The modification and application of Sewage Sludge based in heterogeneous Fenton-like system

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Abstract. In this study, dewatered domestic sewage sludge of moisture content of 65.6% was used as a pore-forming agent to sinter Ceramics with kaolin clay, coal ash and sodium silicate at 1050-1100 °C for 20 min. The weight percentage of sludge of total dried solids was 60% with pore rate >45% and compressive >20 MPa. The Ceramics could be used as catalysts in heterogeneous Fenton-like system to treat phenol wastewater through modification by FeSO₄ solution. After reaction with ceramics catalyst for 2.5 h, phenol removal of the wastewater could reach 99.87% from 100 mg/L to 0.13 mg/L and the COD removal is 85.75%. The performance of this catalyst was stable and had no significant in 30d repeat experiments.

1 Introduction

Yu et al. [1] Fenton oxidation as an advanced oxidation method is commonly used in water refractory organic pollutants treatment [2]. Homogeneous Fenton reaction has a high catalytic efficiency, but it will produce a large iron mud, increasing the processing costs, causing secondary pollution due to the loss of the catalyst in the process [3]. While homogeneous Fenton reaction gradually attracted much attention since it is possible to overcome these drawbacks [2, 4]. The catalyst is more prepared by the active metal component to the carrier in heterogeneous Fenton reaction system [7, 9]. Currently, the focus of its research is centered on the development of the catalyst carrier and the optimization of reaction system conditions [10, 11] The porous ceramic as an important support material, has become a subject of intense interest including using of sludge to prepare porous ceramics.

Sludge contains organic matter [12, 14] Si, Al and other elements and can make to porous materials. Organic matter can be pore formation agent by adjusting content of Si, Al and adding binders such as clay [15, 16]. At present, these kinds of materials are used in construction ceramic or biological sewage treatment and other media. The porosity of construction ceramic is closed-cell structure, high strength, low density and used as a lightweight aggregate for construction, roadbed. Fillers and carriers is the open-cell structure, requiring large surface area and strong adsorption capacity; Ceramic filler with biofilm is for biological wastewater treatment processes [17, 19]; The porous ceramic as a catalyst carrier is coated with modifier on its surface by physical or chemical means to improve the adsorption capacity or the specific surface area of the carrier [20,

21], thereby increasing the catalytic effect. When producing the open-cell ceramic of high porosity, vitreous cannot be formed on the surface of the particles to avoid a closed cell, and at the same time, it requires the internal components fully melted with sufficient physical strength. Therefore, sintering temperature and sintering time control requirements is higher than making closed cell ceramic. In this paper, various raw materials like sludge and clay are used to prepare to porous carrier material for catalyst in heterogeneous Fenton-like system of wastewater catalytic oxidation by a certain sintering curve which has a high porosity, excellent adsorption and switching properties, good mechanical strength and stable chemical properties.

2 Experimental details

2.1 Chemicals

Kaolin clay, GR, 1250 mesh screens, Shanxi ju feng co., LTD.; coal ash, 800 mesh screens, a coal-fired power plant; water glass, AR, mod 3.1-3.4, Dujiangyan Hongyu plastic factory in Sichuan province; FeCl₃, AR, Huihong reagent co., LTD. in Hunan province. The dewatered sludge was taken from a municipal wastewater treatment plant, 34.4% concentration of solids and 65.6% of moisture content. Organic matter was 51% and inorganic matter was 49%. Inorganic matters contained Al₂O₃, SiO₂, FeO, CaO and covered 43.75% of the solids, 89.3% of the inorganic matters.

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2.2 Materials Preparation

Deeply dehydration urban sewage sludge was crushed and added kaolin clay, coal ash and water glass in addition of $38\% \pm 2\%$ moisture, and mixed by a mixer, and squeezed into columnar blank of $\phi 3$ mm by granulator, constant temperature dried for 4 h at 105°C , then cut off to short columnar dry blank. Dry blank was then sintered in an electric muffle in air atmosphere, and charged at temperature of 500°C by $10^\circ\text{C}/\text{min}$, then maintained at this temperature for 40 min, and charged at temperatures of $1000\text{--}1200^\circ\text{C}$ by $10^\circ\text{C}/\text{min}$, then maintained at this temperature for 30 min and left them to cool naturally to get Ceramics.

Ceramics was soaked in 0.05 mol/L FeCl_3 solution for 12 h, liquid to solid ratio was 5:1, and dried at 105°C after filtering solution. After that the Ceramics was calcined at 650°C for 2 h, and gained heterogeneous Fenton-like catalyst after naturally cooling.

2.3 Catalyst Application Experiments

Filling the modified catalysts in a 500 ml glass packed column to prepare simulated phenol wastewater with concentration of 100 mg/L , then adjusting the pH to 6 and the amount of H_2O_2 was 30 mmol/L . Take 1 L wastewater to go through the catalysts packed column by upper-lower path and have cyclic reaction of 3 h. Detect the change of the COD value and the phenol content both before and after treatment, and compare the catalytic effect of homogeneous Fenton, zeolite catalyst, Al_2O_3 ball catalysts. Wastewater (phenol content: 100 mg/L , pH = 6, H_2O_2 : 30 mmol/L) go through the catalysts packed column by upper-lower path with residence time of 2.5 h. Use the prepared ceramic as the heterogeneous catalyst for a continuous month experiment.

2.4 Analytical Methods

TG characteristics of sludge and Ceramics were determined by SDTQ600 simultaneous thermogravimetric analysis (TA co., LTD.), heating rate was $10^\circ\text{C}/\text{min}$ and max temperature was 1200°C . Porosity and apparent density were determined by physisorption analyzer (ASAP2020HD88, micromeritics co., LTD.). Surface and section morphology of Ceramics were determined by SEM (Helios Nanolab 600i, FEI co., LTD.). Phase identification of Ceramics and modified Ceramics was determined by XRD (siemens co., LTD.). COD value was determined using the traditional dichromate method in accordance with the standard methods issued by the China National Environmental Protection Agency.

3 Results and analysis

3.1 Raw Material Characterization

From Figure 1, sludge DTG curved has four obvious weightlessness interval, $0\text{--}155^\circ\text{C}$, $175\text{--}355^\circ\text{C}$, $350\text{--}505^\circ\text{C}$, $505\text{--}615^\circ\text{C}$, with weightlessness of 5.02% , 26.62% , 14.90% , 3.17% , respectively. The weight loss of sludge

become small after the temperature is higher than 615°C , and the total weight loss is 51.72% until 1200°C . The loss of the first part due to the structured water evaporation and volatile substances volatile of sludge; According to the Conesa's research results, the second part loss results from the degradation process by biomass, in which produce a lot of combustible gas and release heat. The weight loss rate reaches the maximum at the temperature of 254.1°C . The third part loss component is mainly organic polymers in cell and sludge stabilization process or natural polymers in the original material. The fourth part is mainly cellulose and other refractory substances [22]. There are two distinct segments of weightlessness in blank DTG curve c. The main weight loss interval is $175\text{--}355^\circ\text{C}$ with 10.70% loss. The weight loss rate reached the maximum when the temperature is 273.5°C . It has increased by about 20°C when compared to the sludge temperature at the maximum rate of weight loss. Followed by $345\text{--}440^\circ\text{C}$, which the weight loss is 2.94% . The blank total weight loss is 17.98% to 1200°C . When the temperature reaches 500°C , sludge and ceramic blank weight loss are 46.54% , 17.15% respectively. Choose the calcining temperature of 500°C for most of the volatile organic compounds have been burning and the pores are formed inside the ceramic.

Fig. 1. Material TGA (a) Ceramics dry blanks TG curve, (b) sludge TG curve, (c) Ceramics dry blanks DTG curves, (d) sludge DTG curves. Blank raw material composition: 55% sludge (moisture content 65.6%), kaolin 30%, 7.5% sodium silicate, 7.5% ash.

3.2 Effect of Sintering Temperature on Porous Materials

As the sintering temperature increases, the porosity rate of Ceramics decreases. From the Figure 2, the porosity rate changed little in the range of $1000\text{--}1050^\circ\text{C}$ because the pores during this period are formed due to the combustion of organic matter. While the temperature is above 1050°C , the silicon oxide, aluminum oxide and other substances start to liquefy and fully melt, thus fill the pore, and the volume is compressed, resulting in decreased porosity, increased density and compressive strength. When producing lightweight aggregate and other closed-cell ceramic, it takes more than 1150°C sintering temperature. In this research, the alkali metal oxide component is high, and the formation of low-temperature eutectic with alumina and silicon oxide

improves the content of the liquid phase and reduces the sintering temperature.

Fig. 2. Effect of sintering time on ceramics.

3.3 Effect of Sintering Time on Porous Materials

During sintering, the ceramic material begins to melt from the point to the surface, the surface to the interior. The material molten and crystallization are insufficient and the strength is relatively small due to the short time. From the Figure 3, when sintering 10 mins under the temperature of 1100 °C, compressive strength is only 18.7 MPa and a porosity rate of 43.24%. With the extension of sintering time, the substances melt sufficiently, and the formed aluminosilicate has better physical framework strength. Due to the strong strength and porosity rate for a long time, the ceramics start a closed shrink from the surface to the inside, and the porosity rate decrease while the strength increase. After sintering 40 min at the 1100 °C, the compressive strength is up to 30.3 MPa with a porosity of 28.92%.

Fig. 3. Effect of sludge addition on ceramics.

3.4 Effect of Sludge Addition on Porous Materials

The strength of Ceramics is reduced with the increasing amount of the sludge. The increase of the amount of the sludge results in the increase of organic porogen, gas production and porosity rate. The porosity rate reached 52.46% when sludge dosage is 60% and sintering 20 mins under the temperature of 1050 °C. The compressive strength is reduced with the increased porosity rate. The higher the porosity, the smaller the compressive strength is. The inorganic mineral starts to melt and liquefied under 1050-1150 °C. The more sludge is added, the higher porosity and faster melt rate are. And the porosity decrease when sintering temperature increase. When added to the 60% of the sludge, the porosity can be reduced 26.09%. When the temperature is above 1150 °C, little change in the porosity with a difference of below 1%. In this case, the porosity is a closed cell. Pore structure will change, but little change in pore volume.

3.5 Catalyst SEM and XRD Characterization Analysis

The weight loss decrease of the ceramics is smaller than 0.5% after soaking 72 h with 1:1 hydrochloric acid. The heavy metals Cr, Ni content in sludge is high due to some industrial wastewater in the municipal wastewater treatment plant. They are solidified in high temperature sintering process, thus stabilized. The toxic heavy metal dissolution rate of obtained material is very low with less than 1%. The concentration of heavy metals in the

leachate is far below the national hazardous waste leaching standard and landfills leaching standard. The leaching toxicity heavy metal is very low.

From SEM pictures of particles of Figure 4, they are open-cell structure with a pore size of several hundred nanometers and roughness surface of good adsorption and exchange properties.

The ceramic samples are mainly oxides and silicate crystal. From Figure 5, there are a lot of mullite ($\text{Al}_6\text{Si}_3\text{O}_{13}$) characteristic peaks in the range of $2\theta = 10^\circ$ – 90° , and the strongest peak appears at $2\theta = 26.78^\circ$, indicating it's the main substance in ceramics. Characteristic peak is also very strong at $2\theta = 26.22^\circ$, indicating the content of kyanite (Al_2SiO_5) is also high. As it can be seen that the sintered ceramics have high crystallinity, good heat resistance and thermal stability. In addition, there are also characteristic peaks of $\text{Ca}_3\text{Al}_2\text{O}_6$ ($2\theta = 33.32^\circ$), Mg_4Zn_7 ($2\theta = 21.00^\circ$), $\text{Fe}_7\text{SiO}_{10}$ ($2\theta = 64.77^\circ$) and other substances, because the sludge contains high Ca, Mg, Fe and other elements. Compare the characteristic peaks between a and b, it is found that the peak of $\text{Fe}_7\text{SiO}_{10}$ increased, indicating the Fe content in the catalyst increases and has entered the crystal lattice which is not easily dissolved.

Fig. 4. Ceramics's SEM (a) porous Ceramics surface (b) a porous Ceramics sectional.

Fig. 5. Ceramic XRD pattern (a) catalyst, (b) fired ceramic.

3.6 Catalytic Oxidation Verification Experiment

As shown in Figure 6, there is a comparison between the heterogeneous Fenton reaction of ceramics a, zeolite b, alumina balls catalyst c and homogeneous Fenton reaction of liquid catalyst d (ferrous sulfate solution). As for the degradation catalytic effect to phenol, d is superior to a, while a is superior to b and c, and the difference between b and c is not significance. When the

reaction time is about 60 min, d has a 14% higher removal rate to phenol than a, it is because the reactants are well mixed in homogeneous system, and the reaction rate is much faster. While in the a catalytic reaction, there is a decrease in the number of active sites for the catalytic decomposition of

H_2O_2 on the surface of the catalyst, thus affect the $\bullet\text{OH}$ radical generation rate, which reduces the rate of reaction system. It is because the concentration of phenol is relatively high and the competitive adsorption between phenol molecule and its degradation intermediates occurs on the catalyst surface. The catalytic results have little difference between a and d until 2 h, respectively, 91% and 93%. Because phenol content is low, and the generation rate and the effective utilization rate of $\bullet\text{OH}$ radical not vary much. In the first 0.5 h, there is no apparent difference among a, b, and c. Later the disparities increase is because the acid dissolution rate of b and c reached 3%. During the reaction, there is a certain waste of the catalyst that makes the reaction rate slow down.

Fig. 6. Different catalysts to COD removal efficiency.

3.7. Service-Life of Ceramic Catalyst

As shown in Figure 7, A reactor is employed to study the service-life of the ceramic catalyst, and the operation strategy is introduced in Section 2.3. In the Figure 8, as for the simulated phenol wastewater, the effluent phenol content is less than 1 mg/L after 30 days of continuous operation process using the ceramic catalyst with more than 99% of phenol removal efficiency and 83.0–85.5% of COD removal efficiency. It shows that ceramic catalysts have relatively stable treatment effect to the phenol containing wastewater. From the SEM image, it can be seen that there is no debris attached to the inner surface of the pores and has angular, indicating a strong adhesive force. And the XRD pattern of the catalyst shows that Fe has entered the crystal lattice and not easy to be dissolved, therefore the material life is relatively long.

4 Conclusion

The catalyst prepared in this research is a porous material which has a good strength that compressive strength can

reach 20-30 MPa, stable chemical performance that acid output rate is less than 0.5%, a higher ratio of surface area and porosity rate that porosity rate is more than 45%, a good adsorption performance and exchange performance which increase the contact between the catalyst and waste water, oxidizer system so that improve the catalytic efficiency. Ceramic used as the catalyst in phenol wastewater treatment can remove 99.85% of phenol after reaction for 2.5 h. Reactor running for 30 days, effluent phenol content is less than 1 mg/L and the removal rate stabilized at 99%. These indicate that the effect of ceramic catalyst is better than the zeolite catalyst and alumina ball.

Fig. 7. Continuous operation device of catalyst.

Fig. 8. The catalyst effect.

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