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Potential Application of A Novel Bimetallic Cation Exchanger For The Catalytic Degradation of Malachite Green From Aqueous Solution

M.A. Dhanitha[1], S. Siji[2] and C. Janardanan[3*]

*Post Graduate and Research Department of Chemistry, Sree Narayana College, Kannur, Kerala 670007, **INDIA**

Email: dhanithabiju@gmail.com

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ABSTRACT

The present investigation focused on the degradation ability of a novel inorganic cation exchanger Zirconium cerium molybdate (ZCM) against malachite green dye in aqueous solution. This exchanger was characterized by some physicochemical properties like FTIR, XRD, TGA-DTA, SEM and ion exchange properties to validate the structure and ion exchange behavior. The exchanger shows high ion exchange capacity of 1.64 meqg^{-1} *as well as good chemical and thermal stability. The pH titration studies revealed mono functional behavior of the exchanger. The distribution studies of various metal ions showed that the material was highly selective for* Pb^{2+} *and* Mn^{2+} *ions. In order to explore the environmental applicability of the newly synthesized ion exchanger, its degradation potential towards malachite green dye was studied. The batch experiments were carried out by the treatment of aqueous dye solution with the exchanger. About 88% of the dye was degraded within 6 hours contact with the exchanger. The effect of process parameters viz. reaction time, pH, temperature, initial dye concentration and the amount of catalyst on degradation of dye has also been assessed with the help of UV-Visible Diffuse Reflectance Spectrophotometer. The entire studies revealed that ZCM was an effective catalyst for the removal of malachite green, which showed the applicability of material towards environmental remediation.*

Keywords: Malachite green, dye degradation, distribution studies, batch experiments etc.

INTRODUCTION

Environmental problem caused by toxic organic pollutants from the domestic and industrial output is now the subject of considerable concern from environmental remediation point of view [1]. Pollution from the effluents has become increasingly alarming with the usage of a wide variety of dyes in industries [2]. Synthetic dyes are used extensively for textile dyeing, paper printing, leather dyeing, color photography and as additives in petroleum products because of their ease and cost effectiveness in synthesis, firmness, high stability to light, temperature, detergent and microbial attack and variety in color compared with natural dyes. This has resulted in the discharge of highly colored effluents that affect water transparency and gas solubility in water bodies [3]. They also decrease or stop capacity of water reoxygenation by blocking sunlight thereby increasing BOD value. Therefore these conditions can prevent or disturb the growth of aquatic plants and animals [4].

Malachite green (MG), a triphenylmethane dye is highly soluble in water and used in aquacultures and animal husbandry as an antifungal, anti-bacterial, anti-parasitical therapeutic agent. MG dye is used extensively in silk, wool, jute and leather industries for dyeing process and in the manufacturing of paints and printing inks. MG in high concentration causes harmful effects on liver, kidney, intestine and gonads of aquatic organisms [5]. Many environmental remediation techniques such as analytical, biochemical and physicochemical methods are used for characterization and elimination of hazardous dyes from water. But each conventional method has its shortcomings since the dyes are stable to light and oxidizing agents, and are resistant to aerobic digestion [6,7].

Ion exchangers are now extensively used in heterogeneous catalysis. During the catalytic reaction, especially when catalytic degradation of dyes present in effluents of various industries is carried out, knowledge of the interaction of certain ions with the cations in the exchanger is very essential since the catalytic reactions are usually carried out in aqueous medium which may contain various cations. Cerium based materials got great interest due to their redox properties, because of conversion between Ce^{3+} to Ce^{4+} valence states under oxidation and reduction conditions. Cerium containing catalysts are broadly used as effective oxidation systems due to their unique properties such as redox, oxygen release and storage abilities [8]. Cerium based ion exchangers are reported having enhanced applications like decolorization of water by adsorption or degradation of organic dyes [9,10].

In the present study the catalytic potential of new inorganic cation exchanger, ZCM was evaluated for the degradation of malachite green without any irradiation and external catalyst. The effect of process parameters viz. reaction time, pH, temperature, initial dye concentration and the amount of catalyst on degradation of dye has also been assessed and the optimum conditions for maximum degradation was determined.

MATERIALS AND METHODS

Materials: Malachite green (oxalate) obtained from Merck, dye solutions were prepared by dissolving the dye in deionised water. Zirconium oxychloride(Loba Chemie,India) Ammonium ceric(IV) nitrate (E.Merck) and sodium molybdate(E.Merck) were used for the synthesis of the exchanger. All other reagents and chemicals used were of analytical grade.

Instruments: ELICO LI613 pH meter was used for pH measurements and an electric thermostat oven was used for heating the sample at various temperatures. UV-Visible spectrophotometer model JASCO V660 was used for spectrophotometric measurements. FTIR spectrometer model Thermo Nicolet Avtar370 for IR studies, X-ray diffractometer Bruker AXS D8 Advance for X-ray diffraction studies, Perkin Elmer Diamond TG/DTA Analysis System for thermal analysis and an electric shaking machine for shaking were also used. Jeol Model JSM - 6390LV for Scanning Electron Microscopic analysis and chemical composition was determined using EDS.

Synthesis of the exchanger: Different samples were prepared by adding a 0.05M solution of sodium molybdate to a mixture of 0.05M zirconium oxychloride solution and 0.05M ammonium ceric (IV) nitrate solution, in different volume ratios with intermittent shaking of the mixture and keeping the pH at 1.0 as given in table 1. It was then filtered, washed with deionized water and dried. The exchanger was then converted in to the H^+ form by treating with 1M nitric acid for 24 h with occasional shaking and intermittent changing of acid. It was then washed with deionized water to remove excess acid, dried and sieved to obtain particles of 60-100 mesh [11].

Ion exchange capacity (IEC): The ion exchange capacity of the material was determined by column method [10]. The exchange capacity in $meqg^{-1}$ was calculated using the formula;

$$\text{IEC} = \frac{av}{w}$$

Where ‘a’ is the molarity, ‘v’ is the volume of alkali used during titration and ‘w’ is the weight of the exchanger taken.

pH titration: Topp and Pepper method [12] was used for pH titration using NaOH/NaCl, KOH/KCl systems. 500 mg of exchanger was equilibrated with varying amounts of metal chloride and metal hydroxide solutions. pH of each solution was measured after attainment of equilibrium and plotted against milliequivalents of OH^- ions.

Chemical stability: The chemical stability of the exchanger was assessed in mineral acids like HCl, HNO_3 and H_2SO_4, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this 500 mg of the exchanger was kept separately in 50 mL of different solvents at room temperature for 24 h. The change in color and weight were noted.

Effect of temperature on IEC: The effect of temperature on IEC was studied by heating several 100 mg sample of the exchanger at different temperatures for three hours in an air oven and Na^+ ion exchange capacity in $meqg^{-1}$ was determined by column method after cooling them to room temperature.

Distribution studies (K_d): Distribution studies were carried out for various metal ions in demineralised water by batch method [13]. The distribution before and after equilibrium were determined volumetrically using EDTA as the titrant. The K_d values as depicted in table 2, were obtained from the formula;

$$K_d = \frac{I-F}{F} \times \frac{V}{w}$$

Where 'I' is the initial volume of EDTA used, 'F' is the final volume of EDTA used, 'v' is the volume of the metal ion solution and 'w' is the weight of the exchanger.

Catalytic degradation of MG using ZCM: The catalytic activity of ZCM on the degradation of malachite green dye was evaluated in laboratory conditions. For this a stock solution (50 ppm) of malachite green dye was prepared in deionized water and was diluted as and when required. The catalytic degradation was observed by the addition of 200 mg of ZCM to the dye solution at room temperature without any irradiation and external catalyst. Decolourisation of media was measured by taking optical density at different time intervals using UV-Vis DRS. The degradation efficiency was calculated [14] using Beer's law as;

$$\% \text{ Degradation} = \frac{Initial\ \ absorbance\ -final\ \ absorbance}{Initial\ \ absorbance} \times 100$$

Optimization of process parameters: The catalytic activity of the exchanger towards MG degradation was optimized under different conditions and parameters. The effects of catalyst dosage, initial concentration of dye solution, pH, temperature and time of contact of dye solution with the catalyst etc were studied. The removed ion exchangers from each of the dye solutions after equilibrium were collected and dried. The extent of degradation of the dye under different optimization conditions were determined by measuring the absorbance using UV-Vis DRS.

Recycling power of the catalyst: The catalyst's life time is an important parameter of the catalytic process, due to the fact that its use for a longer period of time leads to a significant cost reduction of the treatment. For this reason, the catalyst was recycled three times. After the optimized conditions for the degradation of the dye solution were determined, the catalyst was recovered by acid wash using dilute HCl and hot water and again used to study its recyclability.

RESULTS AND DISCUSSION

Synthesis and characterization of the exchanger: The result from the sodium ion exchange capacity of various samples of Zirconium cerium molybdate is presented in table 1. Ion exchange capacity and chemical stability seem to be much higher for sample ZCM2 and, therefore, this sample was chosen for detailed studies. Ion exchange capacity of the material was found to be $1.64meqg^{-1}$.

Table1: Conditions of synthesis and properties of different samples of Zirconium cerium molybdate

Sample	Molar Conc. (M)			Mixing Volume Ratio	pH	Appearance	I.E.C. (meq/g)
	Zr	Ce	Mo				
ZCM1	0.05	0.05	0.05	1:1:1	1	Yellow glassy solids	1.06
ZCM2	0.05	0.05	0.05	1:1:3	1		1.64
ZCM3	0.05	0.05	0.05	1:2:3	1		1.02
ZCM4	0.05	0.05	0.05	2:1:3	1		0.94
ZCM5	0.05	0.05	0.05	2:1:4	1		0.87

The energy dispersive spectrometry (EDS) was used to identify the elements exist in the prepared sample. The elemental composition in percentage of atomic elements in the sample and its spectral images are given in Figure 1(a). Composition of the ZCM was found as Zr: Ce: Mo; 1: 1.4: 2.1

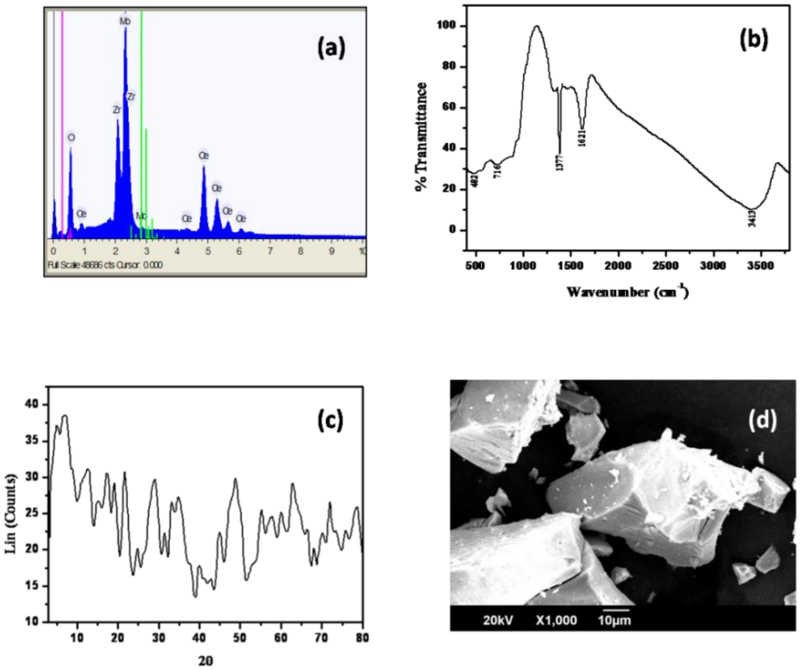

Figure 1: (a) EDS, (b) FTIR, (c) XRD and (d) SEM

FTIR spectra (Figure 1(b)) shows broad band in the region ~3413 cm^{-1} attributed to symmetric and asymmetric –OH stretching, while band at ~1621 cm^{-1} is due to H-O-H bending Band ~1377 cm^{-1} showed the presence of molybdate. The bands at 716 cm^{-1} and 482 cm^{-1} express the metal oxygen stretching vibrations [15]. The X-ray diffraction studies (Figure 1(c)) of cation exchanger ZCM reveal that there was no definite angle of diffraction line to tell about the crystallinity [16]. The scanning electron microscope image (figure 1(d)) of ZCM explains the particles were broad in size range, having an irregular shape and no sign of crystalline structure [16].

The thermogram of ZCM (Figure 2) suffers a first weight-loss of approximately 11.3% up to 100^{o}C, attributed to the loss of moisture and hydrated water [17]. Then a second weight loss of about 4% from 324^{0}C to 417^{0}C is due to the condensation of structural hydroxyl groups. The sample retained 75% of its original weight till the temperature reaches 850^{0}C. This clearly reveals that the material was quite stable at high temperatures and can be used in high temperature applications.

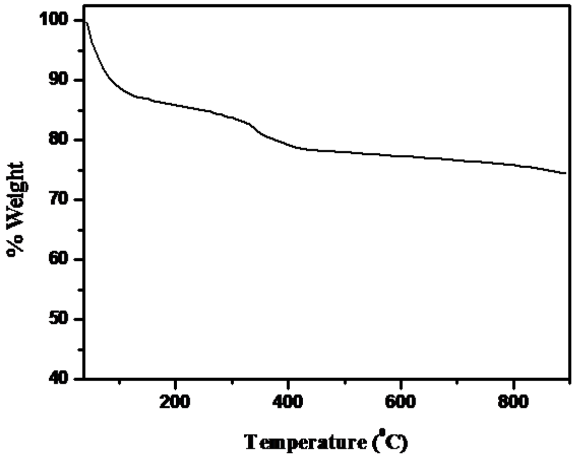

Figure 2: TGA of ZCM

pH titration studies (Figure 3(a)) using NaCl/NaOH, KCl/KOH systems show nearly monofunctional behaviour indicating only one ionizing group. The exchange capacity obtained from the curve is in agreement with that obtained by the column method [15]. It was observed that on heating at different temperatures for 1hr, the ion exchange capacity of the material was changed as the temperature increased as shown in Figure 3(b). Up to 400^{o}C the material shows prominent ion exchange capacity.

Distribution studies of various metal ions (Figure 4) were carried out with the sample. This showed that the exchanger has very high affinity towards Pb2+ and Mn2+ ions in comparison to other metal ions studied. The selectivity was found to be in the order $Pb^{2+} > Mn^{2+} > Bi^{3+} > Mg^{2+} > Co^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+} > Ca^{2+} > Hg^{2+} > Al^{3+}$.

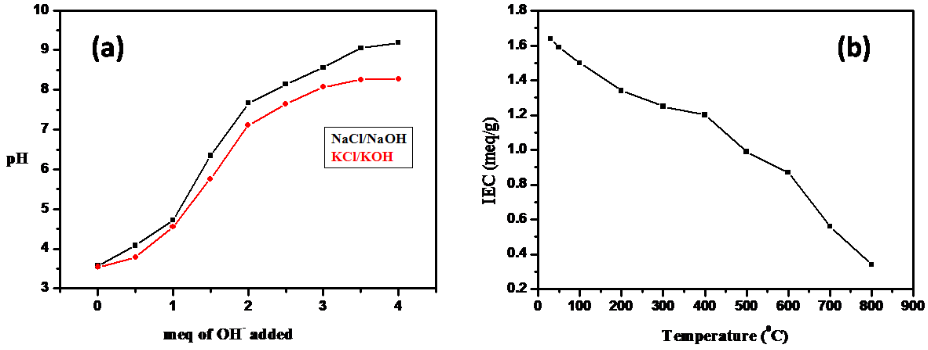

Figure 3: (a) pH titration curves and (b) Effect of temperature on IEC

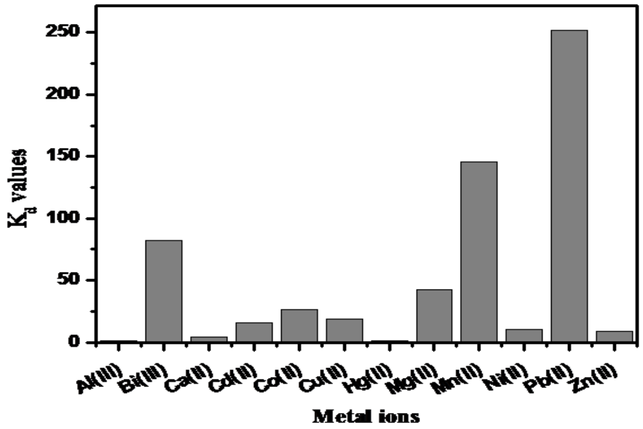

Figure 4: Distribution studies of metal ions on ZCM

Catalytic activity of ZCM towards dye degradation: Preliminary experiments were performed to check the catalytic activity of the exchanger, ZCM for the degradation of malachite green dye from aqueous solution. The results of UV-Visible DRS studies depict a visible outcome suggesting the degradation of malachite green solution. A drastic change in intensity of original peaks was observed after catalytic degradation and gave about 90% degradation after 24 h treatment at room temperature (Figure 5(a)). The removed ion exchangers from the dye solution after equilibrium were collected and dried. Absorbance recorded for these samples show close agreement with that of pure sample of ZCM (Figure 5(b)). These results indicate the strong catalytic activity of the new exchanger towards Malachite green dye degradation.

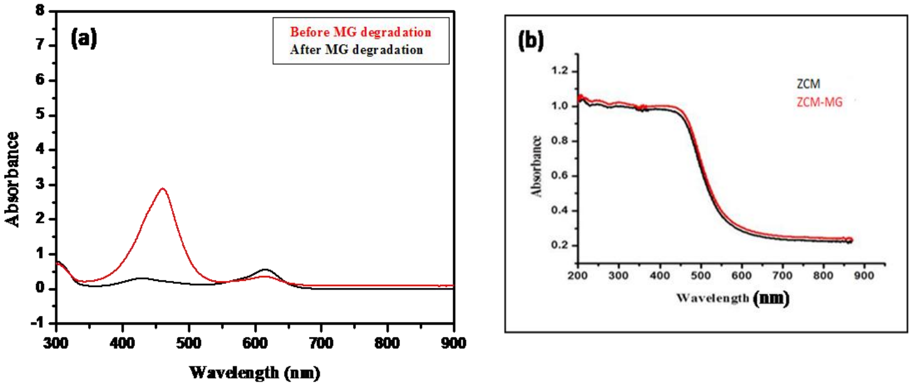

Figure 5: UV-Visible Spectra of (a) degradation of MG on ZCM and (b) solid samples of ZCM before and after treatment with MG

Optimization of process parameters

Effect of initial dye concentration: The effect of initial dye concentration on the rate of degradation was investigated by varying the initial concentration from 10ppm to 50ppm at constant catalytic dosage of 200mg at room temperature. The results are shown in figure 6(a). As seen in the figure the concentration of dye increases the rate of degradation decreases. The reason for this decrease is attributed to the shielding effect of dye at high concentration that retards the rate of dye degradation [18].

Effect of reaction time: To optimize the effect of reaction time on the degradation of MG 200mg of ZCM was shaken with 20 mL of 40ppm MG dye solutions at room temperature, keeping the pH of the medium neutral. Decolorization of media was measured by taking optical density at different time intervals using UV-Vis DRS. Results shown in figure 6(b) illustrates that the rate of degradation increases with increasing reaction time and reaches equilibrium at about 6 hours of contact of the dye solution with the catalyst.

Effect of pH: The pH of the dye solution is likely to affect the catalytic degradation of the dye; hence the effect of pH on the rate of degradation of MG dye was investigated in the pH range 2-10. The results are presented in figure 6(c). It has been observed that the rate of dye degradation was maximum at pH 6. In high acidic condition, rate of dye degradation remained very slow since the catalyst shows more affinity towards hydronium ions than dye molecules. In alkaline condition at higher pH, the formation of OH$^-$ ions is favored. This leads to decrease in the degradation rate because of the repulsion between excess OH-species on the catalytic surface and the dye surface [18].

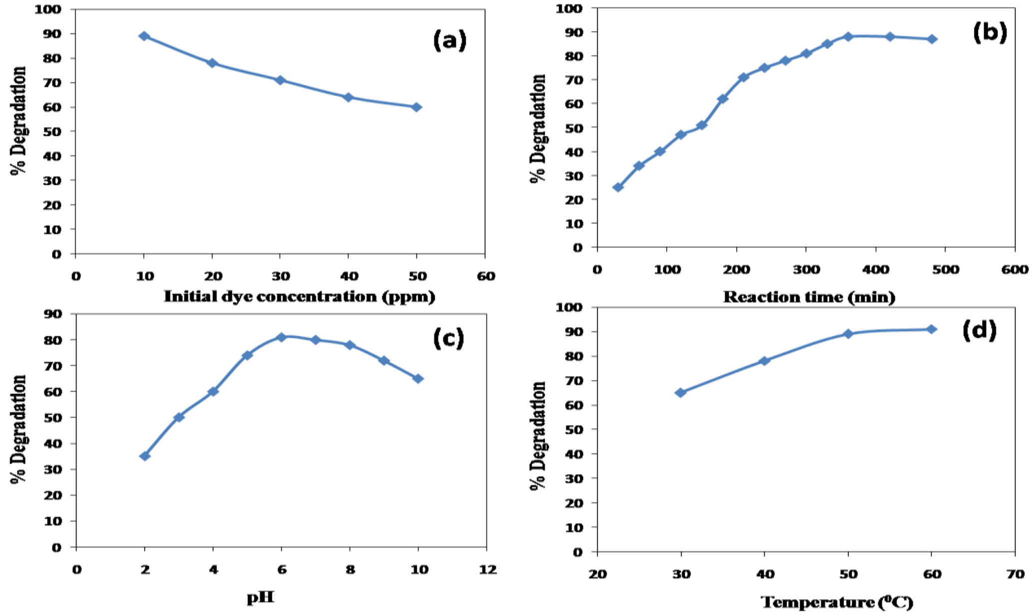

Figure 6: Effect of (a) initial dye concentration, (b) reaction time, (c) pH and (d) Temperature

Effect of temperature: Temperature is also again a very important factor for all processes associated with catalytic dye degradation. For this degradation experiments were performed at different temperatures, keeping a constant initial dye concentration, amount of catalyst and pH. It observed from the results (Figure 6(d)), the rate of dye degradation increases with increase in temperature.

Effect of amount of catalyst: The effect of catalyst concentration on the degradation rate of malachite green dye was investigated (figure 7(a)) by employing different concentrations of ZCM varying from 100 mg to 400 mg, maintaining the initial dye concentration 40 ppm. It is observed that the degradation rate increase with increase in catalyst concentration because of availability of more catalyst surface area for absorption and interaction of molecules of reaction with catalyst [19].

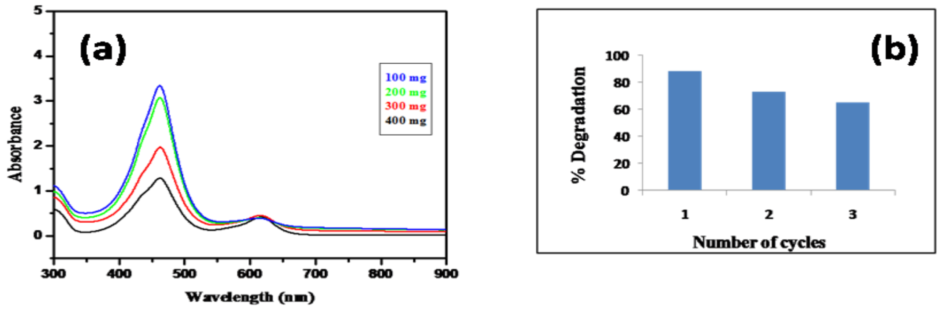

Figure 7: (a) Effect of amount of catalyst and (b) Recycling power of catalyst

Recycling of the catalyst: Catalyst can be recycled effectively, which makes the process cost effective. For this reason, the catalyst was recycled three times as shown in figure 7(b). After the optimized conditions for the degradation of MG dye were determined, the catalyst was recovered by giving acid wash and again used to study its recyclability. The results of the study showed that the efficiency decreases from 88% to 65%, may be due to the fouling of the catalyst and loss due to repeated acid wash.

APPLICATIONS

The present results reveals that ZCM was found to be an effective catalyst for the removal of malachite green, which showed the potential applicability of material towards environmental remediation.

CONCLUSIONS

The present study revealed the ability of the ion exchange material to remove Malachite Green from aqueous solution. The results of UV-Visible DRS studies showed that ZCM possessed high degradation efficiency, reusability and stability. The rate of degradation can be controlled by initial dye concentration, reaction time, pH, amount of catalyst and temperature. The entire studies revealed that ZCM was an effective catalyst for the removal of malachite green, which showed the potential applicability of material towards environmental remediation.

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