Synthesis of CaO_2 in Aqueous at Room Temperature and Its Application in Wastewater Treatment*

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Abstract: In this paper, peroxide calcium (CaO_2) was synthesized at room temperature from industrial $Ca(OH)_2$ and H_2O_2 with the addition of stabilizer, the purity of the product is over 70%. On this basement, the application of CaO_2 in the treatment of wastewater was studied. ① The treatment of dye wastewater by $FeSO_4$ catalysis—CaO_2 oxidation process. The results show that this process is effective to the decolorization of some kinds of dyes. Moreover, the decolorizing rate is related to the quantity of CaO_2, the quantity of $FeSO_4$ and the reaction time. At the optimum condition decided by the experiment, the decolorizing rate can reach to about 100%, COD_{Cr} removal efficiency is more than 90%. ② The treatment of wastewater containing heavy metals Cd^{2+}, Pb^{2+}, Cu^{2+}, Mn^{2+}, AsO_2^- using alkalescence and oxidation of CaO_2. The results show that the residual concentration of Cd^{2+}, Pb^{2+}, Cu^{2+}, Mn^{2+}, AsO_2^- is less than the emission standard set down by country, and removal efficiency of heavy metals is more than 99.9%. Therefore, CaO_2 is an effective, safe, nontoxic, environmental friendly green water-treatment reagent.

Key words: peroxide calcium; wastewater treatment; dye wastewater; heavy metal
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CaO_2 is a kind of newfashioned and much functional inorganic chemicals, which can be applied in coating materials for rice seeds for the enhancement of budding, oxygen generator, maintaining freshness of fruits and vegetables, strengthening rubber and so on[1]. Seen from numerous increasingly exploited application fields, the production and application of CaO_2 is promising. But at present, it is usually synthesized at below 0 ℃[2], which results in equipment complication and product instability. Therefore, the synthesizing method is outdated and very unfitting with its status, which greatly restrict its application. So, in this paper, a new process has been exploited to synthesize CaO_2 at room temperature from industrial $Ca(OH)_2$ and H_2O_2 with the addition of stabilizer. The advantage of this process is simple operation, high recovery and high stability of product. On this basement, the application of CaO_2 in the treatment of wastewater containing dye or heavy metal was studied. The results show that CaO_2 is an effective and environmental friendly green water – treatment reagent.

1 Experiment

1.1 Preparation and characterization of CaO_2

The procedure used to prepare CaO_2 is as follows. First, 10 g $Ca(OH)_2$ (industrial) was mixed with some water in 250 mL flask under strong and consecutive stirring to ensure the homogeneous slurry. Next, The stabilizer was added into the slurry. Subsequently, 16 mL H_2O_2 (30%, industrial) was dropped into the slurry. After dropping was over, the suspension was stirred for some time. Then, the suspension was filtered, the wet filtration residue was put into oven and dried at 150 ℃ for 2 h to obtain the sample.

Phase of the sample was identified by X-ray diffraction analysis (XRD). The content of CaO_2 was analyzed by chemical method[3].

1.2 Making up and treatment of dye wastewater

Three dyes such as Reactive Orange Ⅱ, Acidic Red B and Acidic Black 10B, were respectively dissolved in water to obtain the simulative dye wastewater with the initial concentration 30 mg/L. The treatment procedure is as follows. First, a certain amount of CaO_2 was added into 100 mL dye wastewater under violent and consecutive stirring for 5 min. Then a certain amount of $FeSO_4$ was added in to the suspension with consecutive stirring for some time. Finally, the suspension was placed for 10 min, then filtered. The absorbency, COD_{Cr} and pH of the filtrate were measured.

1.3 Treatment of wastewater containing heavy metal and determination of the residual

The treatment procedure is as follows: a certain amount of CaO_2 was added into 100 mL wastewater containing heavy metal under violent and consecutive stirring. The heavy-metal ions were oxidized and/or

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precipitated because of the properties of oxidation and alkalescence of CaO_2.

At the same time, a certain amount of $FeSO_4$ was added into the suspension, using its flocculent property to make the heavy-metal ions precipitating completely. Then, the suspension was filtered. The residual As in the filtrate was determined by hydride · generation-atomic fluorescence spectrometry. The residual Cd, Pb, Cu, and Mn were determined by atomic absorption spectrometry.

2 Results and Discussion

2.1 Characterization of the sample

The XRD analysis proves that the main component of the sample is CaO_2. The content of CaO_2 is over than 70% determined by chemical method.

2.2 Treatment of dye wastewater

2.2.1 Mechanism of the decolorization

The mechanism of the decolorization is that CaO_2 is catalyzed by Fe^{2+} and release ·OH. ·OH has very strong oxidation ability and can destroy the chromophoric groups in the molecular structure of the dye, which results in the decolorization[4].

2.2.2 Determination of the maximum absorption wavelength of dye wastewater

The maximum absorption wavelength of Reactive Orange Ⅱ, Acidic Red B and Acidic Black 10B is 480, 510 and 620 nm respectively determined by measuring their absorption curves.

2.2.3 Experiment results of disposing dye wastewater

(1) Effect of CaO_2 dosage on the decolorizing rate

From Fig. 1, it can be seen that the dosage of CaO_2 affects remarkably the decolorizing rate. When no CaO_2 is added, the decolorizing rate is almost equal to 0. With increasing the dosage of CaO_2, the decolorizing rate increases. When the dosage of CaO_2 increases to 600, 800 and 1000 mg/L respectively for Reactive Orange Ⅱ, Acidic Red B and Acidic Black 10B, the decolorizing rate is close to 100%. By measuring the absorption curves of the finial filtrate, it is found that the characteristic absorption peak of the dye has disappeared, which shows that the chromophoric groups of the dye has been destroyed. Therefore, the optimum dosage of CaO_2 for these three dyes is 600, 800 and 1000 mg/L respectively.

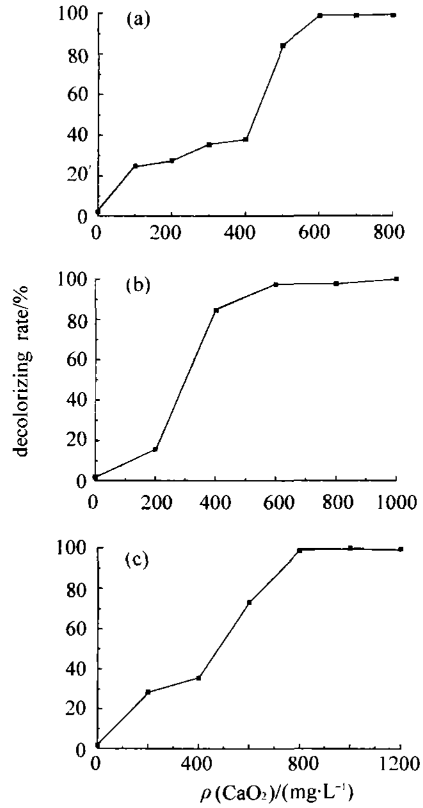

Fig. 1 The effect of CaO_2 dosage on the decolorizing rate
a: Reactive Orange Ⅱ ($FeSO_4 \cdot 7H_2O$ 50 mg/L); b: Acid Red B ($FeSO_4 \cdot 7H_2O$ 100 mg/L); c: Acid Black 10B($FeSO_4 \cdot 7H_2O$ 100 mg/L)

(2) Effect of $FeSO_4 \cdot 7H_2O$ dosage on the decolorizing rate

From Fig. 2, it can be seen that the dosage of $FeSO_4$ affects remarkably the decolorizing rate. When no $FeSO_4$ is added, the decolorizing rate is relatively low. With increasing the dosage of $FeSO_4$, the decolorizing rate increases. When the dosage of $FeSO_4$ increases to 50, 100 and 100 mg/L respectively for Reactive Orange Ⅱ, Acidic Red B and Acidic Black 10B, the decolorizing rate is close to 100% and the filtrate presents colorless. Therefor, the optimum dosage of $FeSO_4 \cdot 7H_2O$ for these three dyes is 50, 100 and 100 mg/L respectively.

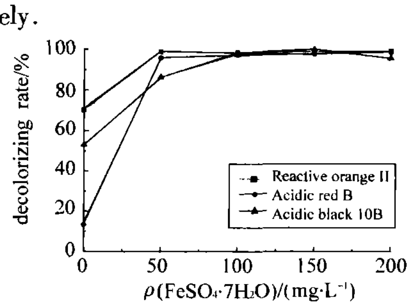

Fig. 2 The effect of $FeSO_4 \cdot 7H_2O$ dosage on the decolorizing rate

(3) Effect of reaction time on the decolorizing rate

From Fig. 3, it can be seen that when the reaction time is prolonged to 30 min, the decolorizing rate is close to 100%. Therefor, the optimum the reaction time is 30 min.

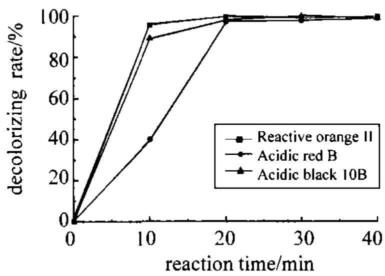

Fig.3 The effect of reaction time on the decolorizing rate

(4) Change of COD_{Cr} and pH of the dye wastewater

From Tab. 1, it can be seen that COD_{Cr} removal efficiency of the dye wastewater is over 90% under the optimal operating conditions. The final COD_{Cr} is lower than the emission standard set down by country. The initial pH value of the dye solution is 7. After being disposed by $FeSO_4$ catalysis – CaO_2 oxidation process under the optimal operating conditions, the final pH value is between 7 and 8. Therefor, the final filtrate conforms to emission standard, and can be directly discharged or reused.

Tab.1 Removal efficiency of COD_{Cr} of the dye wastewater

dye	Initial COD_{Cr} ($mg \cdot L^{-1}$)	Final COD_{Cr} ($mg \cdot L^{-1}$)	Removal efficiency of COD_{Cr}/%
Reactive Orange Ⅱ	520	25	95.2
Acidic Red B	750	32	95.7
Acidic Black 10B	278	15	94.6

2.3 Treatment of wastewater containing heavy metal

The experiment results are showed in Tab.2. From Tab.2, it can be seen that the residue concentration of Cd^{2+}, Pb^{2+}, Cu^{2+}, Mn^{2+} and AsO_2^- is all less than the emission standard set down by country, and removal efficiency of heavy metal is more than 99.9%.

Tab.2 The experiment results of disposing heavy-metal wastewater

Heavy metal	The emission standard/10^{-6}	$\frac{n(\text{metal ion})}{n(CaO_2)}$	pH	$\frac{c(\text{Initial})}{10^{-6}}$	$\frac{c(\text{Residual})}{10^{-6}}$	$\frac{\text{Removal efficiency}}{\%}$
Cd^{2+}	0.1	1:2	10.66	112.4	0.042	99.96
Pb^{2+}	1.0	1:2	9.84	207.2	< 0.055	> 99.97
Cu^{2+}	0.5	1:3	11.39	100	0.05	99.95
Mn^{2+}	2.0	1:2	11.26	55	0.004	99.99
AsO_2^-	0.5	1:8	11.49	80	0.04	99.95

3 Conclusion

(1) The simulative dye wastewater was disposed by $FeSO_4$ catalysis – CaO_2 oxidation process. The optimal operating conditions determined by experiments are as following: when the initial concentration of the dye is 30 mg/L, the optimal dosage of CaO_2 is 600, 800 and 1000 mg/L respectively for Reactive Orange Ⅱ, Acidic Red B and Acidic Black 10B. The optimal dosage of $FeSO_4 \cdot 7H_2O$ is 50, 100 and100 mg/L respectively for Reactive Orange Ⅱ, Acidic Red B and Acidic Black 10B. The optimal the reaction time is 30 min. Under these conditions, the decolorizing rate is close to 100%, and the removal efficiency of COD_{Cr} is over 90%.

(2) By controlling the dosage of CaO_2 and pH, the removal efficiency of Cd^{2+}, Pb^{2+}, Cu^{2+}, Mn^{2+} and AsO_2^- is over 99.9%, and the residual concentration is less than the emission standard set down by country.

(3) The above results show that CaO_2 is an effective, economical, safe, nontoxic and environmental friendly green water treatment reagent. It is promising in dye wastewater treatment.

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过氧化钙的常温水相法合成及其在废水处理中的应用试验研究

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摘 要：以 $Ca(OH)_2$ 和 H_2O_2 为原料，通过添加稳定剂，实现了过氧化钙的常温水相合成。在此基础上，研究了其在废水处理中的应用。采用硫酸亚铁催化—过氧化钙氧化法对染料废水进行了处理实验研究。结果表明：染料的脱色率与 CaO_2 用量、$FeSO_4 \cdot 7H_2O$ 用量、反应时间均有关系。在本试验确定的最佳处理条件下，染料的脱色率均能达到 100%，且 COD 去除率达 90%以上。利用过氧化钙的碱性及氧化性，对 Cd^{2+}、Pb^{2+}、Cu^{2+}、Mn^{2+}、AsO_2^- 等重金属废水进行处理，结果表明：通过控制过氧化钙的加入量及 pH 值，这几种重金属离子的去除率均达到 99.9%以上，残留浓度均低于国家排放标准。由此可见，过氧化钙是一种有效、安全、无毒的“环境友好型”绿色水处理剂。

关键词：过氧化钙；废水处理；染料废水；重金属

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