Study on the Adsorption Performance of Cr^{6+} by Zr-Loaded Coal Gasification Waste Slag

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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 Zr-loaded coal gasification slag adsorbent The adsorption performance of Cr^{6+} 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 Zr-loaded coal gasification slag are: pH=3, dosage of adsorbent is 0.7g, temperature is 50℃, reaction time is 120min, and concentration is 100mg/L. At this time, the adsorption capacity were 3.256 mg/g and 6.816mg/g, and the removal rates were 44.19% and 81.42%, respectively. The adsorption behavior of Cr^{6+} by raw coal gasification slag and Zr-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

Zirconium; Coal gasification slag; adsorption; Cr(Ⅵ).

1. INTRODUCTION

With the rapid development of industry, chromium and its compounds are used in many fields and are essential raw materials for many industries. Chromium and its compounds are widely used in industrial production and processing such as electroplating, metal processing, tanning, metallurgy, printing and dyeing, etc. A large amount of chromium-containing wastewater will be produced during the production or processing process [1]. Among chromium and its compounds, hexavalent chromium is the most toxic, and hexavalent chromium compounds have systemic toxicity, stimulation, accumulation, carcinogenesis and mutagenic effects on the body. Therefore, it is urgent to develop a simple, effective and economical method for the treatment of chromium in wastewater [2].

Coal gasification is the reaction of coal with a gasifier (air, oxygen or water vapor) at a certain temperature and pressure to convert the combustible part of the coal into a combustible gas, and the unburned and incompletely burned part of the coal is waste The process of form discharge [3-5], the waste slag generated in this process is called coal gasification waste slag.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202003_6(3).0004

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, so that the land stacked with gasification slag cannot be recultivated [6]. However, it has high porosity and can degrade and adsorb pollutants. Therefore, this research will use coal gasification slag to treat Cr^{6+} wastewater by adsorption method, so as to achieve the purpose of waste treatment.

In this paper, the main solid waste produced in the coal gasification process, coal gasification waste slag, is used as a raw material to prepare a Zr-loaded coal gasification waste sorbent and study the Cr^{6+} adsorption performance of the two. At the same time, the effects of adsorption time, pH, dosage of adsorbent, and temperature on the modification effect were investigated, which provided ideas for the resource utilization of coal gasification waste slag.

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 passed through a 28 mesh sieve. The slag is separated, passed through a 100-mesh sieve, washed with distilled water until clear, and dried for later use.

Cr^{6+} solution configuration: Weigh 0.2829g of potassium dichromate and dissolve it in distilled water, make up to the mark in a 1000mL volumetric flask, and configure it to a standard stock solution of 100mg / L. During the experiment, draw a certain amount of standard stock solution in the capacity Dilute the bottle to the required concentration to prepare a standard use solution. Potassium dichromate and analytical reagents are of analytical grade.

Configuration of the developer: Weigh 0.2 g of diphenylcarbazide, dissolve it in 50 mL of acetone, add water to a 100 mL volumetric flask, dilute to the mark, and shake well. Store in the refrigerator. Do not use after darkening.

2.2. Preparation of Zr-loaded Coal Gasification Waste Slag Adsorbent

Weigh a certain amount of coal gasification waste slag in a 2% zirconium nitrate solution, leave it for 16 hours, and wash it with ultrapure water for several times. Place the washed solution in a 0.1mol/L NaOH solution. The precipitate ($Zr(OH)_4$) still needs to be washed. If there is no precipitate, it means that the washing is clean. The washed waste is placed in a 60℃ constant temperature drying box until it is dried.

2.3. Adsorption Experiment

1.3.1 Adsorption kinetics

Weigh out 0.5g each of coal gasification waste and Zr-loaded coal gasification waste. Add them to a 30mg/L Cr^{6+} solution. At the same shaking speed, perform constant temperature shaking at 25℃ for adsorption experiments, and periodically take the supernatant for analysis.

1.3.2 Adsorption isotherm

In 50mL of different concentrations of Cr^{6+} solution, 0.7g each of coal gasification slag and Zr-loaded coal gasification slag were added. At the same shaking speed, the adsorption experiment was performed at 25℃ with constant temperature shaking. The supernatant was taken for analysis after 2h.

2.4. Analysis Method

Cr^{6+}: diphenylcarbazide spectrophotometric method. A L5S ultraviolet-visible spectrophotometer was used to determine the standard curve of Cr^{6+} in aqueous solution at the

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202003_6(3).0004

maximum absorption wavelength of 540nm. The concentration of Cr^{6+} can be calculated from the standard curve and the measured absorbance of the sample solution.

3. RESULTS AND DISCUSSION

3.1. Selection of Adsorption Conditions

2.1.1 Effect of reaction time on adsorption effect

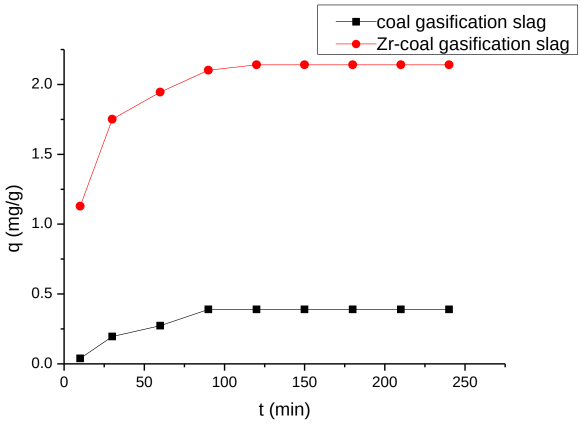

Figure 1. Effect of adsorption time on Cr^{6+} removal effect

Take 50mL of Cr^{6+} solution with an initial concentration of 30mg/L, add 0.5g of coal gasification slag and Zr-loaded coal gasification slag at a pH of 7 and a temperature of 25℃, and shake in a constant temperature water bath for 10, 30, and 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 Cr^{6+} with an ultraviolet spectrophotometer, and calculate the adsorption amount to get the optimal reaction time. The results are shown in Figure 1.

From Figure 1, with the increase of the adsorption time, the adsorption amount of Cr^{6+} by raw coal gasification slag and Zr-loaded coal gasification slag showed an upward trend. During the 30 minutes before adsorption, the adsorption rate of Cr^{6+} by the adsorbent was faster, because at the beginning there are a large number of active adsorption sites on the surface of the adsorbent, which is conducive to adsorption. As the adsorption time increases, the number of vacant adsorption sites on the adsorbent decreases, and it gradually stabilizes at 120 minutes to reach the equilibrium of adsorption. The adsorption capacity of Zr-loaded coal gasification slag is greater than that of unmodified raw coal gasification slag, because the Zr-loaded coal gasification slag has more pores and a larger specific surface area, thus enhancing its adsorption.

2.1.2 Effect of pH on adsorption effect

Take 50mL of Cr^{6+} solution with initial concentration of 30mg/L, and adjust the Cr^{6+} 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 Zr-loaded coal gasification slag, respectively, at a temperature of 25℃, take a sample in a constant temperature water bath for 2 hours, sample after filtration, separate it by filtration, remove a certain amount of filtrate and dilute it with a UV spectrophotometer to measure the Cr^{6+}. Absorbance, and calculate the amount of adsorption to determine the optimal pH. The results are shown in Figure 2.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202003_6(3).0004

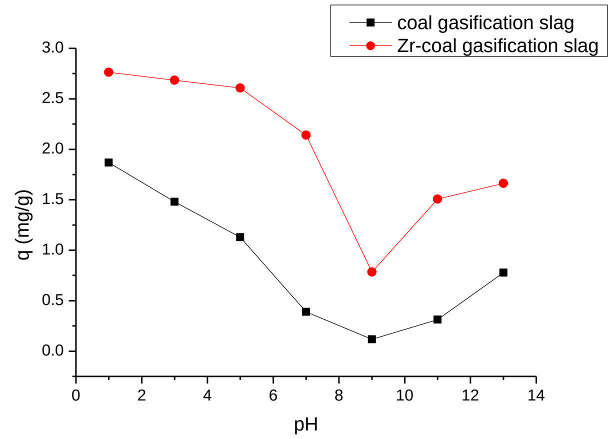

Figure 2. Effect of pH on Cr^{6+} removal effect

It can be seen from Fig 2 that as the pH of the solution increases, the adsorption amount of Cr^{6+} by the raw coal gasification slag and the Zr-loaded coal gasification slag decreases first and then increases. This is because when the pH is low, the concentration of H^+ in the solution is high, and H^+ will neutralize the negative charge on the surface of the waste slag, reducing the repulsive force of the negative charge to Cr^{6+}, which is beneficial to the adsorption of Cr^{6+}. When the pH is high, a large amount of OH^- will neutralize the positive charge on the surface of the waste slag, reducing the attractive force of the positive charge to Cr^{6+}, which is not conducive to the adsorption. As can be seen from the figure, when the pH is 1, the adsorption amount is the largest. However, too low pH will increase the difficulty of treating strongly acidic wastewater and is corrosive. Comprehensive consideration, the optimal pH for this experiment is 3.

2.1.3 Effect of Dosage of Adsorbent on Adsorption Effect

Take 50mL of Cr^{6+} 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 Zr load at a pH of 3 and a temperature of 25℃.Coal gasification slag was sampled after shaking in a constant temperature water bath for 2 hours, filtered and separated. A certain amount of filtrate was removed and diluted. The absorbance of Cr^{6+} was measured with an ultraviolet spectrophotometer, and the adsorption amount was calculated to determine the optimal dosage of the adsorbent. The results are shown in Figure 3.

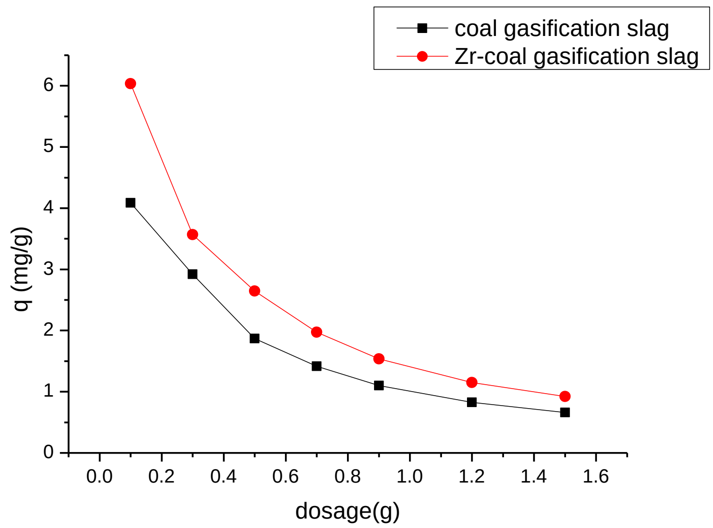

Figure 3. Effect of sorbent dosage on Cr^{6+} removal effect

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202003_6(3).0004

It can be seen from the figure that different dosages of adsorbent have a certain removal effect on Cr^{6+}. As the amount of adsorbent added increases, the amount of adsorption gradually decreases. When the concentration and volume of Cr^{6+} in the solution are constant, the smaller the amount of sorbent added, the higher the amount of sorbent. This is because the Cr^{6+} per unit mass of sorbent absorbs more, and the higher the amount of sorbent. With the increase of the added amount, the equilibrium adsorption amount decreases, because the adsorbent provides a larger specific surface area and active sites for adsorption, but the number of unit mass adsorbents combined with Cr^{6+} decreases, resulting in a decrease in equilibrium adsorption amount. Therefore, considering the overall consideration, the optimal dosage for this experiment is 0.7g.

2.1.4 Effect of temperature on adsorption effect

Take 50mL of a Cr^{6+} solution with a concentration of 30mg/L, and adjust the pH of the Cr^{6+} solution to 3 with a 0.1mol / L HCl or NaOH solution. Add 0.7g of raw coal gasification slag and Zr-loaded coal gasification slag, respectively, adjust the temperature to 30, 40, 50, 60, 70, 75℃, shake in a constant temperature water bath for 2h, 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.

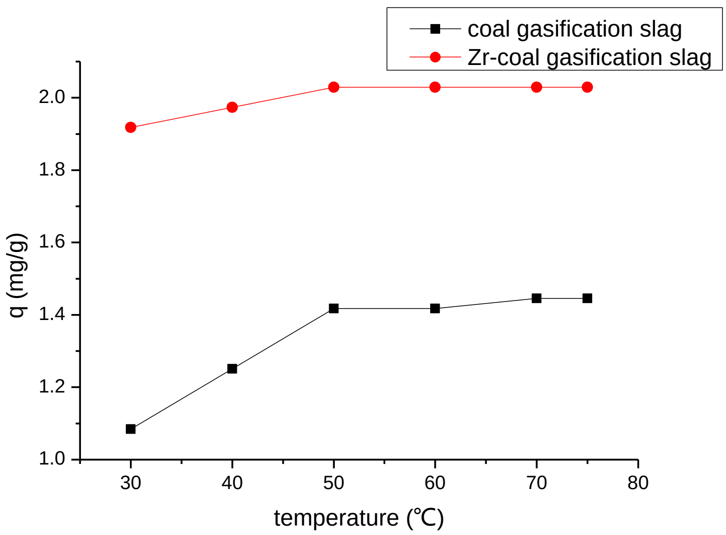

Figure 4. Effect of temperature on Cr^{6+} removal effect

It can be seen from the figure that the change in temperature has a certain effect on the adsorption of Cr^{6+} by the adsorbent. As the temperature increases, the amount of Cr^{6+} adsorbed by the adsorbent gradually increases and stabilizes. 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℃, 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℃.

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.

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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, q_t is the adsorption amount at time t, mg/g; q_e is the equilibrium adsorption amount, mg/g; k_1 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.

Table 1. Kinetic model parameters for adsorption of Cr^{6+} by raw coal gasification slag and Zr-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
Cr^{6+}	Coal gasification slag	0.3896	0.0263	0.4636	0.9776	0.0207	0.6895	0.9997
	Zr-coal gasification slag	2.1402	0.0387	1.4706	0.9752	0.0405	2.3310	0.9995

3.3. Adsorption Isotherms

Experimental conditions: To 50 mL of 10, 20, 40, 70, 100, 150, 200 mg/L Cr^{6+} solutions were added 0.7g of raw coal gasification slag and Zr-loaded coal gasification slag adsorbent, at 50℃, pH=3. Under the condition of constant temperature water bath shaking for 2h, samples were taken, filtered and separated. A certain amount of filtrate was diluted to measure the absorbance of Cr^{6+}, and the adsorption amount was calculated.

Figure 5 shows the adsorption isotherm of Cr^{6+} adsorption by the raw coal gasification slag and Zr-loaded coal gasification slag adsorbent. As can be seen from Figure 5, as the concentration increases, the adsorption amount of coal gasification slag and Zr-loaded gasification slag gradually increases. At the same concentration, the adsorption effect of Zr-loaded coal gasification slag is higher than that of raw coal gasification slag.

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

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202003_6(3).0004

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: Q^0 is the unit saturation adsorption amount when forming monolayer adsorption, mg/g; C_e is the equilibrium mass concentration of the solution, mg/L; q_e 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: K_F and n are adsorption constants related to factors such as temperature and specific surface area of the adsorbent.

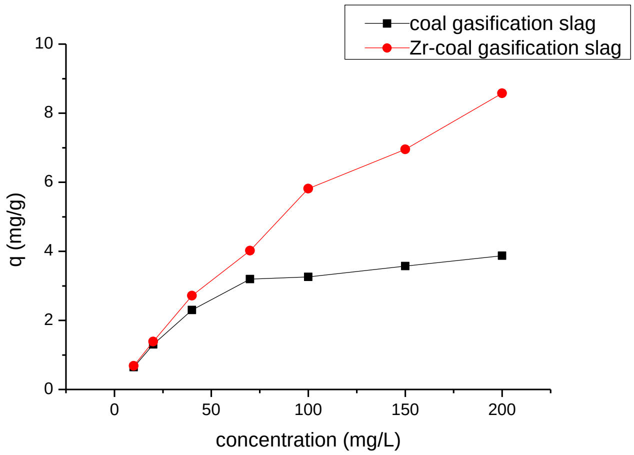

Figure 5. Adsorption isotherms of Cr^{6+} adsorption by coal gasification slag and Zr-loaded coal gasification slag

Table 2. Isotherm regression data for adsorption of Cr6+ on raw coal gasification slag and Zr-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
Cr^{6+}	Coal gasification slag	6.6050	1.113×10-3	0.9896	0.2140	1.7147	0.9190
	Zr-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 Cr^{6+} adsorption by coal gasification slag and Zr-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 Cr^{6+} by coal

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gasification slag and Zr-loaded coal gasification slag adsorbent is more consistent with the Langmuir adsorption isotherm equation, and the corresponding linear correlation coefficients R^2 are 0.9896 and 0.9987, respectively, which are larger than the Freundlich adsorption isotherm equation. This shows that the adsorption of Cr^{6+} by the adsorbent is a monolayer adsorption.

4. CONCLUSIONS

(1) The optimal adsorption conditions for raw coal gasification slag and Zr-loaded coal gasification slag are: pH=3, the amount of adsorbent added is 0.7g, the temperature is 50°C, the reaction time is 120min, and the concentration is 100mg/L. At this time, the adsorption amounts were 3.256 mg/g and 6.816 mg/g, and the removal rates were 44.19% and 81.42%, respectively.

(2) When the adsorption kinetics data of Cr^{6+} for two adsorbents, raw coal gasification slag and Zr-loaded coal gasification slag, were regressed using the two-stage adsorption kinetic equation, the correlation coefficient R^2 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 Zr-loaded coal gasification slag conforms to the Langmuir adsorption isotherm, and their correlation coefficients R^2 are all greater than 0.9, so the adsorption is a monolayer adsorption.

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