.

2.7 Adsorption experiment

RhB and MO were used as target adsorbates. First, a section of hot-pressed PSA paper was put into a 10 mL white capped bottle, and then 10 mL of dye solution was added at a certain concentration. After standing for a set time, dye solution absorbance was measured by taking before and after UV-visible spectrophotometer readings. The dye concentration was calculated according to the standard curve, and the adsorption amount was calculated by applying Equation (1).

$$Q = (C - C_i)V/m \quad (1)$$

Where, Q is the adsorption amount; C is the initial concentration of dye; C_i is the concentration of dye after adsorption; V is the dye volume; m is the adsorbent mass.

3 Results and discussion

3.1 Effect of hot pressing on pore structure of PSA paper

In order to compare the changes of morphology and pore structure in PSA paper from hot pressing, SEM images of PSA papers (PSA short fiber to pulp ratio of 6:4) before and after hot pressing were obtained, and the images are shown in Fig.1. As shown in Fig.1(a), the structure of PSA paper without hot pressing was

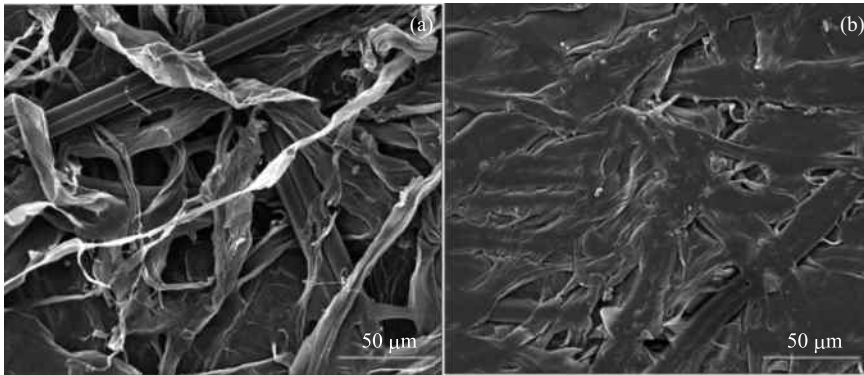


Fig.1 SEM images of PSA paper materials before (a) and after (b) hot pressing

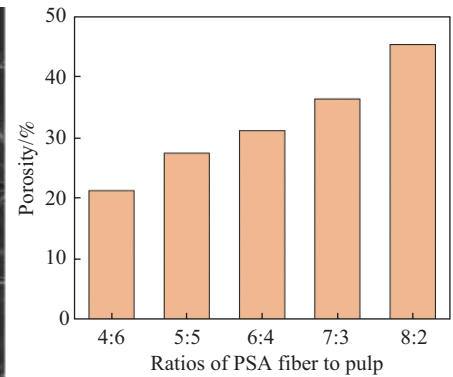


Fig.2 The porosity of PSA papers made using different PSA fiber/pulp ratios

relatively loose, with pulp wrapped around the PSA short fibers in a ribbon-like manner, and connected by weak hydrogen bonds to form a porous, 3D network structure. In this form, the bonding force was weak and the mechanical strength poor—to the extent that the paper could not meet the strength demands of usage. After hot pressing, the unmelted PSA short fibers formed a skeleton, and the molten pulp filled the pores formed by the PSA short fibers overlapping each other, as a binder.

Due to the disordered and uneven bonding between the fibers, a relatively complex pore structure was formed. As shown in Fig.1(b), after hot pressing, part of the pulp melted to fill the pores between the fibers, which became more tightly bonded, which increased the skeleton connection strength of the PSA paper. The melted pulp showed good interfacial adhesion between the PSA short fibers, and much improved tensile stress, in a result consistent with the test results of the mechanical strength of the PSA paper. Hot pressing works to melt the pulp, to a certain extent, and fibers become tightly bonded, to form a structure similar to reinforced concrete^[9-10].

3.2 Effect of fiber content on pore structure of PSA paper

The pore structure of the paper was obtained by using the MIP tester. Porosity is an important pore structure parameter, as it affects the mechanical strength, electrical properties, and adsorption effects of PSA papers. The porosity test results for different proportions of PSA papers are shown in Fig.2, where

it can be seen that, as the proportion of PSA fibers increased, the porosity of PSA paper increased. This was due to the fact that, after hot pressing, the pulp melted and filled the gaps in the fibrous skeleton, but the increased proportion of fibers meant that the molten pulp was insufficient to completely fill the pores—and so porosity increased^[11]. This increased porosity benefitted adsorption performance.

3.3 Effect of fiber content on the mechanical properties of PSA paper

Tensile strength is mainly determined by the bonding strength between PSA fiber and pulp, and the strength of the PSA fiber itself. PSA fiber is rigid and straight, showing an almost rod-like form and a smooth, ungrooved circumference. In this form, although the PSA fiber itself has high strength, it does not easily combine with other fibers. When used as paper raw material, it is usually necessary to add a certain amount of pulp to increase its bonding strength, and due to the different pulp fiber lengths, they become finely fibrillated, with surface splitting clearly evident.

Mechanical and compressive strengths for PSA paper with different PSA fiber/pulp ratios are shown in Fig.3. It can be seen in Fig.3(a) that, the tensile index of PSA paper decreased gradually with increased PSA fiber content, decreasing from 40.7 N·m/g at a ratio of 4:6, to 29.0 N·m/g at a ratio of 8:2. So, as the proportion of pulp in the paper decreased by 40%, its tensile index decreased by 28.7%, and this occurred because the PSA

binder between the PSA fibers was reduced when there was less pulp, resulting in a looser bond between the fibers. Therefore, when the paper was stretched by an external force, the fibers were easily separated, whereas when the pulp content was high, the fibers were more tightly bound together. This meant that the break in the paper was caused by a different mechanism; with higher pulp content, when the paper is stretched by an external force, the fibers themselves snap, and the paper is broken. Because the strength of the PSA fiber itself is high, it requires a lot of external force to break it. When the pulp content is reduced, and the maximum tension that the paper can withstand is reduced, so its tensile strength is lowered.

Elongation is a suitable indicator of paper toughness, and is an important factor influencing tearing. Elongation of the paper is linear with the tightness of the paper. Because papers with different PSA fiber to pulp ratio have the same quantitative characteristics and the papers were hot-pressed under the same conditions, the tightness theory still applies. This explains why

elongation decreased from 9.01% to 5.27% as the PSA short fiber to pulp ratio increased from 4:6 to 8:2, as shown in Fig.3(a). Mechanistically, this may be because as the mass of the pulp was reduced, it was not able to fill the pores between the PSA fibers after hot-pressing completely, meaning that some fibers were freed from the pulp during the elongation testing, instead of showing elongation, leading to the paper breaking more easily.

Tear strength is an important physical property indicator for paper and paper board, and porosity is an important parameter affecting tear strength. It can be seen from Fig.3(b) that as the proportion of pulp decreased, the tear index of PSA paper increased. Specifically, when the PSA short fiber to pulp ratio was increased from 4:6 to 8:2, the tear index increased by 66%, from 28.1 $\text{mN}\cdot\text{m}^2/\text{g}$ to 46.7 $\text{mN}\cdot\text{m}^2/\text{g}$. In the tear strength test, paper is subjected to an external force to tear the fibers, however, since the fiber itself is strong, the external force required to break the paper structure is increased. Porosity also has an effect on paper tear strength: as the proportion of PSA fiber increases, its pulp content decreases, and paper porosity increases. When hot-pressed, the pulp can no longer completely fill the pores, thereby increasing the tear strength of the paper, and the most comprehensive performance was achieved by PSA paper with a PSA fiber to pulp ratio of 6:4.

3.4 Adsorption performance of PSA paper

The excellent properties of PSA paper allow for its application in many fields. In our study, we considered its application in an environmental management field, in the hope of expanding its range of applications. While mechanical strength of materials is an important consideration in the process of environmental management, it is necessary to avoid secondary pollution during processing to achieve this. Therefore, in the PSA papers prepared with different PSA fiber/pulp ratio, considering tensile strength and tear strength options, PSA paper with a PSA fiber to pulp ratio of 6:4 was selected for the adsorption test.

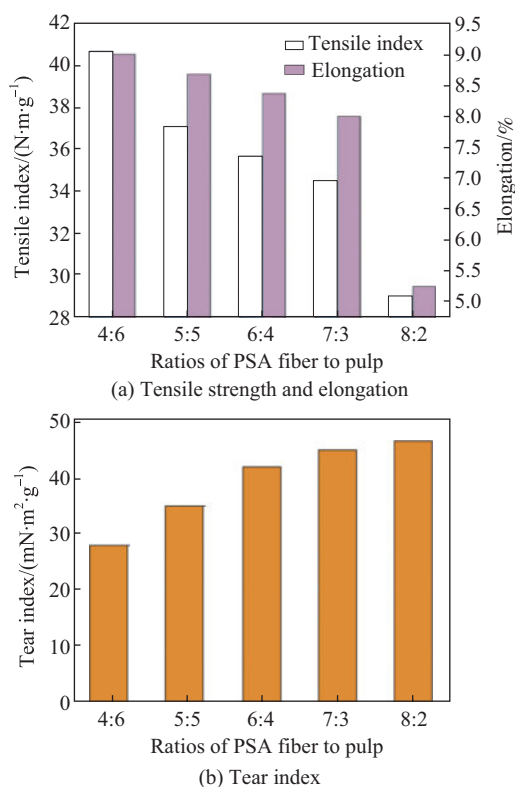


Fig.3 Mechanical and compressive strengths for PSA paper with different PSA fiber/pulp ratios

3.4.1 Adsorption kinetics of MO and RhB onto PSA paper

The adsorption performance of the as-prepared PSA paper toward MO and RhB was tested, with the adsorption results over time were shown in Fig.4. Adsorbents were able to reach adsorption equilibrium relatively quickly, reaching close to 80% of the adsorption equilibrium after 120 min reaction time. The regression parameters for the kinetics, according to pseudo-first-order and pseudo-second-order models, were shown in Fig.5 and Table 1.

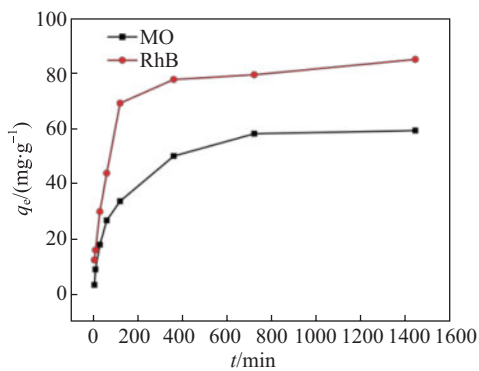
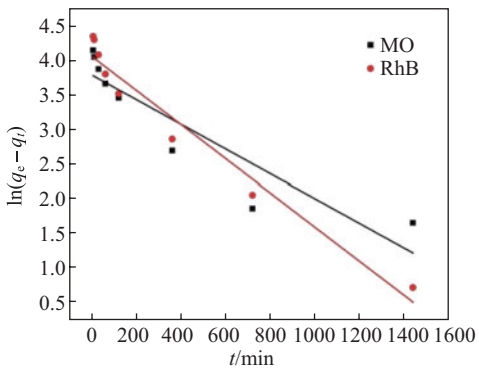
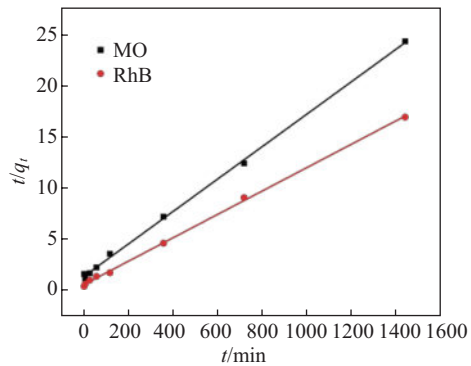


Fig.4 Effect of adsorption time on adsorption capacity



(a) Pseudo-first-order model



(b) Pseudo-second-order model

Fig.5 Adsorption kinetic models of PSA paper

Table 1 Adsorption kinetic parameters

Dyes	Pseudo-first-order model			Pseudo-second-order model		
	q_e /(mg·g ⁻¹)	k_1 /min ⁻¹	R^2	q_e /(mg·g ⁻¹)	k_2 /(g·mg ⁻¹ ·min ⁻¹)	R^2
MO	42.7129	0.0018	0.8442	62.8931	1.91×10^{-4}	0.9990
RhB	55.8461	0.0025	0.9615	86.9565	2.45×10^{-4}	0.9992

To investigate the adsorption kinetics further, the results have been formulated using pseudo-first-order and pseudo-second-order models to study the adsorption process of several adsorbates^[12], as shown in Equation (2) and Equation (3):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (3)$$

Where, q_e and q_t (mg/g) refer to the adsorption amount of the adsorbate at the equilibrium state and at time t , respectively, and k_1 (min⁻¹) and k_2 (g/(mg·min)) are the rate constants of the pseudo-first-order adsorption and the pseudo-second-order adsorption models, respectively.

It can be seen from Table 1, the R^2 values of the pseudo-second-order model were larger than 0.999, indicating the pseudo-second-order model was more suitable to describe the adsorption process of PSA paper on different adsorbates.

3.4.2 Adsorption isotherms of MO and RhB onto PSA paper

The adsorption isotherms for MO and RhB onto PSA paper were shown in Fig.6, where it can be seen that the saturated adsorption capacities of RhB and MO onto PSA paper were 108.70 mg/g and 89.29 mg/g,

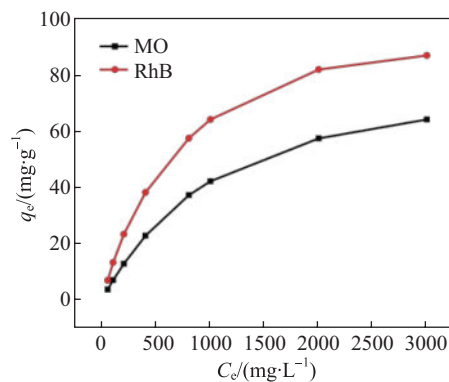


Fig.6 Effect of initial concentration of dye aqueous solution on adsorption capacity

respectively. The actual adsorption amounts achieved were 61.24 mg/g and 85.92 mg/g, respectively, indicating that PSA paper displayed good adsorption capacity for MO and RhB, suggesting that PSA paper would be a good adsorbent for dye pollutants.

To investigate the adsorption isotherms further, the results were formulated using Langmuir and Freundlich isotherm models, to study the adsorption process of different adsorbates^[13], as shown in Equation (4) and Equation (5).

$$C_e/q_e = 1/(q_m k_L) + C_e/q_m \quad (4)$$

$$\ln q_e = 1/n \ln C_e + \ln k_F \quad (5)$$

Where, q_m and k_L are the Langmuir constants representing the maximum adsorption capacity of adsorbents (mg/g) and the energy of adsorption, respectively. k_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

The regression adsorption isotherm details for the Langmuir and Freundlich model were listed in Fig.7 and Table 2. Usually, the Langmuir isotherm describes homogeneous adsorption, in which all sites have equal affinity for the adsorbate, while the Freundlich

Table 2 Isothermal adsorption model parameters

Dyes	Freundlich isotherm model			Langmuir isotherm model		
	k_F $/(L \cdot mg^{-1})^{1/n}$	n	R^2	q_m $/(mg \cdot g^{-1})$	k_L $/(L \cdot mg^{-1})$	R^2
MO	0.0123	1.0930	0.7178	89.2857	0.0009	0.9993
RhB	0.7761	1.6087	0.9652	108.6957	0.0014	0.9992

isotherm model commonly assumes that the adsorption phenomena on heterogeneous adsorbent surfaces follows an empirical equation. For MO and RhB, the PSA paper isotherms were fitted better by the Langmuir model than by the Freundlich model.

4 Conclusions

The results have shown that the PSA paper exhibited good performance, and the most comprehensive performance was achieved with a PSA fiber to pulp ratio of 6:4, including tensile index (35.7 N·m/g), tearing index (42.1 mN·m²/g), elongation (8.38%), and porosity (31.05%). Adsorption experiments showed that the Langmuir isotherm adsorption model and the pseudo-second-order kinetic equation could describe the adsorption properties of MO and RhB onto PSA paper surface well, indicating that the adsorption of RhB by PSA paper was consistent with a monolayer chemical adsorption process. This study has provided an improved theoretical and scientific basis to conduct additional research into the application of PSA paper.

Acknowledgments

This work was supported by the International Joint Research Center for Biomass Chemistry and Materials, Shaanxi International Science and Technology Cooperation Base (2018GHJD-19), the Key Scientific Research Plan (Key Laboratory) of Shaanxi Provincial Education Department (No.17JS016) and by the Natural Science Basic Research Plan, of Shaanxi Province, China (Grant No. 2017JQ2019).

Reference

- [1] Yan X, Wang X W. Research Progress in Paper-based Materials [J]. China Pulp & Paper, 2018, 37(7): 76-79.
- [2] Jin W, Feng Y P, Yan X, et al. Study on Preparation of Polysulfonamide by Low- temperature Solution Polycondensation[J]. Synthetic Fiber in China, 2007,

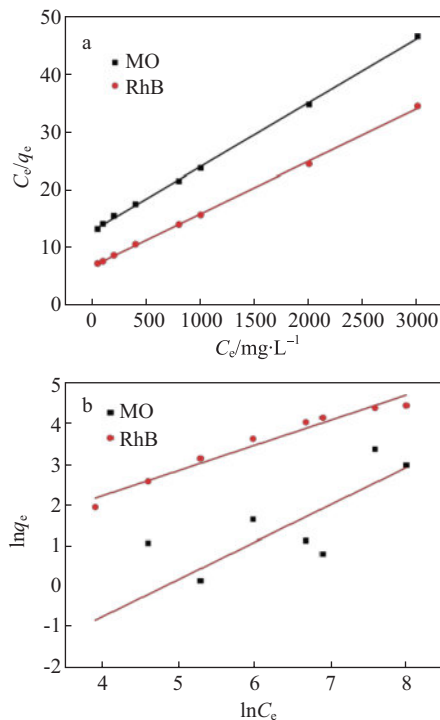


Fig.7 Isothermal adsorption models of PSA paper: (a) Langmuir model; (b) Freundlich model

- 36(10): 27-30.
- [3] Liu L, Zhou J, Gao T, et al. Recent advance in study of polysulfonamide[J]. Journal of Functional Materials, 2011, 42(S5): 781-783.
 - [4] Sun S X, Lu Z M, Shi F J, et al. Structure and Properties of Polysulfonamide Fiber[J]. He'nan Science, 2013(2): 161-164.
 - [5] Yu J C, Yang C L, Chen S H, et al. Progress of aromatic polysulfonamides fiber[J]. Technical Textiles, 2014, 32(12): 1-8.
 - [6] Li H, Zhu Y, Xu B, et al. Preparation and characterization of all para-position polysulfonamide fiber[J]. Journal of Applied Polymer Science, 2013, 127(1): 342-348.
 - [7] Chen Z M. Preparation and Characterization of Functional Polysulfonamide Composites[D]. Shanghai: Shanghai University of Engineering Science, 2011.
 - [8] Wang F H. Application of Polysulfonamide Fiber in the Gas Filtration of Cement[J]. Synthetic Fiber in China, 2017, 46(7): 21-23,26.
 - [9] Zhao H, Zhang M, Zhang S, et al. Influence of Fiber Characteristics and Manufacturing Process on the Structure and Properties of Aramid Paper[J]. Polymer-Plastics Technology and Engineering, 2012, 51(2): 134-139.
 - [10] Lu Z Q, Jiang M, Zhang M, Y, et al. Structure and Properties of Para-Aramid Fibrid and Its Para-Phenylene Terephthalamide Paper[J]. Polymer Materials Science & Engineering, 2015, 31(2): 88-92,97.
 - [11] Zhang S F, Li P H, Liu Y, et al. Effect of hot pressing temperature on inter-binding feature between para-aramid fiber and meta-aramid fibrils in composite paper[J]. Acta Materiae Compositae Sinica, 2017, 34(5): 1003-1008.
 - [12] Wei M P, Chai H, Cao Y L, et al. Sulfonated Graphene Oxide as an Adsorbent for Removal of Pb^{2+} , and Methylene Blue[J]. Journal of Colloid & Interface Science, 2018, 524: 297-305.
 - [13] Li W H, Yue Q Y, Gao B Y, et, al. Preparation and utilization of sludge-based activated carbon for the adsorption of dyes from aqueous solutions[J]. Chemical Engineering Journal, 2011, 171(1): 320-327. PBM