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Treatment mechanism of chromium-containing wastewater with carbonate minerals

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ABSTRACT

The pH scope for neutralization precipitation of chromium ion is comparatively narrow (6.3 ~ 9.5) and the dosage must be controlled strictly when NaOH or CaO is used as regulator. Slight dissolution of carbonate minerals such as calcite ($CaCO_3$) and magnesite ($MgCO_3$) makes it possible that the solution has buffer pH which can match with the condition of neutralization precipitation of chromium ion. The hydroxide precipitation of Cr(III) occurs more easily in the interface area than in solution because the interfacial solubility product of $Cr(OH)_3$ formed on the surface of $MgCO_3$ ($K_{SP}^{S} = 10^{-33.50}$) is less than the solubility product in solution ($K_{SP} = 10^{-30.27}$). After the surface precipitation is formed, the dynamic electricity behavior of $MgCO_3$ becomes similar to that of $Cr(OH)_3$. Using $MgCO_3$ as a purifier, the wastewater containing high concentration of chromium ion has been purified and advantages such as good purification effect, fast subsiding speed, and little sediment volume are manifested.

Keywords: Carbonate mineral; Chromium ion; Wastewater treatment

1. Introduction

Because heavy metals are not biodegradable and tend to accumulate in organisms causing various diseases [1,2], heavy metals pollution has become a serious problem for human health and environment [3]. As is well known, chromium is generated from various industrial processes like leather tanning, wood preservations, paint, electroplating, and manufacturing of dye and paper [4,5], and it is a common heavy metal contaminant in industrial regions throughout the world. In addition, many Cr(VI) species are known as carcinogens [6–10].

Currently, the amount of Cr(VI) effluented in wastewater from chemical, textile, and metallurgy industries is larger than that of the allowed limits by the United States Environmental Protection Agency (USEPA, 2002). Nowadays, activated carbon is the well known and proved most efficient adsorbent, but it is expensive [11–13]. There is still a considerable interest in the research of new solids with similar efficiency and price but easier regeneration than carbons [14,15]. Other different solids, such as zeolites, clay minerals, clino-pyrrhotite, metal oxides, organic

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polymers, and biomaterials, have been tested as insoluble adsorbents [6,16–21].

Chemical precipitation is one of the most widely used methods due to the simple usage [22–25]. And the traditional reduction, such as NaOH and CaO precipitation, has good results in treating wastewater with low concentration of chromium ion. Whereas, when the concentration of chromium ion in the wastewater is high, the adverse conditions like poor purification results and slow subsiding speed will occur in this process [26].

In this work, carbonate minerals (e.g. calcite and magnesite) as purifiers have been used to treat the wastewater with a high concentration of chromium ion. Compared with the NaOH and CaO precipitation, the utilization of carbonate minerals (e.g. calcite and magnesite) as purifiers to treat the artificial preparation wastewater which contains chromium ion has better purification and precipitation effects, especially the treatment with magnesite on wastewater containing more than 900 mg/L chromium ion. And eventually the total residual concentration of chromium ion in the wastewater is less than 0.4 mg/L.

2. Experimental methods

All reagents were of chemical grade and the wastewater was prepared by mixing tap water with $K_2Cr_2O_7$. The mass percentage of the carbonate minerals such as calcite ($CaCO_3$) and magnesite ($MgCO_3$) ($CaCO_3$ from Flour Mill Ore of Changsha, Hunan, China and $MgCO_3$ from Xingan County of Guilin, Guangxi, China) was 98.89% and 98.56%, respectively, and the mineral size was less than 0.074 mm. Reduction of Cr(VI) to Cr(III) took place when a strong chemical reducing agent (e.g. $NaHSO_3$) was added in the wastewater containing Cr (VI). The analysis of dynamic electricity properties for $MgCO_3$ and the precipitation of $Cr(OH)_3$ were measured by standard procedures with a Malvern Zeta Sizer III using a quartz capillary cell with a 4 mm diameter. Solutions were prepared using 1.0×10^{-3} mol/L KCl as background electrolyte at a set pH using a total volume of 100 mL.

3. Results and discussion

3.1. The optimum pH scope for neutralization precipitation of Cr(III) and the purification effects of NaOH and CaO

In the experiments, the reduction reaction occurred when the initial pH was adjusted to 2–2.5 with H_2SO_4. The purification treatment occurred when the color of wastewater turned into bright green from orange red.

In terms of the solution of Cr(III), there exists an equilibrium as follows:

$$Cr^{3+} + OH^- \rightarrow Cr(OH)^{2+} \qquad \beta_1 = 10^{9.99} \tag{1}$$

$$Cr^{3+} + 2OH^- \rightarrow Cr(OH)_2^+ \qquad \beta_2 = 10^{11.88} \tag{2}$$

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3(aq) \qquad \beta_3 = 10^{25.37} \tag{3}$$

$$Cr^{3+} + 4OH^- \rightarrow Cr(OH)_4^- \qquad \beta_4 = 10^{29.87} \tag{4}$$

$$Cr(OH)_3(s) \rightarrow Cr^{3+} + 3OH^- \qquad K_{SP} = 10^{-30.27} \tag{5}$$

According to the equilibrium relationship of Cr(III) in solution, a logarithmic diagram of solubility for $Cr(OH)_3$ is drawn (Fig. 1).

As shown in Fig. 1, the optimum pH scope for the removal of Cr(III) using neutralization precipitation ranges from 6.3 to 9.5. At $pH < 6.3$, the dominating species in the solution was $Cr(OH)^{2+}$, and Cr(III) was not fully transferred into the precipitation of $Cr(OH)_3$. At $pH > 9.5$, $Cr(OH)_4^-$ became the dominating species in the solution due to $Cr(OH)_3$ which dissolved again.

The purification effects in the wastewater containing different concentrations of chromium ion treated by NaOH and CaO are shown in Figs. 2 and 3, respectively.

The results suggest that there are two problems needed to be solved in the purification process. Firstly, the optimum pH value for neutralization precipitation of chromium ion is comparatively narrow and adjusted at a weakly alkaline scope, so the dosage must be strictly controlled when NaOH or CaO is used as regulator. Furthermore, the dosage added too little or too much will result in loss of purification effects.

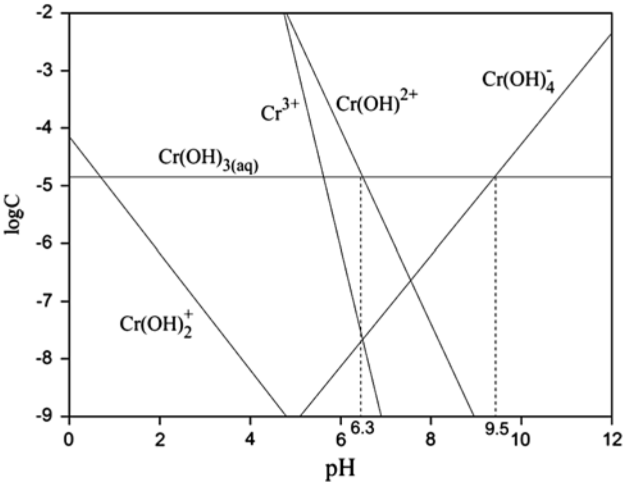

Fig. 1. Logarithmic diagram of solubility for $Cr(OH)_3$.

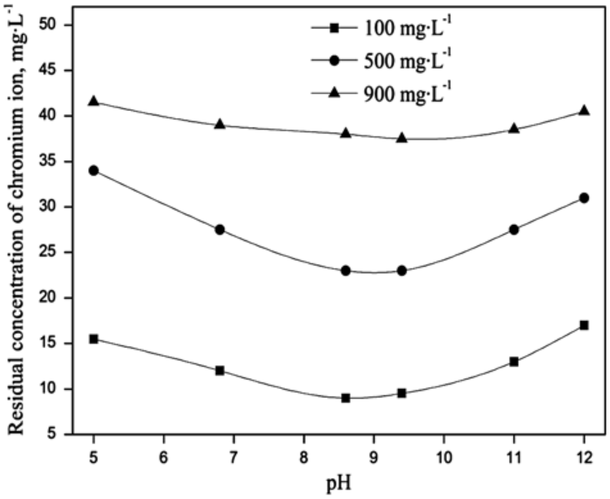

Fig. 2. Purification effects of wastewater containing different concentrations of chromium ion treated by NaOH.

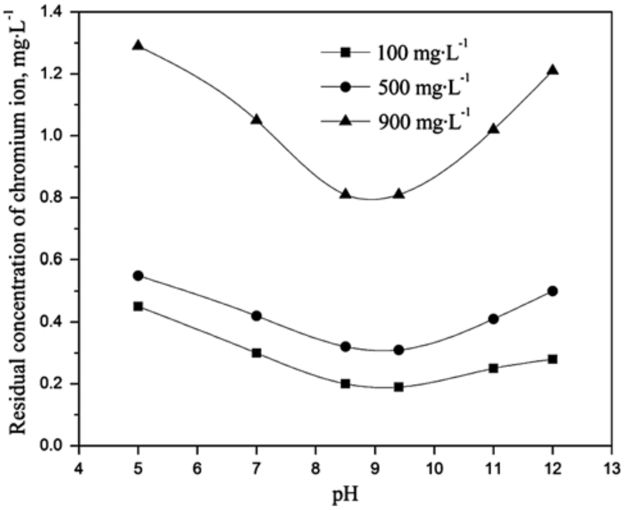

Fig. 3. Purification effects of wastewater containing different concentrations of chromium ion treated by CaO.

Secondly, if the concentration of the wastewater containing chromium ion is too high, the purification will be difficult, especially for NaOH.

3.2. The dissolution of carbonate mineral and buffer pH

Various minerals have some solubility in a certain solution system, especially the salt-type minerals, and the solubility of the minerals can directly affect the pH value of the system. Taking $MgCO_3$, for example, in an open system, the dissolution of carbonate minerals influences by partial pressure of CO_2 in the atmosphere and there exist equilibriums as follows:

$$MgCO_3(s) \rightarrow Mg^{2+} + CO_3^{2-} \qquad K_{SP} = 10^{-7.46} \tag{6}$$

$$Mg^{2+} + OH^- \rightarrow Mg(OH)^+ \qquad \beta_1 = 10^{2.58} \tag{7}$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_{2(aq)} \qquad \beta_2 = 10^{1.00} \tag{8}$$

$$H^+ + CO_3^{2-} \rightarrow HCO_3^- \qquad K_1^H = 10^{10.33} \tag{9}$$

$$H^+ + HCO_3^- \rightarrow H_2CO_3 \qquad K_2^H = 10^{6.35} \tag{10}$$

$$H_2CO_3 \rightarrow CO_{2(g)} + H_2O \qquad K_0 = 10^{1.47} \tag{11}$$

P_{CO2} is the partial pressure of CO_2 in the atmosphere, the value of which is 32.03 Pa, and taking it into the equilibrium reaction formula (11), it can be obtained from (9) to (11) that:

$$[CO_3^{2-}][H^+]^2 = 10^{-21.65} \tag{12}$$

The initial concentration of CO_3^{2-} can be approximately calculated from the solubility of $MgCO_3$ (K_{SP}); the calculated value is $10^{-3.73}$ and 8.96 is the pH value obtained from Eq. (1) by taking $10^{-3.73}$ into it. The side reaction coefficients of Mg^{2+} and CO_3^{2-} can be obtained on the basis of this pH value as follows:

$$\alpha(Mg^{2+}) = 1 + 10^{2.58} \times 10^{-5.04} + 10^{1.00} \times (10^{-5.04})^2 = 1.00$$

$$\alpha(CO_3^{2-}) = 1 + 10^{10.33} \times 10^{-8.96} + 10^{16.68} \times (10^{-8.96})^2 = 24.50$$

So the conditional solubility product of $MgCO_3$ (K'_{SP}) is $K'_{SP} = 10^{-7.46} \times 1.00 \times 24.50 = 8.49 \times 10^{-7}$, the solubility of $MgCO_3$ is $s_m = \sqrt{K'_{SP}} = 9.22 \times 10^{-4}$ mol/L.

Based on the calculated results above, the more accurate concentration of CO_3^{-2} is $[CO_3^{-2}] = s_m/24.50 = 3.76 \times 10^{-5}$ mol/L, and a more accurate pH (8.61) can be obtained by taking $[CO_3^{2-}]$ into Eq. 12. In this open system, the accurate solubility of $MgCO_3$ ($s_m = 3.22 \times 10^{-4}$ mol/L) and pH (8.4) can be calculated by using the successive approximation method, repeatedly.

Using the same method of the calculation of $MgCO_3$, the solubility of $CaCO_3$ ($s_m = 1.18 \times 10^{-4}$mol/L) and pH (8.2) can also be calculated.

The calculations indicate that no matter what the initial pH is, the pH of mineral–water system will eventually tend to a narrow range after equilibrium for a period of time because of the dissolution of carbonate minerals. Fig. 4 shows the relationship between the stirring time and the changes in the pH of calcite or magnesite–water system, respectively. The initial pH was adjusted with H_2SO_4.

The results show that the carbonate minerals–water systems such as calcium carbonate and magnesium carbonate minerals have buffer pH which accords with the range of neutralization precipitation of chromium ion.

3.3. Surface precipitation of chromium ions on the surface of mineral particles

Due to the existence of electric field, the dielectric constant of medium in the mineral–water interface is much lower than that in the solution. In fact, the condition forming hydroxide precipitation for metal ions in solution or interface is different. When the product is $Cr(OH)_3$, it can be described as formulae (13) and (14):

$$Cr(OH)_{3(S)} = Cr^{3+} + 3OH^- \qquad K_{SP} = 10^{-30.27} \tag{13}$$

$$\Delta G^0 = -RT \ln K_{SP} \tag{14}$$

where K_{SP} is the solubility product of hydroxide formed in the bulk solution for Cr(III); ΔG^0 is the change of standard Gibbs free energy in hydroxide dissociation equilibrium.

The following equation Eq. (15) can be obtained in the interface:

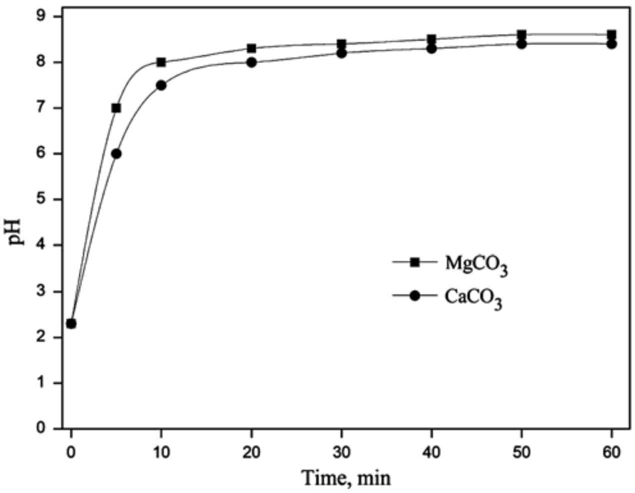

Fig. 4. Relationship between the stirring time and the changes in the pH of calcite or magnesite–water system.

$$\begin{aligned}\Delta G^{0\prime} = {} & G^0(Cr^{3+}) + G'(Cr^{3+}) + G^0(OH^-) \\ & + G'(OH^-) - G^0(Cr(OH)_{3(S)}) \\ & - G'(Cr(OH)_{3(S)})\end{aligned} \tag{15}$$

where G' is the contribution of electric field on the standard Gibbs free energy. Because the influences of the electric field on the ions are much stronger than that on the neutral or polar substances, $G'(Cr(OH)_{3(S)})$ can be neglected, and Eq. (15) can be simply described as follow:

$$\Delta G^{0\prime} = \Delta G^0 + (G'(Cr^{3+}) + G'(OH^-)) \tag{16}$$

Assuming K_{SP}^S is the solubility product of chromium metal hydroxide precipitation in the interface, the following equation can be obtained:

$$\Delta G^{0\prime} = -RT \ln K_{SP}^S \tag{17}$$

Another equation Eq. (18) can be obtained according to Eqs. (16) and (17):

$$\log(K_{SP}/K_{SP}^S) = (G'(Cr^{3+}) + G'(OH^-))/(2.303RT) \tag{18}$$

According to Born charging equation [27–29]:

$$G' = \frac{(ze)^2 N}{8\pi(r_i + 2r_w)\varepsilon_0} \times \left(\frac{1}{\varepsilon_i} - \frac{1}{\varepsilon_b}\right) \times g(\theta) \tag{19}$$

where G' (J/mol) is the excess free energy; z is the charge on ion; e is the electronic charge, 1.6×10^{-19} C; N is the Avogadro's number, $6.02 \times 1{,}0^{23}$; r_i is the ionic radius, $r(OH^-) = 1.33 \times 10^{-10}$ m, $r(Cr^{3+}) = 0.69 \times 10^{-10}$ m [29]; r_w is the radius of water molecule, 1.38×10^{-10} m; ε_0 is the permittivity of free space, 8.85×10^{-12} C/(Vm); ε_i is the dielectric constant of the interface, and commonly value of ε_i used for aqueous systems is 20 at 298 K as the previous studies [30,29]; ε_b is the dielectric constant in bulk solution, 78.5; and $g(\theta)$ is the geometrical function whose value is 0.25 as the previous studies [30,29]. So Eq. (19) can be expressed as follows:

$$G'(Cr^{3+}) = 16852.2 \quad (J/mol)$$

$$G'(OH^-) = 1579.5 \quad (J/mol)$$

And the result can be calculated as follows:

$$\log(K_{SP}/K_{SP}^S) = 3.23$$

So the results can be shown as follows: $K_{\mathrm{SP}} = 10^{-30.27}$, $K^{S}_{\mathrm{SP}} = 10^{-33.50}$.

The results indicate that it is easier to form hydroxide precipitation for Cr(III) in the interface area than in solution because the interfacial solubility product of $Cr(OH)_3$ formed on the surface of carbonate is less than the solubility product in solution.

The generation of surface precipitation has an impact on the dynamic electricity behavior of $MgCO_3$. Fig. 5 shows that whether the Cr(III) exists or not and the zeta potential of $MgCO_3$ varies with pH. It indicates that the coverage of $Cr(OH)_3$ on the mineral surface changes the dynamic electricity behavior of $MgCO_3$, and the surface precipitation began to occur when the pH was about 6.3. After the surface precipitation is formed, the dynamic electricity behavior of $MgCO_3$ becomes similar to that of $Cr(OH)_3$.

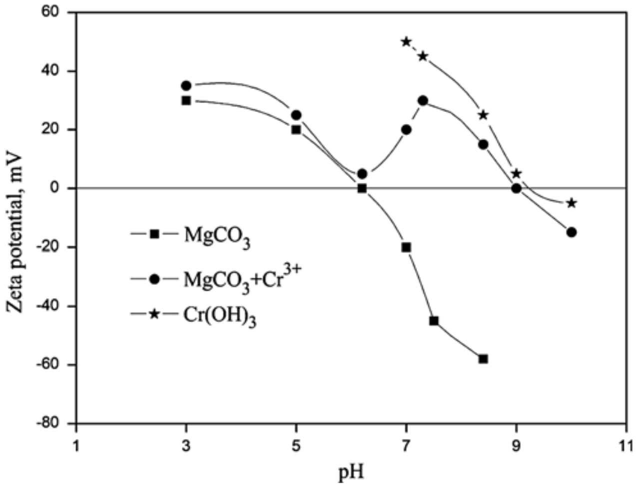

Fig. 5. Influence of Cr^{3+} on the zeta potential of $MgCO_3$.

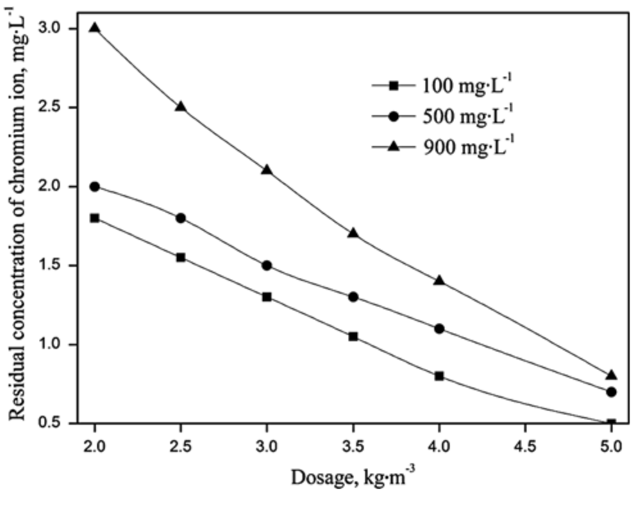

Fig. 6. Purification effects of wastewater containing different concentrations of chromium ion treated by calcite.

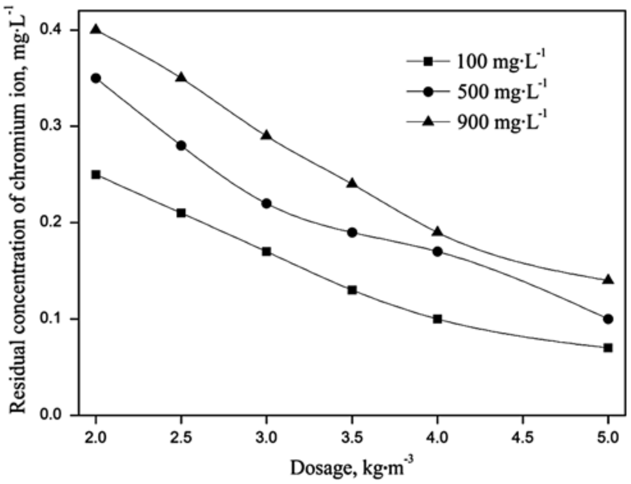

Fig. 7. Purification effects of wastewater containing different concentrations of chromium ion treated by magnesite.

3.4. Purification effects of calcium and magnesium carbonate minerals on chromium ion wastewater

The purification effects of calcite and magnesite on chromium ion wastewater are shown in Figs. 6 and 7, respectively.

The results indicate that it has some advantages of the purification effects of carbonate minerals (e.g. calcite and magnesite) on wastewater containing chro-

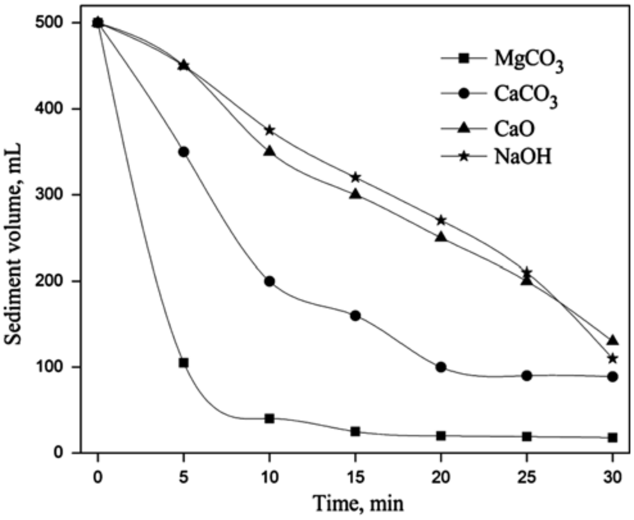

Fig. 8. Relationship between subside time and sediment volume.

mium ion, especially the utilization of $MgCO_3$. Furthermore, the residual concentration of chromium ion in wastewater decreased from 100 to 900 mg/L to less than 0.4 mg/L through a small amount of magnesite (2 kg/m^3), and the removal percentage could be up to 99.6%. Meanwhile, when compared with the treatment of NaOH or CaO using magnesite as purifier, advantages such as good purification effects, fast subsiding speed, and little sediment volume were manifested. The result of subsiding test is shown in Fig. 8.

4. Conclusions

The utilization of NaOH or CaO as regulator to purify wastewater containing chromium ion has some disadvantages, for example, the pH of the solution is difficult to control, the purification effect is poor, and the subsiding speed is slow.

The hydroxide precipitation for Cr(III) in the interface occurs more easily than in solution because the interfacial solubility product of $Cr(OH)_3$ formed on the surface of $MgCO_3$ ($K_{SP}^{S} = 10^{-33.50}$) is less than the solubility product in solution ($K_{SP} = 10^{-30.27}$). After the surface precipitation is formed, the dynamic electricity behavior of $MgCO_3$ becomes similar to that of $Cr(OH)_3$.

Slight dissolution of carbonate minerals like $CaCO_3$ or $MgCO_3$ makes it possible that the solution has buffer pH that can match with the conditions of neutralization precipitation of chromium ion, meanwhile, it shows good results in the purification of wastewater containing chromium ions. The residual concentration of chromium ion in the wastewater has been decreased to less than 0.4 mg/L from 100 to 900 mg/L with adding a small amount of magnesite (2 kg/m^3), and the removal percentage could be up to 99.6%. Meanwhile, when compared with the treatment of NaOH or CaO, using magnesite as purifier, advantages such as good purification effects, fast subsiding speed, and little sediment volume are manifested.

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