Academic Journal of Science and Technology
ISSN: 2771-3032 | Vol. 4, No. 2, 2022

The Study on Kaolin/corn Stalk Composite Adsorbent Materials Prepared by H_3PO_4 Activation Method

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Abstract: Using single factor method and orthogonal experiment,the study takes Kaolin and corn straw as raw materials and H_3PO_4 as activator and dips them in different activator concentration,different kaolin and corn straw mass ratio as well as different impregnation ratio under different conditions, and then carbonize them in low temperature by electric furnace, muff calcining to prepare kaolin/corn straw composite adsorption material.The adsorption capacity for methylene blue solution was characterized by T6 visible spectrophotometer,and automatic specific surface area and porosity analyzer was used to characterize the composite adsorption material under the optimal experimental conditions. The results show that the optimal experimental conditions are: Under the conditions of 25% Concentration of H_3PO_4 , 1:4 mass ratio of kaolin to corn stalk and 2.5:1 impregnation ratio, the adsorption value of methylene blue on the composite adsorbent is 1.116mg/g, the specific surface area is $7.56m^2 \cdot g^{-1}$ and the single specific surface area is $6.82m^2 \cdot g^{-1}$. The microporous volume was $1.24\times10^{-8}mL \cdot g^{-1}$ and the microporous area was $0.57m^2 \cdot g^{-1}$, the results show that the pore structure of the composite adsorbent is not uniform, and there are a lot of micropores and a certain amount of mesopores in the samples.

Keywords: Kaolin, Corn Straw, Zinc Chloride, Composite Adsorption Material.

1. Introduction

EmbroideryCorn stalks account for a large proportion of all kinds of crop stalks, with an annual output of more than 300 million tons. Because it contains rich cellulose and lignin, it is an important raw material for preparing adsorption materials, so it can be reused. Kaolin is a common porous material in nature, but its raw ore purity is not high, leading to its lower adsorption performance, so it needs to be modified to improve its adsorption performance.

H3PO4 activation method has the advantages of low carbonization temperature low cost, relatively low pollution, uniform and stable products, simple equipment demand, and good precipitation performance, which is the primary development direction of adsorption material activation process.

In this experiment, the H_3PO_4 activation method was used to prepare the kaolin/corn straw composite adsorption material. With methylene blue adsorption value as the inspection index, the single factor method and orthogonal experiment were used to determine the most appropriate process conditions for preparing the kaolin/corn straw composite adsorption material, and the specific surface area and pore structure of the prepared composite adsorption material were analyzed to develop and comprehensively utilize agricultural waste corn straw Kaolin resources provide a theoretical reference.

2. Preparation of Composite Materials

(1) Material Science

H_3PO_4,KH_2PO_4,$Al_20_3 \cdot 2Si0_2 \cdot 2H_20$,$C_{16}H_{18}N_3ClS$,Corn straw,$Na_2HPO_4$

(2) Preparation of composite adsorption materials by single factor method

Dry the corn stalks planted in the right wing front banner of Chahar, Ulanqab City, wash them and put them into an oven to dry them to constant weight, then crush them for standby. Weigh a certain amount of kaolin and pretreated corn straw in proportion, put them into a crucible, add H_3PO_4 of different mass concentrations as an activator, stir and mix them evenly, soak the mixed liquid at room temperature for a certain time, filter them, place the filter cake in an electric blast oven at 90 □ for drying, carbonize it in an electric furnace, and then put it into a muffle furnace for calcination at a certain temperature. After it is completely cooled, the sample is loaded to obtain kaolin/corn straw composite adsorption material.

(3) Drawing of methylene blue standard curve

Take 2g/L methylene blue solution as the mother solution, dilute it into methylene blue solutions with concentrations of 2mg/L,4mg/L,6mg/L,8mg/L,10mg/Land15mg/L respectively. With UP water as the reference, measure the absorbance values Aof different concentrations, record the data and draw a graph.

The standard curve is drawn by the absorbance versus the concentration of methylene blue solution. The linear regression equationis A=0.2285C-0.0524 (Aisthe absorbance of methylene blue solution, C is the concentration of solution at a certain time, mg/L), and the correlation coefficient is 0.9972.

3. Study on Adsorption Performance

Take 20mL 7.5mg/L methylene blue solution into iodine measuring flask, weigh 0.1g of composite adsorption material prepared by single factor method, adsorb it in iodine measuring flask for 3h without light, centrifuge, take the upper clear solution and put it into a cuvette, measure its absorbance A at the wavelength of 663nm with T6 visible spectrophotometer, and according to the formula A=0.2285C-0.0524,Qt=(C0-Ct)V/m(C0:initial concentration of methylene blue solution (mg/L), V: volume of methylene blue solution (L), m: mass of activated carbon (g)) Calculate the adsorption amount Qt, and plot and analyze according to the data sheet.design. At present, many designers will actively try embroidery techniques in the process of design, so as to enhance the artistic value of clothing design, and even properly use embroidery techniques in foreign high-definition clothing, so as to further improve the quality of clothing.

It can be seen from Figure 1 that the adsorption capacity increases first and then decreases with the increase of H_3PO_4 mass concentration, which may be because the lignin, hemicellulose and cellulose molecules in kaolin and straw cannot be swelled in low concentration H_3PO_4 solution, and the intermolecular crystalline zone cannot be fully damaged; When the concentration of H_3PO_4 solution is too high, lignin, hemicellulose and cellulose in kaolin and straw will change at high temperature, so intercalated composite materials cannot be formed. When the concentration of H_3PO_4 is 30%, the adsorption capacity is the largest and the adsorption effect is the best. The adsorption value is 0.962mg/g

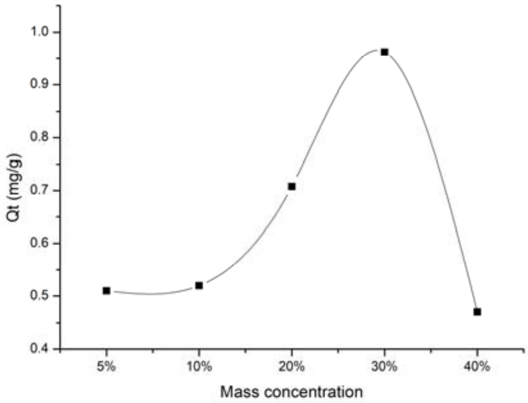

Figure 1. Effect of H_3PO_4 mass concentration on adsorption capacity of composite adsorption materials

It can be seen from Figure 2 that the adsorption capacity first increases and then decreases with the increase of biomass mass. When the biomass proportion is high, it is not conducive to the adsorption of methylene blue. It may be analyzed that when the biomass proportion is high, the excess biomass will insert into the soil layer of kaolin, preventing methylene blue molecules from entering the orbit of kaolin, reducing its adsorption performance . When the mass ratio of kaolin to biomass is 1:4, the adsorption capacity is the largest, and the adsorption value is 1.011mg/g.

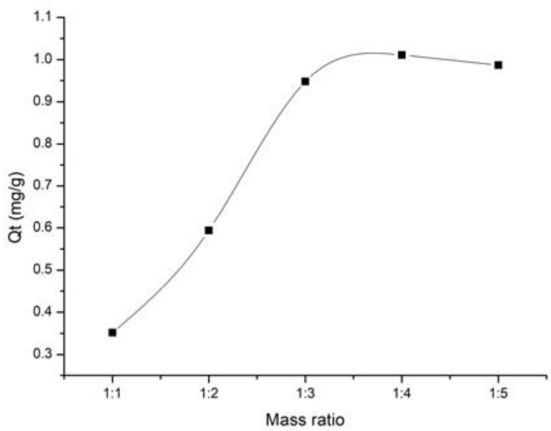

Figure 2. Effect of mass ratio of kaolin to biomass on adsorption capacity of composite adsorption materials

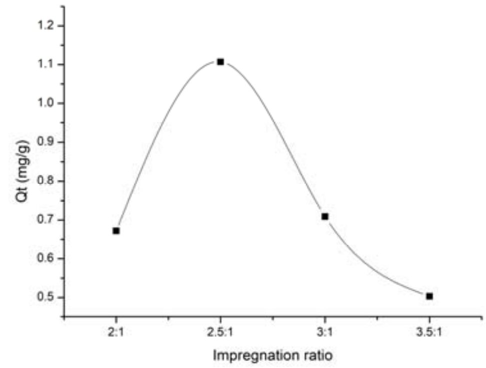

Figure 3. Effect of impregnation ratio on adsorption capacity of composite adsorbent

It can be seen from Figure 3 that the adsorption capacity increases first and then decreases with the change of impregnation ratio. H_3PO_4 has the ability of dehydration and coordination, and plays a skeleton role during activation, making the oxygen atom and hydrogen atom in the carbon containing raw material molecule volatilize mainly in the form of water molecules. The surface area of the mixture is exposed, becoming the internal surface area of the composite adsorption material. However,when the impregnation ratio is large, the adsorption capacity decreases. The analysis may be related to the carbon containing raw materials in biomass and kaolin. The impregnation ratio gradually increases,and the excessive amount of H_3PO_4solution gradually increases, which cannot form intercalated composite materials. The surface area of composite adsorption materials gradually decreases, reducing the adsorption capacity. When the impregnation ratio is 2.5:1,the maximum adsorption amount is 1.107mg/g.

4. Design Orthogonal Experiment to Prepare Composite Adsorption Materials and Study Their Adsorption Properties

In the single factor experiment of preparing kaolin/corn straw composite adsorption material by H_3PO_4 activation method, the best adsorption conditions were: the mass concentration of H_3PO_4 was 30%, the impregnation ratio was 2.5:1, and the mass ratio of kaolin to biomass was 1:4. In order to reduce the error affecting the optimal adsorption conditions, the orthogonal experiment was designed with the adsorption amount of methylene blue adsorbed by composite adsorption materials as a single index, and theH_3PO_4 mass concentration, impregnation ratio, and kaolin biomass mass ratio as three factors. The initial set values of each factor are as follows: Factor A (H_3PO_4 mass concentration): 25%, 30%, 35%; Factor B (immersion ratio): 2.25:1, 2.5:1, 2.75:1; Factor C (mass ratio of kaolin to biomass): 1:3.5, 1:4, 1:4.5. The experimental results are as follows:

Table 1 shows the adsorption amount of methylene blue by kaolin/corn straw composite adsorption material under the conditions of three factors and three levels. It can be seen from the table that R1>R2>R3, factor A (H_3PO_4 concentration) has the largest impact on the adsorption amount of methylene blue, followed by the impregnation ratio, R_1,R_2 is 0.492 and 0.084 respectively, and the smallest impact factor is kaolin: corn straw mass ratio, R_3 is 0.072.

Table 1. Orthogonal Experiment Results

SerialNo	A	B	C	Absorbance	Adsorption capacity
1	25%	2.25:1	1:3.5	0.513	1.096
2	25%	2.5:1	1:4	0.491	1.116
3	25%	2.75:1	1:4.5	0.513	1.096
4	30%	2.25:1	1:4	0.681	0.949
5	30%	2.5:1	1:4.5	0.661	0.967
6	30%	2.75:1	1:3.5	0.737	0.900
7	35%	2.25:1	1:4.5	0.598	1.022
8	35%	2.5:1	1:3.5	0.556	1.059
9	35%	2.75:1	1:4	0.552	1.062
Ij	3.308	3.067	3.055		
IIj	2.816	3.142	3.127		
IIIj	3.143	3.058	3.085		
R_j	0.492	0.084	0.072		

In the horizontal experiment of factor A (H_3PO_4 concentration), since I_1>III_3>II_2, it is better to have a H_3PO_4 concentration of 25%; In the horizontal experiment of factor B (impregnation ratio), II_2>I_1>III_3, so the liquid-solid impregnation ratio 2.5:1 is the best; In the horizontal experiment of factor C (kaolin: corn straw mass ratio), II_2>III_3>I_1, so the proportion of kaolin: biomass 1:4 is the best; It is concluded that the best adsorption condition is A1B2C2, that is, the concentration of H_3PO_4 is 25%, the impregnation ratio is 2.5:1, and the mass ratio of kaolin to corn straw is 1:4. Under this condition, the adsorption capacity of the kaolin corn straw composite adsorption material for methylene blue reached the maximum value of 1.116mg/g.

According to the classification of the IUPAC adsorption isotherm, the N_2 adsorption desorption isotherm belongs to type I. When the relative pressure is low, the adsorption rate is very slow, indicating that the adsorption capacity of the prepared composite adsorption material for N_2 increases slowly with the increase of the relative pressure, indicating that there are a large number of micropores in the sample. In the high pressure area of the relative pressure (P/P_0=0.9-1.0), the curve has an obvious upward trend, indicating that the adsorption capacity of the composite adsorption material is still increasing and there is no saturation state, It shows that the pore structure is not uniform, and it is not simple adsorption of single layer, but also multi-layer adsorption . In the middle area (P/P_0=＞0.4), there is an obvious H4 hysteresis loop. The adsorption curve and the desorption curve of the isotherm do not coincide. At the same time, there is a hysteresis loop, indicating that there are mesopores in the composite adsorption material . It is concluded that there are a large number of micropores and a certain amount of mesopores in this sample, which is conducive to adsorbing some wastewater dyes and organic substances.

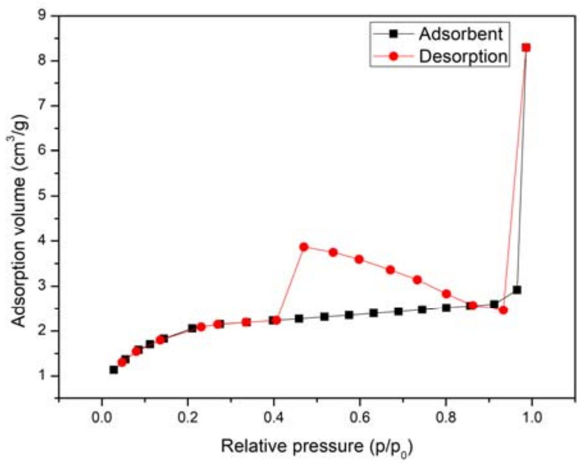

Figure 4. Adsorption desorption isotherms of composite adsorption material

5. Conclusion

In this experiment, kaolin and corn straw were used as raw materials to prepare composite adsorption materials by H_3PO_4 activation method. The best process conditions were determined by single factor method and orthogonal experiment method, and the structure of the prepared composite adsorption materials was characterized. The main conclusions are as follows:

(1) The optimum technological conditions for preparing kaolin/corn straw composite adsorption materials by single factor method are as follows: the mass concentration of H_3PO_4 is 30%, the mass ratio is 1:4, and the impregnation ratio is 2.5:1;

(2) According to the orthogonal experiment of single factor design, the optimal experimental conditions are as follows: the concentration of H_3PO_4 is 25%, the mass ratio of kaolin to corn straw is 1:4, and the impregnation ratio is 2.5:1. Under this condition, the specific surface area of the composite adsorption material is7.56m^2/g, the specific surface area of a single point is 6.82m^2/g, and the micropore volume is 1.24×

10^{-8} mL/g, micropore area 0.57 m^2/g, and the adsorption capacity of methylene blue is 1.116mg/g.

(3) According to the test and analysis of specific surface area and pore diameter, the pore structure of the prepared composite adsorption material is not uniform, there are multi-layer adsorption phenomena, and there are a lot of micropores and a certain amount of mesopores.

(4) Although the specific surface area of the composite adsorption material after activation modification is larger than that of the original kaolin, it does not increase much. In the later stage, the experimental method needs to be improved to prepare products with larger specific surface area.

Acknowledgment

The author would like to thank Jining Normal University for its financial support of the key university level project (jsky 2019009).

References

[1] HE Longqiang, HU Peng, LIU Zhongyang. Preparation of composite super absorbent resin from kaolin and corn straw [J]. Jiangsu Agricultural Science 2017,45 (23): 296-298

[2] LI Weixin, CAO Xiangyu, TIAN Junyang Study on the adsorption performance of mixed adsorbent of activated carbon and kaolin for methylene blue [J]. Leather and Chemical Industry, 2021, (01): 6-8+30

[3] XIN He, ZHANG Na, CHAI Yangyang, GUO Qingqi. Preparation and characterization of thin skinned walnut shell based activated carbon [J]. Journal of Central South University of Forestry and Technology, 2021 (02): 176-183

[4] WANG Zuoying. Supporting the comprehensive utilization of straw is an effective model to achieve targeted poverty alleviation [J] China Economic and Trade Guide, 2018 (10): 46

[5] ZHU Ling, KANG Chunli, TIAN Tao, etal. Preparation of hickory shell corn straw mixed based activated carbon by zinc chloride method [J]. Science, Technology and Engineering, 2017, 17 (23): 115-119.