Ba, Co modified activated clay and their adsorption performance characterization

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Abstract. A series of modified activated clay composite materials were prepared by solvothermal method. The modified samples were tested and characterized by a series of instrument methods. The modified activated clay materials with good adsorption effect, simple process and low cost were synthesized by doping different metal ions. The adsorption properties of the modified activated clay materials were investigated. The results show that the (Ba, Co)-activated clay modified samples can be used as adsorbents to remove Congo red organic dye wastewater, and the activity is greatly improved compared with the activated clay, the adsorption capacity is greatly enhanced. The particle size is small, and it has good thermal stability. When the initial Congo red concentration is 100 mg/L and the adsorption time is 140 minutes, the maximum adsorption capacity of Ba-activated clay is 371 mg/g, and that of Co-activated clay is 338 mg/g.

1. Introduction
In recent years, China's sewage treatment project is imminent, because the activated clay has excellent decolorization, adsorption, catalysis and ion exchange properties [1-4]. At present, the state and local governments attach great importance to wastewater treatment. However, the average treatment rate of Congo red and other dye wastewater in China is not very high due to the large amount of discharged dye wastewater, difficult degradation, high content of organic matter, high alkalinity, deep color and high COD [5-6]. For this reason, many scholars at home and abroad are committed to low-cost natural mineral materials such as clay, zeolite, carbon to remove organic matter or heavy metal ions in wastewater [7-10]. The surface silica structure of natural clay has strong hydrophilicity and the hydrolysis of a large number of exchangeable cations between layers, so there is usually a thin water film on its surface, which can not effectively adsorb hydrophobic organic matter, limiting its application. Therefore, in order to meet the needs of different industries and improve the application effect of activated clay products, it is necessary to modify the natural clay. After high-temperature calcination, acid or oxidation, doping and other activation treatment processes, the removal rate of Congo red and other dye organics and chromaticity in wastewater is significantly improved, the specific surface area is increased, the pore structure is loose, and the adsorption performance is improved [11-13].
In view of the development and trend of Congo red organic dye wastewater treatment, considering that the prepared products can not cause secondary pollution to the environment, low cost and easy availability, a series of modified activated clay samples were synthesized. The modified samples were tested by scanning electron microscope (SEM), thermogravimetry differential scanning calorimetry (TG-DSC), X-ray diffraction (XRD), infrared spectroscopy (FT-IR) and other methods. It is of great practical significance to study the economic and effective wastewater treatment technology [14-16].

2. Experimental
The modified activated clay was modified activated clay (AC) of 4.0g bentonite, For short, MAC), 2.0g barium chloride (analytical pure), 2.0g sodium hydroxide (analytical pure), 20mL of distilled water shall be taken, stirred by magnetic stirrer for one and a half hours, and then placed in ultrasonic cleaner for 2 hours to make it mix evenly distributed, and the mixture shall be poured into the reactor, and placed in the oven at the temperature of 80 ℃, and taken out after 15 hours, and then the mixture shall be put into the reactor. After filtration and washing, half of the samples are poured into the small crucible, put into the oven for 7 hours, and the set temperature is 120 ℃, the other part is poured into the small crucible and put into the oven for 12 hours, and the set temperature is 120 ℃, and the dried samples are ground into powder respectively. Similarly, 4.0g of active clay, 2.0 g of cobalt chloride (analytical pure), 2.0 g sodium hydroxide (analytical pure), 20mL of distilled water were measured to prepare the active clay doped with cobalt. Then, the modified samples were tested and characterized by a series of methods.

The morphology of the modified activated clay was analyzed by Hitachi SU8010 cold field emission scanning electron microscope. The structure was characterized by Rigaku smartlab 9 KW X-ray diffractometer (Cu Kα radiation, wavelength 0.154056 nm), Nicolet Fourier transform FT-IR 850 infrared spectrometer. Netzsch TG-DSC comprehensive thermal analyzer was used to test thermogravimetric analysis, and UV-2501 PC ultraviolet visible absorption spectrometer was used to test visible absorption spectrum.

3. Results and discussion
The SEM images of a series of activated clay in figure 1 show that the particles are relatively loose and dispersed, and can not effectively adsorb Congo red dye, while the surface structure of the particles passing through (Ba, Co)-activated clay is relatively compact, which is conducive to adsorbing Congo red and other substances. According to the different time of Ba-activated clay reaction and drying, the mixing time is 1.5 hours, the reaction time is 15 hours at 80 ℃ and the drying time is 120 ℃. The results show that the composite prepared by drying for 12 hours is more compact than the composite prepared by stirring for 0.5 hours, reacting at 80 ℃ for 15 hours and drying at 120 ℃ for 7 hours, and the particles are relatively small, which is more conducive to the adsorption of organic matter. The surface morphology of Ba-activated clay is smaller than that of Co activated clay, and the particles of Co-activated clay may be slightly aggregated into flakes.
In the infrared spectrum of (Ba, Co)-activated clay, 3632 cm\(^{-1}\) absorption peak is active, Al-O-H stretching vibration band in the structure of activated clay, 1662 cm\(^{-1}\) O-H bending vibration band, 1018 cm\(^{-1}\) ~ 1237 cm\(^{-1}\) asymmetric stretching vibration band of Si-O-Si, 527 cm\(^{-1}\) and 465 cm\(^{-1}\) bending vibration band of Si-O-Al and Si-O-Si in the structure of activated clay, 3632 cm\(^{-1}\) and 1058 cm\(^{-1}\) asymmetric stretching vibration band of natural clay. The characteristic absorption peaks of Al-O-H and Si-O-Si appeared at 1439 cm\(^{-1}\), which indicated that the doped Ba and Co formed a stable structure with activated clay.

By comparing the XRD patterns of Ba and Co doped activated clay with those of undoped metal activated clay, it is found that the positions and widths of the peaks are similar. It can be seen from figure 3 that the absorption peaks of both are sharp without obvious dispersion, which proves that the crystal form is relatively complete. However, the intensity of the absorption peak decreases slightly after modification, which indicates that the active clay after modification is active. At the same time, the diffraction absorption peak of the modified activated clay moves to the left, which indicates that the interlayer spacing of the modified activated clay is increased, and the diffraction peaks are obviously widened, especially for the Ba modified activated clay prepared after 12 hours drying, which indicates that the powder particles are fine and microcrystalline or amorphous.
Figure 4 shows the curve of residual percentage of (Ba, Co)-activated clay adsorption at different times under sunlight conditions. The effect of materials on the removal rate of Congo red solution in simulated wastewater. The amount of (Ba, Co)-activated clay adsorbent was 40 mg, the adsorption time was 160 min, the volume of Congo red solution was 200 mL, and the initial concentration was 100 mg/L. It can be seen from figure 4 that the adsorption effect of modified Ba-activated clay adsorbent is the best, with the removal rate reaching 98.8%, and the adsorption effect of Co-activated clay component is also better, with the removal rate reaching 89.5%, and the adsorption removal effect of all series of products with different compositions is better with the extension of time.

Figure 5 shows the curve of adsorption amount, removal time and material composition of residual Congo red solution adsorbed by (Ba, Co)-activated clay under sunlight. The amount of the sample modified adsorbent material is 50 mg, the adsorption time is 140 min, and the volume of Congo red solution is 500 mL. According to figure 5, the adsorption effect of Ba-activated clay samples is the best for 12 hours drying, with the maximum adsorption capacity reaching 371 mg/g, the maximum adsorption capacity of Co-activated clay in 12 hours reaches 338 mg/g, and the better the adsorption and removal effect of all the products of different composition over time. After the adsorption time reaches 120 minutes, the adsorption amount tends to be stable with the increase of time. When the adsorption time is 140 minutes, the adsorption amount is not increasing, indicating that the adsorption process is mainly completed in 120 minutes, and the adsorption effect is very good.
Fig. 5 Adsorption capacity curve of Congo red adsorbed by (Ba,Co)-activated clay

With the increase of adsorption time, the residual concentration of the solution after adsorption of Congo red dye decreased, and the visible adsorption rate increased, and reached the maximum value gradually. The adsorption effect of Ba and Co modified activated white soil on Congo red dye is obviously stronger than that of the undoped metal, and the adsorption effect is better. Moreover, the adsorption gap is obvious from the beginning. This is mainly because the adsorption in the initial stage occurs on the surface of the adsorbent, and a large number of active adsorption sites are conducive to the improvement of adsorption rate, while the modified activated clay is modified by doping. The adsorption of the active adsorption sites gradually saturated with the increase of adsorption time, and the adsorption rate was almost unchanged. It can be seen from the adsorption curve that the adsorption capacity of Ba-activated clay is slightly stronger than that of Co-activated clay. The adsorption effect of Ba-activated clay is similar to that of 7 hours drying for 12 hours. This shows that adsorption has active site control at first. After the adsorption is stable, the adsorption process is mainly controlled by activated clay base. It can be seen that the modified (Ba, Co)-activated clay can be treated as adsorbent, such as Congo red dye wastewater.

4. Conclusion
A series of modified active clay composites were prepared by solvent heat. The modified samples were tested by a series of characterization methods. The adsorption effect was obtained by doping different metal elements. The synthesis process was simple and the cost of the composite material was low. The results show that the modified (Ba, Co)-activated clay samples can be used as adsorbents to remove organic dye wastewater. Compared with natural clay, the activity of (Ba, Co)-activated clay is greatly improved, the adsorption capacity is greatly enhanced, the particle size is small and the thermal stability is better. It is expected to further expand the active clay and its application in environmental pollution control, such as enrichment of some rare metals and treatment of toxic gas pollution.

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