Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22910

125 (2018) 296–301
September

Study on dye wastewater treatment of tunable conductivity solid-waste-based composite cementitious material catalyst

Le Kang*, Hui Ling Du*, Xian Du, Hai Ting Wang, Wan Li Ma, Ming Liang Wang, Feng Bo Zhang

College of Materials Science and Engineering, Xi'an University of Science and Technology, Xi'an 710054, China, Tel. 86 29 85587373, email: kangle20140805@126.com (L. Kang), hldu@foxmail.com (H.L. Du)

Received 25 April 2018; Accepted 3 August 2018

ABSTRACT

At present, dye wastewater pollution and solid wastes storage become the main environmental issues in China. Thus, it is of great significance to develop low–cost and efficient technologies to remove dyes from aquatic environment. In this paper, the mixture of magnesium slag and steel slag were used as the raw materials, $Na_2SiO_3·9H_2O$ as alkali activator, silica fume as toughening agent, conductive carbon black as conductive medium, a novel conductive alkali-activated-steel-slag-magnesium-slag-based composite cementitious material (CACCM) was successfully prepared and applied to dye wastewater treatment. The results indicated that the compressive strength of the prepared specimens with carbon black was decreased, and the electrically conductive property was improved significantly with growing of carbon black content. When carbon black content reached 4.5 wt%, the stable conductivity was 0.3997 S/m for the curing period of 28 d. PL spectrum revealed that the photoluminescence intensities progressively decreased with increasing of carbon black content. The incorporation of carbon black could improve the photo catalytic degradation rate of the composite cementitious material, and the conductivity was positively correlated with the degradation rate. 4.5CB/CACCM specimen showed the best photo catalytic degradation activity and the degradation rate of malachite green dye could reach 90.58% at 80 min. The photo catalytic degradation reaction belongs to the second-order reaction kinetics.

Keywords: Malachite green; Water pollution control; Alkali–activated; Composite cementitious material; Carbon black; Photo catalysis

1. Introduction

In recent years, with the accelerated process of industrialization and increasing population, China has now developed into a printing and dyeing industry power [1]. It is reported that China had produced 756 thousand tons of dye in 2010, ranking the top of the world, while more than 700 m^3 of waste water was discharged in the production of one ton of dye [2]. Moreover, in daily textile printing and dyeing, as about 15% of the dye enters the water environment, more than 100 thousand tons of dye without effective treatment was directly discharged into the water environment [3]. These dyes which have stable chemical structures are very difficult to be degraded by the environment itself. So even the dyes with low concentration can also produce clear color, thus affects the normal life activities of aquatic animals and plants, and then destroy the ecological balance of water. More seriously, most of dyes and intermediates have carcinogenic, teratogenic and mutagenic effects, such as triphenylmethane dyes [4,5], which are great threat to the health of humans and animals through the food chain [6–8]. Therefore, dye wastewater is one of the most serious factors that threaten the safety of water body in China [9–12]. How to treat dye wastewater has obviously become a problem to be solved urgently.

---

*Corresponding author.

Presented at the 4th Annual Science and Technology Conference (Tesseract'17) at the School of Petroleum Technology, Pandit Deen Dayal Petroleum University, 10–12 November 2017, Gandhinagar, India

1944-3994 / 1944-3986

With the rapid development of national economy, the emissions of steel slag and magnesium slag as the main solid waste produced by the steel industry and the magnesium industry have increased sharply. According to statistics, in 2016, the emission of steel slag in China was about 121 million tons [13], and the emission of magnesium slag was more than 6 million tons [14], so it is imminent to improve the application of this kind of solid waste as resources. In recent years, numerous scholars at home and abroad have made a lot of researches on the basic performance and comprehensive utilization of steel slag and magnesium slag. For example, the steel slag is mainly used as a raw material for calcining cement clinker [15], soil amendments [16], adsorbent used in wastewater treatment [17], and catalyst carrier material [18–20]; Magnesium slag is mainly used in the fields of calcining Portland cement clinker, cement admixture [21], multiphase catalyst [22] and a raw material of catalyst carrier material [14,23]. However, its utilization is still low. The large amount of accumulated steel slag and magnesium slag not only occupy land resources, but also cause serious environmental pollution, and at the same time, it is also a huge waste of secondary resources, which seriously affects the circular economy and sustainable development of the iron and steel industry and the metal and magnesium industry. Therefore, it is imperative to further develop new methods for scientific utilization of steel slag and magnesium slag, explore a new way of high value-added utilization for steel slag and magnesium slag as resources, and expand new fields for its green and harmless utilization.

In this paper, where carbon black is taken as conductive medium, steel-slag-magnesium-slag as raw materials, a novel conductive alkali-activated-steel-slag-magnesium-slag-based composite cementitious material (CACCM) was prepared, and used for photo catalytic degradation of malachite green dye wastewater. The main purposes of the research are as follows: (1) put forward to create a novel photo catalyst in an economical and feasible way; (2) evaluate its photo catalytic performance of the composite cementitious material; (3) resolve the environmental pollutions caused by both wastewater of malachite green dye and steel-slag-magnesium-slag.

2. Experimental

2.1. Reagents

Steel slag with the density of 3.40×10^3 kg/m^3 and the Blaine specific surface area of 485 m^2/kg was purchased from Hancheng Longmen Iron and Steel Co. Ltd., Shaanxi, China. The magnesium slag powder was obtained from Fugu Magnesium Company. The density and the Blaine specific surface area were 1.58×10^3 kg/m^3 and 485 m^2/kg respectively. Silica fume was provided by Xi'an Lin Yuan Co. Ltd. $Na_2SiO_3\cdot9H_2O$ (A.R.) was purchased from Sinopharm Chemical Reagent Co. Ltd. Carbon black with an average particle size of 40 nm was supplied by Tianjin Lihua Chemical Co. Ltd., China.

2.2. Synthesis of photocatalyst

Steel slag and magnesium slag were mixed by the mass ratio of 8:2, and 300 g of mixture were accurately weighed as the measurement basis. In the mixing process, silica fume as the toughening agent and carbon black as conductive medium were added by using external-adding method, whose addition amounts were respectively 10 wt% and 15 wt% of the total mixture, and the addition amount of $Na_2SiO_3\cdot9H_2O$ as the alkali-activator was 10 wt% of the total mixture. The water-slag ratio was 0.39. Referring to the standard of GB/T17671–1999 "cementation sand strength", the solution containing $Na_2SiO_3\cdot9H_2O$ was poured into the SJ-160 type mortar mixer, adding mixture and stirring evenly to form paste. Then, the mixed slurry was placed into a 31.5 mm×31.5 mm×40 mm triplicate steel mold to be shaped on a vibrating table . Four galvanized stainless steel electrode plates were inserted at the equal distance (Electrode size: 20 mm×30 mm). After that, they were put into a sealed plastic bag to cure at 80°C for 6 h in the constant temperature drying box. The test blocks were continuous cured at room temperature for 1 d before the demolding, and it was cured for 2 d in a standard curing box to obtain the novel conductive alkali-activated-steel-slag-magnesium-slag-based composite cementitious material (abbreviated as: 1.5 CB/CACCM). For the comparison, the conductive composite cementitious materials whose addition amounts of carbon black were respectively 0 wt%, 3.5t% and 4.5t% of the total mixture were prepared according to the above method (written as: CACCM, 3.5 CB/CACCM and 4.5 CB/CACCM), and the burden ratio was shown in Table 1. The compressive strength of the test blocks with 3d of curing age were detected, and the four electrode method was used to detect the electrical conductivity of specimens with the curing age of 1 d, 3 d, 7 d, 14 d, 28 d and 60 d. The testing device is demonstrated in Fig. 1.

2.3. Experimental device

The compressive strength of specimen was carried out on a YAW-300 automatic pressure testing machine at the loading speeding of 2.4 kN/s. The morphology analysis was characterized using Hitachi High-resolution field emission scanning electron microscope (FESEM) S-4800. The photoluminescence (PL) spectrum was carried out using an F-4500 fluorescence spectrophotometer with an excitation wavelength of 310 nm.

2.4. Evaluation of photo catalytic activity

The 752N type ultraviolet visible spectrophotometer produced by Shanghai Precision and Scientific Instruments Co. Ltd. was used to detect the absorbance of simulated dye wastewater solution. The light source in the degradation experiment comes from the TL-D type ultraviolet lamp (Power: 18W) produced by PHILPS, and its vertical height with the surface of the dye solution 12 cm. The experimental procedures for evaluating the photo catalytic degradation activity of dye are shown as follows: 6 mg/L malachite green dye solution of 100 ml was prepared at the room temperature to detect the absorbance value at different wavelengths by using spectrophotometer. The photo catalytic degradation of malachite green dye wastewater at its characteristic absorption peak of 616 nm was studied. Before the experiment, the beaker containing the catalyst sample and malachite green dye solution was placed in the dark-

Table 1
Burden ratio of conductive composite cementitious materials

Sample	Steel slag (g)	Magnesium slag (g)	Silica fume (g)	Carbon black (wt%)	$Na_2SiO_3·9H_2O$ (wt%)	Water-slag ratio
CACCM	216	54	30	0	10	0.31
1.5 CB/CACCM	216	54	30	1.5	10	0.39
3.5 CB/CACCM	216	54	30	3.5	10	0.47
4.5 CB/CACCM	216	54	30	4.5	10	0.55

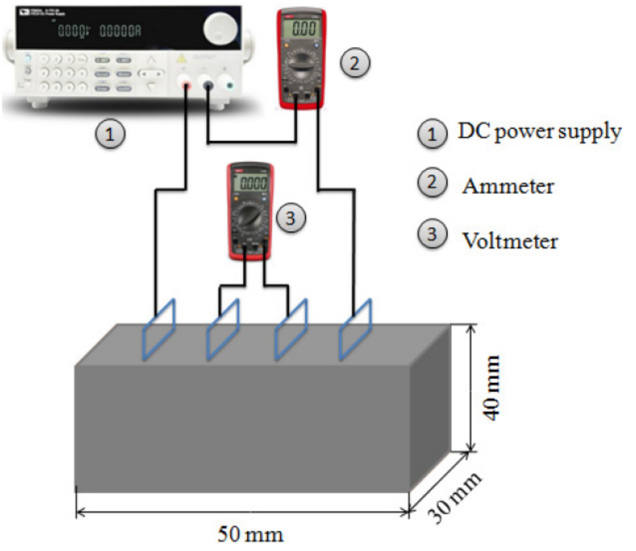

Fig. 1. Schematic diagram of conductivity test of conductive composite cementitious materials.

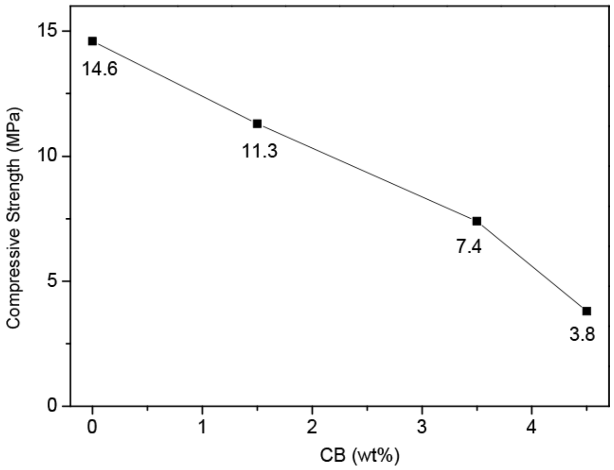

Fig. 2. 3 d compressive strength of specimens.

room for about 30 min, enabling the dye solution to reach the adsorption–desorption balance on catalyst, and then the photo catalytic degradation reaction experiment was carried out. The photo-degradation rate (η) was calculated as shown in the following Eq. (1):

$$(\eta)=\frac{(C_0-C_t)}{C_0}\times 100\%=\frac{(A_0-A_t)}{A_0}\times 100 \quad (1)$$

where C_0 is the initial concentration of malachite green dye and C_t is the concentration of malachite green dye after irradiation for t minutes. A_0 is the initial absorbance of malachite green dye and A_t is the absorbance of malachite green dye after irradiation for *t* minutes.

3. Results and discussion

3 d compressive strength of the conductive composite cementitious materials with different addition amounts of carbon black are shown in Fig. 2. It can be seen that the compressive strength of the conductive composite cementitious materials with carbon black decreased rapidly with the increase of carbon black content. The compressive strength of 1.5 CB/CACCM, 3.5 CB/CACCM and 4.5 CB/CACCM samples were 11.3 MPa, 7.4 MPa and 3.8 MPa, respectively, while the compressive strength of the CACCM sample without carbon black was 14.6 MPa. Compared with the test block without conductive medium, the compressive strength of the test blocks added with 1.5 wt%, 3.5 wt% and 4.5 wt% carbon black decreased by 22.61%, 49.32% and 73.97% respectively, which was probably because of the carbon black with larger surface area and finer particle gradation. The particles were added into the matrix to cause a large accumulation of agglomeration, and then produced the interface effect with the inter phase of gels in the composite cementitious material, reducing the density of hydrated gelatine, thus affecting the mechanical properties of test blocks. Its macroscopic performance was that the compressive strength decreased with the increased of carbon black content.

Fig. 3 shows the FESEM photographs of (a) CACCM and (b) 4.5 CB/CACCM. Compared with CACCM specimen, 4.5 CB/CACCM has some obvious cracks and loosing structure. This may be attributed to the interface effect between a large number of carbon black particles in the matrix and the gel phase in the CACCM sample, reducing the density of hydrated gelatine, thus affecting the mechanical properties of test blocks. This is in accordance with changes for the results of the macroscopic mechanical properties in Fig. 2.

The electrical conductivity of the conductive composite cementitious materials with different ages is shown in Table 2. It can be observed that with the growing of carbon black content, the electrical conductivities of the conductive composite cementitious material increased at the same age. Its order was 4.5CB/CACCM > 3.5CB/CACCM

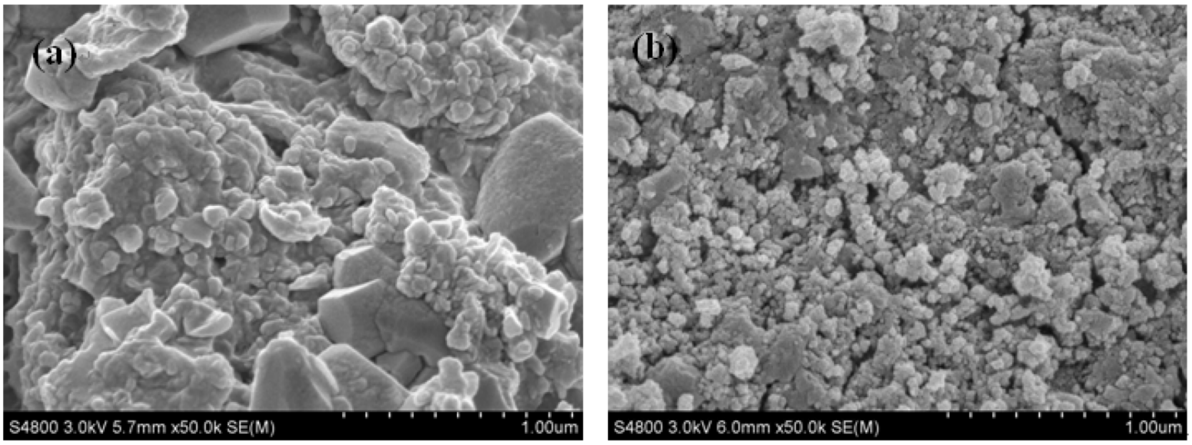

Fig. 3. FESEM photographs of (a) CACCM and (b) 4.5 CB/CACCM.

Table 2
Electrical conductivity of conductive composite cementitious materials at different ages (S/m)

Sample	Carbon black (wt%)	Electrical conductivity of test blocks at different ages (S/m)					
		1 d	3 d	7 d	14 d	28 d	60 d
CACCM	0	0.0770	0.0116	0.0076	0.0026	0.0020	0.0018
1.5CB/CACCM	1.5	0.1370	0.0343	0.0203	0.0138	0.0122	0.0112
3.5CB/CACCM	3.5	0.7221	0.2621	0.1767	0.1333	0.1318	0.1307
4.5CB/CACCM	4.5	1.6662	0.6363	0.4769	0.4069	0.3997	0.3978

> 1.5CB/CACCM > CACCM. The electrical conductivity of the same specimen with different curing ages tended to decrease with the increase of curing age, and the electrical conductivity tended to be stable at the curing age of 28 d. When the content of carbon black was 1.5 wt%, the stable electrical conductivity of the 1.5CB/CACCM sample was 0.0122 S/m, when carbon black content was 4.5 wt%, the stable electrical conductivity of the 4.5CB/CACCM sample was 0.3997 S/m. When the curing age was 60 d, the electrical conductivity was basically equal to the electrical conductivity of the 28 d. Thus it can be seen that the addition of carbon black can obviously improve the electrical conductivity of the composite cementitious material.

As the conductive medium was not added, in the initial stage of hydration reaction, Na^+, Ca^{2+}, OH^- and other electrolytes in the system could migrate freely in their liquid channels, thereby exhibiting excellent electrical conductivity, and at this time, the matrix was dominated by ionic conduction. With the increase of the age, the hydration reaction continued, and a large number of amorphous gelatin hydrated substances were produced, while these hydration products with cementitious property were gradually filled in the voids inside the materials, resulting in the decrease of the number and migration space of ions, and the electrical conductivity of the samples showed a downward trend [24]. Because of its larger surface area and finer particle gradation, the added carbon black were existed in the form of botryoidal and chain structure formed by the aggregation and accumulation of carbon black particles., and were easy to connect with each other in a composite cementitious material system to form a conducting chain conductive network structure [25], which played a leading role. With the increase of carbon black content, the density of carbon black and carbon black aggregates dispersed in the composite cementitious material system increased as well, while the average distance between carbon black particles decreased, the probability of contacting with each other increased, and the formed conductive channels were also on an increase [26], suggesting an excellent electrical conductivity.

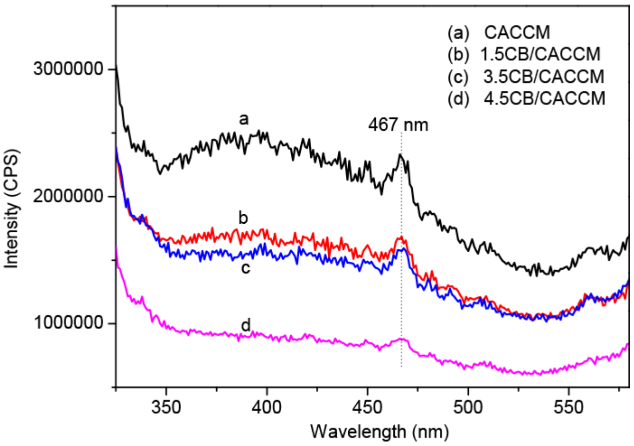

Fig. 4. Photoluminescence spectra of specimens.

Fig. 4 displays the photoluminescence spectra of conductive composite cementitious material catalysts excited by the 150 W xenon lamp. It can be observed that CACCM specimen shows the strongest photoluminescence spectrum with a peak at about 467 nm. Photoluminescence spectrum was generated by the recombination of the photo generated electrons and holes [27]. Spectral intensity of CB/CACCM specimens was clearly weakened. Among them, 4.5CB/CACCM specimen exhibited the weakest spectral intensity, implying that carbon black promotes the transmission of photo generated electrons, and enhancing the separation efficiency of photo generated electron-hole pairs.

CACCM, 1.5 CB/CACCM, 3.5 CB/CACCM and 4.5 CB/CACCM samples with the curing age of 3d were used as the catalyst for photo catalytic degradation of malachite green dye solution, while the amount of catalyst was 0.05 g, malachite green solution was 100 mL, and the dye concentration was 6 mg/L.

Fig. 5 exhibits the photo catalytic degradation rate of malachite green dye by the catalysts with different amount of carbon black. It shows that the photo-degradation rate of malachite green solution irradiated by ultraviolet light for 80 min was about 3.54%, indicating that malachite green dye under the radiation of ultraviolet light was relatively stable and difficult to have its own photolysis reaction. The photo catalytic degradation efficiency of CB/CACCM series of sample with carbon black was higher than that of the sample without carbon black, and the sequence of the degradation of malachite green dye by the catalyst sample was 4.5 CB/CACCM > 3.5 CB/CACCM > 1.5 CB/CACCM > CACCM. The degradation rate of the dye by the 4.5 CB/CACCM, 3.5 CB/CACCM and 1.5 CB/CACCM sample under the irradiation for 80 min were 90.58%, 84.33% and 51.84%, respectively, while the degradation rate of malachite green dye by the CACCM sample without carbon black under the irradiation for 80 min is only 42.68%.

As shown in Table 2, compared with the CACCM specimen without carbon black, the photo catalytic degradation rate by the 4.5 CB/CACCM catalyst sample with 4.5 wt% carbon black increased by 47.90%, for carbon black helped to form the conducting chain conductive network structure in the composite cementitious material system, which significantly improved the conductivity of the composite cementitious material. The electrical conductivity of the 4.5 CB/CACCM sample was 0.3978 S/m, which was 221 times as high as that of the CACCM sample, its excellent electrical conductivity played an important role in electron transport. Under illumination, the conductive network structure speeded up the transmission rate of photo generated electrons, and effectively separated photo generated electrons from photo generated holes, greatly improved the photo catalytic activity of the catalysts.

In order to further explore the reaction kinetics characteristics of malachite green dye, the experimental data were fitted into a linear function to correspond to the mutual relationship. As shown in Table 3, compared with the value of R_0^2, R_1^2, R_2^2, and R_3^2, which represent the correlation coefficients of the zero, first, second and third order correlation coefficients of kinetics equations, the value of R_2^2 was the biggest, indicating that the photo catalytic degradation of malachite green dye wastewater obeys the second-order reaction kinetics. Second-order reaction kinetic curves of photo catalytic degradation of malachite green dye are shown in Fig. 6.

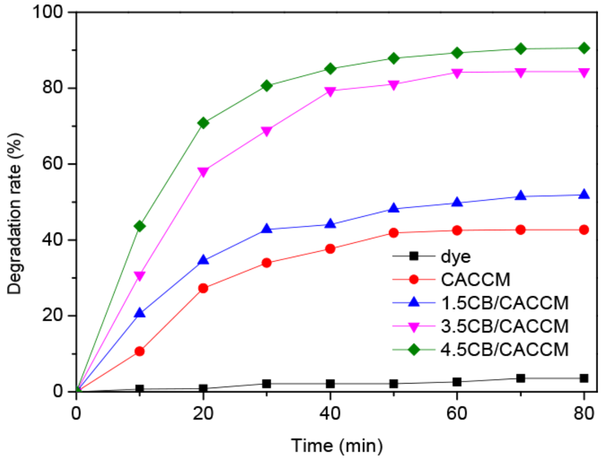

Fig. 5. Photo catalytic degradation rate of malachite green dye of specimens.

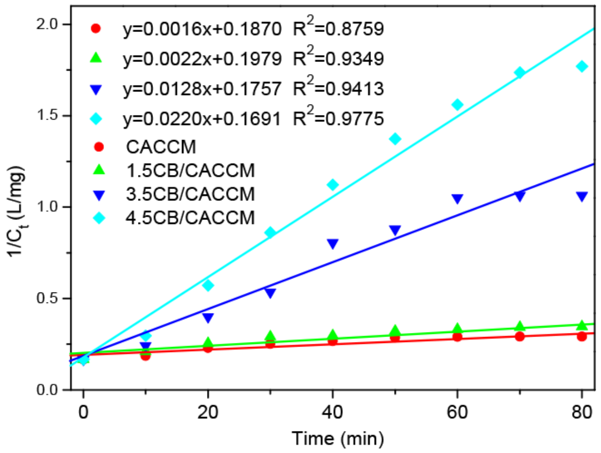

Fig. 6. Second–order reaction kinetic curves of photo catalytic degradation of malachite green dye.

Table 3
Kinetics equations of photocatalytic degradation of malachite green

Sample	Second-order reaction kinetics	R_0^2	R_1^2	R_2^2	R_3^2	k_2 [L/(mg·min)]	$t_{1/2}$ (min)
CACCM	$1/C_t = 0.0016t+0.1870$	0.7579	0.8037	0.8759	0.8436	0.0016	104.17
1.5CB/CACCM	$1/C_t = 0.0022t+0.1979$	0.7402	0.8196	0.9349	0.8859	0.0022	75.76
3.5CB/CACCM	$1/C_t = 0.0128t+0.1757$	0.7153	0.8711	0.9413	0.9349	0.0128	13.02
4.5CB/CACCM	$1/C_t = 0.0220t+0.1691$	0.6204	0.8599	0.9775	0.9662	0.0220	7.58

4. Conclusions

Herein, a novel type of alkali-activated-steel-slag-magnesium-slag-based composite cementitious material catalyst was prepared by polymerization and successfully applied it towards degradation of dyestuff wastewater. The addition of carbon black could significantly improve composite cementitious material electrical conductivity. More importantly, the electrical conductivity of the conductive composite cementitious material is positively related to the degradation rate of malachite green dye, which can be attributed to the conductive network structure connected by carbon black. It has accelerated the transmission rate of photo generated electrons, and made the photo generated electrons to be effectively separated from the bare holes, which thus greatly improved the photo catalytic activity of the catalyst. This photo catalytic degradation reaction belongs to the second order reaction kinetics.

Acknowledgements

This study was financially supported by Natural Science Foundation of China under grant (No.51372197), the Key Innovation Team of Shaanxi Province (No.2014KCT-04), Xi'an University of Science and Technology PhD start-up project (NO. 2018QDJ011).

References

[1] O. Tong, S. Shao, Y. Zhang, S.L. Liu, S.S. Zhang, An AHP-based water-conservation and waste-reduction indicator system for cleaner production of textile-printing industry in China and technique integration, Clean Technol. Environ. Policy, 14 (2012) 857–868.

[2] A.K. Mishra, T. Arockiadoss, S. Ramaprabhu, Study of removal of azo dye by functionalized multi walled carbon nanotubes, Chem. Eng. J., 162 (2010) 1026–1034.

[3] A.M.M. Mawad, N.M.H. Yousef, A.A.M. Shoreit, Robust Aspergillus terreus biofilm supported on graphene oxide/hematite-nano composites for adsorption of anthraquinone dye, Desal. Water Treat., 57 (2016) 24341–24351.

[4] P.S. Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi, S. Sivanesan, Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions, Desalination, 261 (2010) 52–60.

[5] A. Mittal, J. Mittal, A. Malviya, D. Kaur, V.K. Gupta, Adsorption of hazardous dye crystal violet from wastewater by waste materials, J. Colloid Interface Sci., 343 (2010) 463–473.

[6] M.L. Rache, A.R. García, H.R. Zea, A.M.T. Silva. L.M. Madeira, J.H. Ramirez, Azo-dye orange II degradation by the heterogeneous Fenton-like process using a zeolite Y-Fe catalyst-kinetics with a model based on the Fermi's equation, Appl. Catal. B: Environ., 146 (2014) 192–200.

[7] Q. Zhang, Y. Li, P. Phanlavong, Z. Wang, T. Jiao, H. Qiu, Q. Peng, Highly efficient and rapid fluoride scavenger using an acid/base tolerant zirconium phosphate nano flake: Behavior and mechanism, J. Cleaner Prod., 161 (2017) 317–326.

[8] J. Zhou, F. Gao, T. Jiao, R. Xing, L. Zhang, Q. Zhang, Q. Peng, Selective Cu(II) ion removal from wastewater via surface charged self-assembled polystyrene-Schiff base nano composites, Colloids Surfaces A., 545 (2018) 60–67.

[9] H. Fu, X. Liu, Research on the phenomenon of chinese residents' spiritual contagion for the reuse of recycled water based on SC–IAT, Water, 9 (2017) 846.

[10] K. Liu, H. Fu, H. Chen, Research on the influencing mechanism of traditional cultural values on citizens' behavior regarding the reuse of recycled water, Sustainability, 10 (2018) 165.

[11] H. Guo, T. Jiao, Q. Zhang, W. Guo, Q. Peng, X. Yan, Preparation of grapheme oxide-based hydrogels as efficient dye adsorbents for wastewater treatment, Nanoscale Res. Lett., 10 (2015) 272–281.

[12] Y. Liu, C. Hou, T. Jiao, J. Song, X. Zhang, R. Xing, J. Zhou, L. Zhang, Q. Peng, Self–assembled AgNP-containing nano composites constructed by electro spinning as efficient dye photo catalyst materials for wastewater treatment, Nano materials, 8 (2018) 35.

[13] World Steel Association. World steel statistics 2017[EB/OL]. World Steel Association, https://www.worldsteel.org/zh/media–centre/press–releases/2016.html. 2017–06–20.

[14] Y.J. Zhang, L. Kang, L.C. Liu, H.X. Si, J.F. Zhang, Synthesis of a novel alkali-activated magnesium slag-based nano structural composite and its photo catalytic performance, Appl. Surf. Sci., 331 (2015) 399–406.

[15] P.E. Tsakiridis, G.D. Papadimitriou, S. Tsivilis, C. Koroneos, Utilization of steel slag for Portland cement clinker production, J. Hazard. Mater., 152 (2008) 805–811.

[16] M. Makela, G. Watkins, R. Poykio, H. Nurmesniemi, O. Dahl, Utilization of steel, pulp and paper industry solid residues in forest soil amendment: Relevant physico chemical properties and heavy metal availability, J. Hazard. Mater., 207–208 (2012) 21–27.

[17] C. Oh, S. Rhee, M. Oh, J. Park, Removal characteristics of As(III) and As(V) from acidic aqueous solution by steel making slag, J. Hazard. Mater., 213–214 (2012) 147–155.

[18] Y.J. Zhang, L.C. Liu, Y. Xu, Y.C. Wang, D.L. Xu, A new alkali–activated steel slag–based cementitious material for photo catalytic degradation of organic pollutant from waste water, J. Hazard. Mater., 209–210 (2012) 146–150.

[19] L. Kang, Y.J. Zhang, L. Zhang, K. Zhang, Preparation, characterization and photo catalytic activity of novel CeO_2 loaded porous alkali-activated steel slag-based binding material, Int. J. Hydrogen Energy, 42 (2017) 17341–17349.

[20] L. Kang, Y.J. Zhang, L. Zhang, K. Zhang, M.M. Yang, Preparation and photo catalytic activity of CeO_2 loaded porous alkali-activated steel slag-based catalyst, Spectrosc. Spectral Anal., 37 (2017) 875–880.

[21] C.A.S. Oloveira, A.G. Gumieri, A.M. Gomes, W.L. Vasconcelos, Characterization of magnesium slag aiming the utilization as a mineral admixture in mortar, Inernational RILEM conference on the use of recycled materials in building and structures. Federal University of Minas Gerais(UFMG), Spain: Barcrlona., 2 (2004) 919–924.

[22] E.E. Kwon, H. Yi, J. Park, Transesterication of used vegetable oil by magnesium slag as heterogeneous catalyst(MgO–CaO/Al_2O_3), J. Chem. Eng. Japan, 45 (2012) 850–856.

[23] Y.J. Zhang, L. Kang, L.C. Liu, A novel magnesium slag-based cementitious nano-composite for photo catalytic degradation of dye, Rare Metal Mater. Eng., 44 (2015) 3032–3036.

[24] X.S. Wei, Z.J. Li, Study on hydration of port land cement with fly ash using electrical measurement, Mater. Struct., 38 (2005) 411–417.

[25] X. Long, M. Sun, Z. Li, X.H. Song, Piezo-resistive effects in carbon black-filled cement-matrix nano composites, J. Wuhan Univ. Technol., 30 (2008) 57–59.

[26] A.O. Monteiro, P.B. Cachim, P.M.F.J. Costa, Electrical properties of cement-based composites containing carbon black particles, Mater. Today: Proc., 2 (2015) 193–199.

[27] L. Wang, Q. Pang, Q. Song, X. Pan, L. Jia, Novel microbial synthesis of Cu doped $LaCoO_3$ photo catalyst and its high efficient hydrogen production from formaldehyde solution under visible light irradiation, Fuel, 140 (2015) 267–274.