Preparation of the sludge activated carbon with domestic sludge mixed agricultural straw

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Abstract. Urban sewage sludge with complicated composition produce largely each year, pollution problem and resource utilization has increasingly become the focus of attention. Sewage sludge is utilized to prepare adsorbent that is a new type method. Agricultural stalks was added to material (urban sewage sludge) and activator (ZnCl₂), calcined under the condition of no inert gas, and obtained domestic sludge activated carbon. The properties were measured by iodine adsorption value and BET, discussed influence factors of sludge activated carbon preparation, including activator concentration, solid-liquid ratio, calcific temperature and calcific time. The best process condition of orthogonal experiment had explored that activated time is 10 minutes, calcific temperature is 350°C, the activator concentration ZnCl₂ is 3 mol/L and the mixing ratio of raw materials and activator is approximately 1:5. The iodine adsorption value and the optimal BET of as-obtained domestic sludge activated carbon is 445.06 mg/g, 525.31 m²/g, respectively.

1. Introduction

Urban sludge is composed of organic and inorganic substance that contains a variety of fungi and protozoa constitute, its content was 60%~70%. The activated carbon can be made of residual activated sludge through high temperature carbonization and activation, for instance, Rozada [1] Jevaseelan [2] prepared sludge activated carbon with ZnCl₂, the results showed that the ZnCl₂ activation effect is superior to other activator. As-obtained sludge adsorbent with ZnCl₂ as activating agent, research think ZnCl₂ chemical activation is very outstanding that the effect is very good as activator [3]. Tay [4] on the premise of ZnCl₂ as activator, to explore the domestic sludge optimum process condition of preparation of activated sludge carbon. The results show that the activated sludge carbon specific surface area of 867.61 m²/g, when concentration of ZnCl₂ is 5 mol/L, the activation temperature is 500°C, the activation time is 2 h. And so Ren Ai-ling [5] utilize the traditional activated carbon preparation technology, with ZnCl₂ as activator, under optimal technological condition that 40% of ZnCl₂ solution, the activation temperature is 600°C, the activation time 20 minutes, solid-liquid ratio of 1:2~1:3, as-obtained product iodine adsorption value is 514-542 mg/g.

In this study, the activator is zinc chloride solution, the preparation of the sludge adsorbent under the condition of without inert gas protection and use of urban sludge and agricultural straw to calcine. We could determine the product quality by iodine adsorption value, however, optimal reaction condition was necessary to be determinated by orthogonal experiment. The influence factors of sludge activated carbon preparation, including activator concentration, solid-liquid ratio, calcific temperature and calcific time were investigated systematically.
2. Experiment section

2.1. Experimental materials and Instrument
Urban sludge taken sample from the xianyang road wastewater treatment plant in tianjin, the experiment used instruments including: disintegrator, electric heating air-blowing drier, muffle furnace, desktop thermostatic oscillator, molecular sieve. The reagents used in the experiments including: ZnCl₂(AR), HCl(LR), Na₂S₂O₃(AR), iodine standard solution(AR).

2.2. The preparation of sludge activated carbon
The experimental materials adopt domestic sludge moisture content of 89.2%, the reagents used in the test, respectively, 0.5 mol/L hydrochloric acid standard solution configuration, 0.5 mol/L sodium thiosulfate solution configuration, 1 g/L starch indicator configuration, the configuration of a solution of different concentrations of ZnCl₂, iodine standard solution configuration.

2.3. The preparation of activated carbon from digested sewage sludge test
In a typical procedure, the crushed reed straw was put into the solution containing domestic sludge with 3 mol/L concentration of zinc chloride solution impregnated and activated the mixture. The sample was reacted for a day and filtered, and then calcined at 400°C for 15 min in a muffle furnace. After it was cooled down to room temperature, the sample was removed from the autoclave, rinsed with dilute hydrochloric acid, and dried at 60°C in an oven. Through the single factor experiment to determine the single factor effect on the properties of adsorbent, this experiment by orthogonal experiments to determine the experimental parameters: the optimum process conditions of activator concentration, solid-liquid ratio, calcific temperature and calcific time.

3. Results and discussion

3.1. No agricultural straw doping to prepare sludge adsorbent

![Graphs showing the influence of different factors on the iodine adsorption value: (a) ZnCl₂ concentration, (b) temperature, (c) time and (d) solid-liquid ratio.](image-url)
The single factor experiment curve graph of sludge adsorbent without agricultural straw doping obviously reveals different factors impact on the iodine adsorption value, as shown as figure 1. The optional experimental conditions of sludge adsorbent without agricultural straw doping can be clear shown that activator concentration of ZnCl$_2$ is 3 mol/L, calcific temperature is 350°C, calcific time is 15 minutes and the mixing ratio of raw materials and activator is 1:4.

3.2. Doping of agricultural straw to prepare sludge adsorbent

![Figure 2](image-url)

**Figure 2.** The influence curve of different factors on the iodine adsorption value: (e) ZnCl$_2$ concentration, (f) temperature, (g) time and (h) solid-liquid ratio

The single factor experiment curve graph of sludge adsorbent with agricultural straw doping obviously reveals different factors impact on the iodine adsorption value, as shown as figure 2. The optional experimental conditions of sludge adsorbent without agricultural straw doping can be clear shown that activator concentration of ZnCl$_2$ is 3 mol/L, calcific temperature is 350°C, calcific time is 10 minutes and the mixing ratio of raw materials and activator is 1:4. Compared with no agricultural straw doping, the optional experimental conditions of sludge adsorbent are similar, the difference is that calcific time becomes shorter. This may increase the porosity of the sludge, tend to maximize the specific surface area.

3.3. Orthogonal experimental design and analysis

The orthogonal experiment of preparation of sludge adsorbent with domestic sludge and reed straw, as summarized in the table 1 and table 2. Data analysis and experimental results show the important sequence of factors are calcification temperature, calcification time, solid-liquid ratio, activator concentration, respectively. The optional experimental conditions of sludge adsorbent can be
determined by orthogonal test that activated time of 15 minutes, calcific temperature is 350℃, activator concentration of ZnCl₂ is 2 mol/L, the mixing ratio of reed straw and domestic sludge is 1:5. The highest adsorption capacity of the best product in standard iodine is 380.90 mg/g.

Table 1. Factors and levels of orthogonal experiment

| Level | A==Calcific time/min | B==Calcific temperature/℃ | C==Activator concentration/(mol/L) | D==Solid-liquid ratio |
|-------|----------------------|---------------------------|-----------------------------------|-----------------------|
| 1     | 10                   | 300                       | 2                                 | 1:3                   |
| 2     | 15                   | 350                       | 3                                 | 1:4                   |
| 3     | 20                   | 400                       | 4                                 | 1:5                   |

Table 2. Results of orthogonal experiment

| Test number | Factor | Iodine adsorption capacity (mg/g) |
|-------------|--------|-----------------------------------|
| Test number | A      | B      | C      | D      |                               |
| 1           | 1      | 1      | 1      | 1      | 317.56                         |
| 2           | 1      | 2      | 2      | 2      | 351.79                         |
| 3           | 1      | 3      | 3      | 3      | 378.86                         |
| 4           | 2      | 1      | 2      | 3      | 351.78                         |
| 5           | 2      | 2      | 3      | 1      | 379.99                         |
| 6           | 2      | 3      | 1      | 2      | 349.68                         |
| 7           | 3      | 1      | 3      | 2      | 285.35                         |
| 8           | 3      | 2      | 1      | 3      | 380.9                          |
| 9           | 3      | 3      | 2      | 1      | 288.79                         |

K₁: 1048.21 954.69 1048.14 986.34
K₂: 1081.45 1112.68 992.36 986.82
K₃: 955.04 1017.33 1044.2 1111.54
k₁: 349.4 318.23 349.38 328.78
k₂: 360.48 370.89 330.79 328.94
k₃: 318.35 339.11 348.07 370.51
Range: 42.13 52.66 18.59 41.73

Important order: B>A>D>C
Optimal levels: A₂, B₂, C₁, D₃
Optimal combination: A₂B₂C₁D₃

The orthogonal experiment of preparation of sludge adsorbent with domestic sludge and peanut shells, as summarized in the table 3 and table 4. Data analysis and experimental results show the important sequence of factors are calcific time, solid-liquid ratio, calcific temperature and activator concentration. The optional experimental conditions of sludge adsorbent can be determined by orthogonal test that calcific time of 10 minutes, calcific temperature is 350℃, activator concentration ZnCl₂ is 3 mol/L, the mixing ratio of activator and raw materials is 1:5. The highest adsorption capacity of the best product in standard iodine is 445.06 mg/g.
Table 3. Factors and levels of orthogonal experiment

| Level | A==Calcific temperature/℃ | B==Solid-liquid ratio | C==Activator concentration/(mol/L) | A==Calcific time/min |
|-------|--------------------------|----------------------|-----------------------------------|---------------------|
| 1     | 300                      | 1:3                  | 2                                 | 10                  |
| 2     | 350                      | 1:4                  | 3                                 | 15                  |
| 3     | 400                      | 1:5                  | 4                                 | 20                  |

Table 4. Results of doping reed lever of orthogonal experiment

| Test number | F  | A  | B  | C  | D  | Iodine adsorption capacity (mg/g) |
|-------------|----|----|----|----|----|----------------------------------|
| 1           | 1  | 1  | 1  | 1  | 1  | 349.82                           |
| 2           | 1  | 2  | 2  | 2  | 2  | 318.01                           |
| 3           | 1  | 3  | 3  | 3  | 3  | 349.61                           |
| 4           | 2  | 1  | 2  | 3  | 3  | 381.58                           |
| 5           | 2  | 2  | 3  | 1  | 3  | 381.81                           |
| 6           | 2  | 3  | 1  | 2  | 2  | 380.82                           |
| 7           | 3  | 1  | 3  | 3  | 2  | 318.01                           |
| 8           | 3  | 2  | 1  | 3  | 3  | 317.44                           |
| 9           | 3  | 3  | 2  | 1  | 1  | 445.06                           |
| K_1         |    | 1017.44 | 1049.41 | 1048.08 | 1176.69                     |
| K_2         |    | 1144.21 | 1017.26 | 1144.65 | 1016.85                     |
| K_3         |    | 1080.51 | 1175.49 | 1049.43 | 1048.63                     |
| k_1         |    | 339.15  | 349.8    | 349.36  | 392.23                      |
| k_2         |    | 381.4   | 339.09   | 381.55  | 338.95                      |
| k_3         |    | 360.17  | 391.83   | 349.81  | 349.54                      |
| Range       |    | 42.25   | 52.74    | 32.19   | 53.28                       |
| Important order |    | D>B>A>C                                        |
| Optimal levels | A_2 | B_3 | C_2 | D_1 |
| Optimal combination | A_2 B_3 C_2 D_1 |

3.4. The test result of SEM

![Figure 3. SEM images of sludge adsorbent](image)
The SEM images of sludge adsorbent (figure 3) shows similar spherical particles, particle size of nanoscale materials with the size of 200 nm. It is noticed that the major pore size distribution of sludge adsorbent relatively disperse, the formation of this humble pore structure may be the evaporation of moisture and organic small molecules escape in the process of thermal decomposition. The mixture of urban sludge and agricultural straw under the catalysis of activator ZnCl₂ at high temperature calcination, restrained effectively organic carbon decomposition and escape, in favour of adequate mixture and carbonization of organic at high temperature.

3.5. The test result of BET

![Figure 4 N₂ stripping - adsorption isotherm of the sludge adsorbent](image)

(a) the urban sludge mixed reed straw and (b) the urban sludge mixed peanut shells

Specific surface area of the adsorbent (BET) is one of the important factors affecting its properties, so we test the sludge adsorbent mass N₂ stripping - adsorption isotherm. As shown in figure 4, compared to the urban sludge mixed reed straw, coincidence degree of the urban sludge mixed peanut shells is better, this isotherm type is similar to mesoporous material type. The specific surface area of sludge adsorbent materials are 428.15 m²/g and 525.31 m²/g, respectively. High specific surface area and mesoporous structure can improve the contact area of tested material and sludge adsorbent, therefore, we need to prepare as-obtained sludge adsorbent with good adsorption properties.

4. Conclusion

This experiment provides a new way for utilization of the domestic sludge resource and agricultural straw resource. This novel of this experiment is that preparation of calcific sludge adsorbent under no inert gas protection made a systemic analysis of affecting factors of the experiment. Considered fully the effect of single factor on preparation of sludge adsorbent, the single factor tests are individually established. Then optimum condition of sludge adsorbent with doping agricultural straw is that ZnCl₂ is 3 mol/L, calcific temperature is 350°C, calcific time is 10 minutes and the mixing ratio of raw materials and activator is 1:4. And optimum condition of sludge adsorbent without doping agricultural straw is that activator concentration ZnCl₂ is 3 mol/L, calcific temperature is 350°C, calcific time is 15 minutes and the mixing ratio of raw materials and activator is 1:4.

The above-mentioned orthogonal experiments were adopted to determine the optimum process conditions of sludge activated carbon prepared by domestic sludge mixed reed straw or peanut shell. Analysing orthogonal experiment data, optimal combination and data of the factors are determined. The SEM images of sludge adsorbent with optimal combination show that sludge adsorbent particle size is nanoscale and the material aperture is mesopore, the formation of material tends to maximize specific surface area and pore size. And two groups BET tests indicate that BET of product with
domestic sludge mixed reed straw is 428.15 m²/g, BET of product with domestic sludge mixed peanut shell is 525.31 m²/g. Thus, the sample with domestic sludge mixed peanut shell is the best sludge adsorbent.

References
[1] Rozada F, Otero M and Moran A 2005 J. Hazard. Mater. Activated carbons from sewage sludge and discarded tyres: production and optimization 124 181
[2] Jeyaseelan S and Gao Q L 1996 Wat. Sci. Tech. Development of Adsorbent/Catalyst from Municipal Wastewater sludge 34 499
[3] Zan W B, 2005 Chang sha:Hu nan university Academic research on adsorbent derived from sewage sludge based on chemical activation method and its application 57 58
[4] Tay J H, Jeyaseelan S and Graham N S 2001 Chemosphere Optimising the preparation of activated carbon from digested sewage sludge and coconut husk 44 45
[5] Ren A L, Wang Q S and He J 2004 Environ. Sci. Study on activated carbon produced with sewage sludge 25 48