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Study on Adsorption Performance of Ce-Loaded Coal Gasification Slag to Congo Red

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Abstract. *Coal gasification slag is a solid waste that reacts with gasifier (air, oxygen or water vapor) at a certain temperature and pressure. The unburned and incompletely burned part of the coal is discharged as waste slag.Coal gasification slag itself, as a solid waste, causes dust to fly over a long period of time. At the same time, the slag contains a large amount of inorganic substances and heavy metals, which makes it impossible to recultivate the land where gasified slag has been stacked. However, it has a high porosity, which can better degrade and adsorb pollutants. This experiment uses coal gasification slag as a raw material in the coal gasification process, preparation of Ce-loaded coal gasification slag adsorbentThe adsorption performance of Congo Red by both was studied. The effects of adsorption time, pH, dosage of adsorbent and temperature on adsorption performance were also investigated.The results show that the best conditions for adsorption of raw coal gasification slag and Ce-loaded coal gasification slag are: pH=9, dosage of adsorbent is 0.5g, temperature is 50°C, reaction time is 150min, and concentration is 70mg/L. At this time, the adsorption capacity were 2.6392 mg/g and 7.152mg/g, and the removal rates were 30.65% and 95.87%, respectively. The adsorption behavior of Congo Red by raw coal gasification slag and Ce-loaded coal gasification slag is in accordance with the secondary adsorption kinetics, and conforms to the Langmuir adsorption isotherm, which is a monomolecular adsorption.*

Keywords: *Cerium, Coal gasification slag, adsorption, Congo Red*

1. Introduction

Dye wastewater mainly comes from the production of dyes and dye intermediates. It is composed of mother products of various products and intermediate crystals, materials lost during production, and sewage that flushes the

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ground [1]. Azo dyes are currently the most common and used most Dyes, whose structure is stable and difficult to degrade, Congo red is one of the most common benzidine direct azo dyes in the printing and dyeing industry [2]. The chemical name of Congo red containing the substituents —SO3Na and —NH2, has good water solubility. Congo red is widely used in the paper industry, and its wastewater is difficult to degrade and pollute the environment. Harm to human health. At present, domestic methods for treating dye wastewater include oxidation catalysis method [3], adsorption decolorization method [4], etc. The adsorption decolorization method has attracted much attention due to its simple process, convenient operation, economy and good treatment effect [5].

Pollutant emissions from coal gasification during the production process are extremely low, effectively achieving clean and green coal gasification production. At the same time, almost no exhaust gas is emitted during the gasification process [6]. Coal gasification mainly includes several processes: ①Pyrolysis of coal, mainly carboxyl, hydroxyl, carbonyl and other cleavage, dehydration and degassing, tar, methanol and other reactions. ②Oxidative combustion of part of the coal. This stage mainly generates heat and provides conditions for the next gasification reaction. ③ Gasification of coal, the main core stage of coal gasification technology is the production of CO, H_2, CH_4 and other gases [7-10]. In summary, coal gasification is the reaction of coal with a gasifier (air, oxygen, or water vapor) at a certain temperature and pressure, so that the combustible part of the coal is converted to a combustible gas, and the unburned and incompletely burned coal The process in which part of it is discharged in the form of waste residue [11], the waste residue produced in this process is called coal gasification waste residue. Coal gasification slag contains relatively rich SiO2, Al2O3, and Fe2O3, and the sum of the three contents can reach 70% or more [12]. In addition, coal gasification coal slag also contains inorganic substances such as CaO, MgO, TiO, etc., which is an important material resource for coal gasification coal slag for resource utilization technology. In addition, as a solid waste, long-term storage causes dust to fly, and at the same time, the slag contains a large amount of inorganic substances and heavy metals, which makes it impossible to recultivate the land where the gasified slag has been stacked. However, it has high porosity and can degrade and adsorb pollutants.

In this experiment, the main solid waste produced in the coal gasification process, coal gasification residue, was used as raw materials. The effects of adsorption time, pH, and the amount of adsorbent added, and temperature on the modification effect were investigated. The Ce-loaded coal gasification residue was studied. The adsorption performance of Congo red for printing and dyeing wastewater provides ideas for the resource utilization of coal gasification waste residue.

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2. Experimental part

2.1 Experimental materials

The raw materials used in the experiment were taken from the waste slag produced by a coal gasification furnace in a plant in Yulin, Shaanxi Province. The waste slag was crushed with a hammer and mortar, ground and sieved through a 28-mesh sieve. The residue is separated, passed through a 100-mesh sieve, washed with distilled water until clear, and dried for later use.

Congo red solution configuration: Weigh 0.03g of Congo red in distilled water, make up to the mark in a 1000mL volumetric flask, and configure it as a 30mg/L standard stock solution. Congo red and analytical reagents were of analytical grade during the experiment.

2.2 Preparation of Ce-loaded coal gasification waste slag adsorbent

Weigh out a certain amount of coal gasification slag and dissolve it in a 2% cerium nitrate solution, leave it for 16 hours, and then wash it with ultrapure water several times. The washed waste is placed in a 60°C constant temperature drying box until it is dried.

2.3 Adsorption experiment

2.3.1 Adsorption kinetics

Weigh 0.3g each of coal gasification waste and Ce-loaded coal gasification waste. Add them to a 30mg/L Congo red solution. At the same shaking speed, perform constant temperature shaking at 25°C for adsorption experiments, and periodically take the supernatant for analysis.

2.3.2 Adsorption isotherm

In 50 mL of Congo red solution of different concentrations, 0.5 g each of coal gasification waste and Ce-loaded coal gasification waste were added. At the same shaking speed, the adsorption experiment was performed at 25°C with constant temperature shaking. The supernatant was taken for analysis after 150 min.

3. Results and discussion

3.1 Selection of adsorption conditions

3.1.1 Effect of reaction time on adsorption effect

Take 50mL of Congo red solution with an initial concentration of 30mg/L, add 0.3g of coal gasification slag and Ce-loaded coal gasification slag at a pH of 7 and a temperature of 25°C, and shake in a constant temperature water bath for 10, 30, and

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60, 90, 120, 150, 180, 210, 240min. After sampling, filtration and separation, transfer a certain amount of filtrate for dilution and then measure the absorbance of Congo red with an ultraviolet spectrophotometer, and calculate the adsorption amount to get the optimal reaction time. The results are shown in Figure 1.

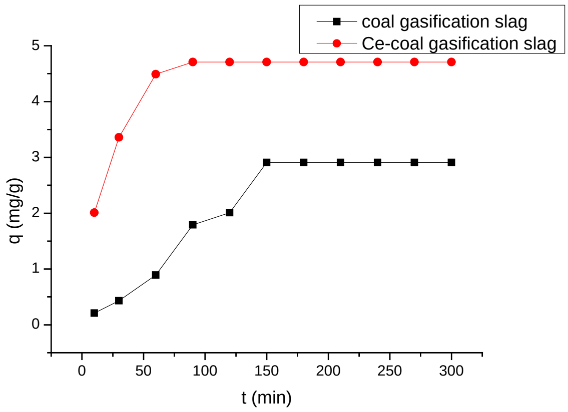

Figure. 1 Effect of adsorption time on Congo red removal effect

From Figure 1, with the increase of the adsorption time, the adsorption amount of Congo red by the raw coal gasification waste and Ce-loaded coal gasification waste slag shows an upward trend. During the 90 minutes before the adsorption, the adsorption rate of Congo red by the adsorbent is faster because at the beginning of adsorption, there are a large number of active adsorption sites on the surface of the adsorbent, which is conducive to adsorption. With the increase of the adsorption time, the vacant adsorption sites of the adsorbent decrease, gradually stabilize at 150 min, and reach the adsorption equilibrium. The adsorption capacity of Ce-loaded coal gasification slag is greater than that of unmodified raw coal gasification slag. The reason is that Ce-loaded coal gasification slag has more pores and a larger specific surface area, thus enhancing its adsorption.

3.1.2 Effect of pH on adsorption effect

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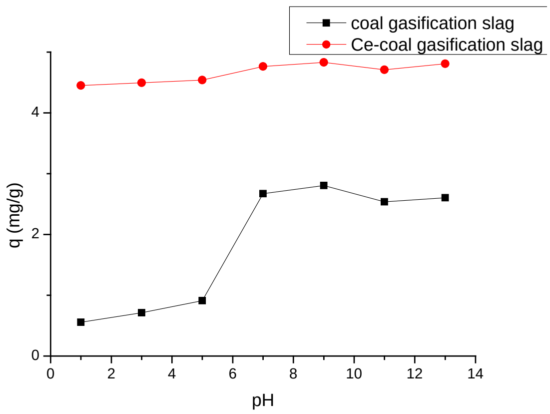

Figure. 2 Effect of pH on Congo red removal effect

Take 50mL of Congo red solution with initial concentration of 30mg/L, and adjust the Congo red solution to different pH with 0.1mol/L HCl or NaOH solution, namely 1, 3, 5, 7, 9, 11, 13. Add 0.5g of coal gasification slag and Ce-loaded coal gasification slag, respectively, at a temperature of 25°C, take a sample in a constant temperature water bath for 2.5 hours, sample after filtration, separate it by filtration, remove a certain amount of filtrate and dilute it with a UV spectrophotometer to measure the Congo red. Absorbance, and calculate the amount of adsorption to determine the optimal pH. The results are shown in Figure 2.

It can be seen from Fig. 2 that with the increase of the solution pH, the adsorption amount of Congo red by the raw coal gasification slag and Ce-loaded coal gasification slag showed a trend of increasing first and then decreasing. This is because Congo red is an anionic dye, which can combine with protonated H+ in the solution to form cations and exchange cations with Al3+, Si2+, etc. in the coal gasification residue to promote the adsorption of Congo red by the coal gasification residue; when the pH of the solution is 5~7, Congo red dye is easily ionized and negatively charged. The surface of the adsorbent is positively charged cations, which electrostatically interact with the dye. When the pH value continues to increase to an alkaline environment, Congo red is easily ionized and negatively charged in aqueous solution. Increasing the value will also increase the OH-concentration in water, which will compete with dyes for adsorption, resulting in a decrease in the amount of Congo red adsorbed by coal gasification residues. Therefore, the pH is taken as 9.

3.1.3 Effect of Dosage of Adsorbent on Adsorption Effect

Take 50mL of Congo red solution with an initial concentration of 30mg/L, and add 0.1, 0.3, 0.5, 0.7, 0.9, 1.2, 1.5g of coal gasification slag and Ce-load at a pH of 9 and a temperature of 25°C. Coal gasification slag was sampled after shaking in a constant temperature water bath for 2.5 hours, filtered and separated. A certain amount of filtrate was removed and diluted. The absorbance of Congo red was measured with an ultraviolet spectrophotometer, and the adsorption amount was

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calculated to determine the optimal dosage of the adsorbent. The results are shown in Figure 3.

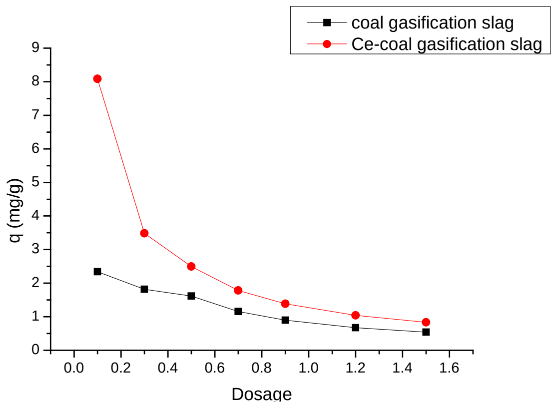

Figure. 3 Effect of sorbent dosage on Congo red removal effect

It can be seen from the figure that different dosages of adsorbent have a certain removal effect on Congo red. As the amount of adsorbent added increases, the amount of adsorption gradually increases. When the concentration and volume of Congo red in the solution are constant, the smaller the amount of adsorbent added, the higher the amount of adsorption. This is because the unit of mass of adsorbent adsorbs more Congo red and the higher the amount of adsorption. As the dosing amount increases, the equilibrium adsorption amount decreases, because the adsorbent provides a larger specific surface area and adsorption active sites, but the number of unit mass adsorbents combined with Congo red decreases, resulting in a decrease in equilibrium adsorption amount . Therefore, considering the comprehensive consideration, the optimal dosage for this experiment is 0.5g.

3.1.4 Effect of temperature on adsorption effect

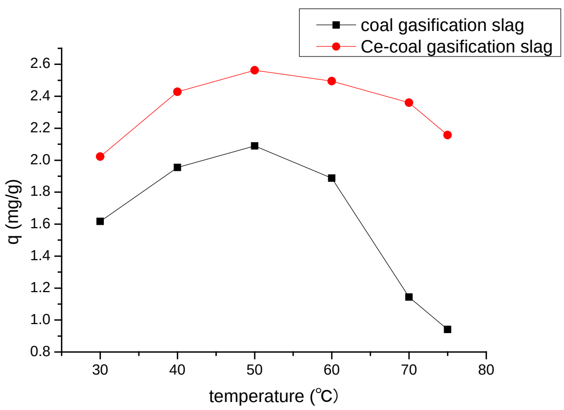

Figure. 4 Effect of temperature on Congo red removal effect

Take 50mL of Congo red solution with a concentration of 30mg/L, and adjust the pH of the Congo red solution to 9 with a 0.1mol/L HCl or NaOH solution. Add 0.5g of raw coal gasification slag and Ce-loaded coal gasification slag, respectively, adjust the temperature to 30, 40, 50, 60, 70, 75°C, shake in a constant temperature water bath for 2.5h, and take a sample. Dilute and measure a certain amount of filtrate Absorbance, calculate the amount of adsorption, and determine the optimal temperature. The results are shown in Figure 4.

It can be seen that the change in temperature has a certain effect on the adsorption of Congo red by the adsorbent. As the temperature increased, the amount of Congo red adsorbed by the adsorbent gradually increased and then decreased. When the temperature is low, it is not conducive to the progress of the reaction. As the temperature increases, the reaction rate increases, the removal rate also increases significantly, and the amount of adsorption increases. When the temperature reaches 50°C, the increase in the amount of adsorption is slow and tends to equilibrium. Therefore, if the temperature is too high, the adsorbent may be decomposed or destroyed, and the temperature is too low to provide sufficient energy to complete the reaction. Comprehensive consideration, this experiment chooses 50°C.

3.2 Adsorption kinetics

In order to study the adsorption kinetics characteristics of coal gasification slag and coal gasification slag after Zr loading, the Lagergren first-order adsorption rate equation and second-order adsorption rate equation were applied to the experimental data.

The linear form of Lagergren's first-order adsorption kinetic equation based on the solid adsorption capacity is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

In the formula, qt is the adsorption amount at time t, mg/g; qe is the equilibrium adsorption amount, mg/g; k1 is the first-order adsorption rate constant, min-1; t is the adsorption time, min.

The second-order reaction rate equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$$

In the formula, k_2 is the second-order adsorption rate constant, g/(mg · min).

The experimental data in Figure 1 were linearly processed using Lagergren's first- and second-rate reaction rate equations. The parameters are shown in Table 1.

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Table 1 Kinetic model parameters for adsorption of Congo red by raw coal gasification slag and Ce-loaded coal gasification slag

Pollutant	Adsorbent	q_e mg/g	Lagergren First-order kinetic model			Second-order kinetic model		
			k_1 min^{-1}	$q_{e.c}$ mg/g	R^2	k_2 $g/mg\cdot min^{-1}$	$q_{e.c}$ mg/g	R^2
Congo red	Coal gasification slag	2.9100	0.0263	0.4636	0.9776	0.0207	0.6895	0.9997
	Ce-coal gasification slag	4.7135	0.0387	1.4706	0.9752	0.0405	2.3310	0.9995

Experimental conditions: To 50 mL of Congo Red solutions with a concentration of 10, 20, 40, 70, 100, 150, and 200 mg/L, add 0.5 g of raw coal gasification residue and Ce-loaded coal gasification residue adsorbent, at 50°C, pH=9, the sample was sampled after shaking in a constant temperature water bath for 150 minutes, filtered, and a certain amount of filtrate was diluted to determine the absorbance of Congo red, and the adsorption amount was calculated.

Figure 5 is the adsorption isotherm of the original coal gasification slag and Ce-loaded gasification slag adsorbent on Congo red. It can be seen from Figure 5 that with the increase of the concentration, the adsorption amount of gasification slag and Ce-loaded gasification slag gradually increases At the same concentration, the adsorption effect of Ce-loaded coal gasification residue is higher than that of the original coal gasification residue.

The experimental data were fitted with Langmuir and Freundlich adsorption isotherm equations.

The Langmuir adsorption isotherm equation is:

$$\frac{1}{q_e} = \frac{1}{Q^0} + \left(\frac{1}{bQ^0}\right)\left(\frac{1}{C_e}\right)$$

In the formula: Q0 is the unit saturation adsorption amount when forming monolayer adsorption, mg/g; Ce is the equilibrium mass concentration of the solution, mg/L; qe is the equilibrium adsorption amount, mg/g; b is the Langmuir equilibrium constant.

Freundlich adsorption isotherm equation is:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

In the formula: KF and n are adsorption constants related to factors such as temperature and specific surface area of the adsorbent.

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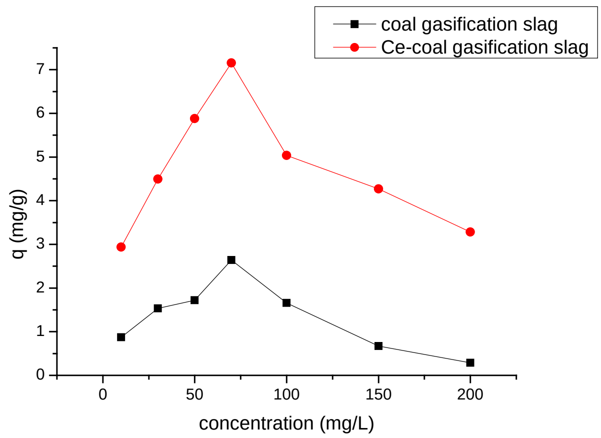

Figure. 5 Adsorption isotherms of Congo red adsorption by coal gasification slag and Ce-loaded coal gasification slag

Table 2 Isotherm regression data for adsorption of Congo red on raw coal gasification slag and Ce-loaded coal gasification slag (25°C)

Pollutant	Adsorbent	Langmuir Isotherm parameters			Freundlich Isotherm parameters		
		Q^0 mg/g	b L/mg	R^2	K_F	n	R^2
Congo red	Coal gasification slag	6.6050	1.113×10^{-3}	0.9896	0.2140	1.7147	0.9190
	Ce-coal gasification slag	25.1889	2.824×10^{-3}	0.9987	0.1093	1.1886	0.9908

Langmuir and Freundlich isothermal adsorption models were used to fit the data of Congo red adsorption by coal gasification slag and Ce-loaded coal gasification slag adsorbent. It can be seen from Table 2 that 2.5. It can be seen from Table 2 that the adsorption behavior of Congo red by coal gasification slag and Ce-loaded coal gasification slag adsorbent is more consistent with the Langmuir adsorption isotherm equation, and the corresponding linear correlation coefficients R2 are 0.9896 and 0.9987, respectively, which are larger than the Freundlich adsorption isotherm equation. This shows that the adsorption of Congo red by the adsorbent is a monolayer adsorption.

4. Conclusion

(1) The optimal adsorption conditions for raw coal gasification slag and Ce-loaded coal gasification slag are: pH=9, the amount of adsorbent added is 0.5g, the temperature is 50°C, the reaction time is 150min, and the concentration is 70mg/L.

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At this time, the adsorption amounts were 2.6392 mg/g and 7.152mg/g, and the removal rates were 30.65% and 95.87%, respectively.

(2) When the adsorption kinetics data of Congo red for two adsorbents, raw coal gasification slag and Ce-loaded coal gasification slag, were regressed using the two-stage adsorption kinetic equation, the correlation coefficient R2 was greater than 0.999. Therefore, the adsorption behavior was consistent with the two-stage adsorption kinetics.

(3) The adsorption of raw coal gasification slag and Ce-loaded coal gasification slag conforms to the Langmuir adsorption isotherm, and their correlation coefficients R2 are all greater than 0.9, so the adsorption is a monolayer adsorption.

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