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Removal of Methylene Blue from Aqueous Solutions Using CeFe_{0.5}Cu_{0.5}O₃

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ABSTRACT

The removal of Methylene blue dye from aqueous solutions using the *B*-site doped perovskite CeFe_{0.5}Cu_{0.5}O₃ was investigated. The perovskite oxides were synthesised using Sol–Gel method and characterised by conventional powder X-ray diffraction technique. The X-ray measurements suggested that doping with Copper ion influences the structural properties of the oxides. It was found that both CeFeO₃ and CeFe_{0.5}Cu_{0.5}O₃ compounds are orthorhombic and have approximate particle size of 54.5 and 72.6 nm respectively. The batch mode study demonstrated that the removal capacity of Methylene Blue for CeFe_{0.5}Cu_{0.5}O₃ (18.8(8) × 10³ mg/g) is larger than that for CeFeO₃ (1.70(5) × 10³ mg/g) at 150 min at pH = 7. However, the two oxides exhibited similar capacities in both strong acidic and basic media. The removal of Methylene Blue was found to be negatively correlated with temperature. The maximum removals of dye were observed at pH = 2 and 12.

KEYWORDS: Removal, Methylene Blue, Perovskite Oxides.

1. INTRODUCTION

The present environmental concerns over organic water pollution have sparked an urgent demand in developing new decontamination techniques. For instance, the textile and printing industries produce and dump tonnes of highly coloured waste effluents per year in wastewater system.^{1,2} These effluents are characterized by strong variation of pH, high chemical oxygen demand and strong resistivity of biodegrading. They affect biodegradation. light penetration and photosynthesis producing imbalance in the ecosystem.³ Moreover, the effluents are classified as toxic and carcinogenic towards aquatic organisms and human. For example, methylene blue is an organic dye usually used in cotton and wool manufacturing, causes serious health problems for human such as vomiting, hard breathing and mental disorder. The absence of effective treatments results to sustain some components in the environment for a long period. The half-life of hydrolysed Reactive Blue-19 is \sim 46 years at pH = 7 and 25 °C.⁴ As a result, the development of wastewater treatment methods is essentially required.

The removal of effluents from wasters can be achieved by several methods, such as precipitation, flocculation, adsorption, oxidation, ultra-filtration, reversed osmosis, ion exchange and membrane separation. Out of these methods, adsorption is believed to be the most simple, economic

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and effective process. Thus, a wide variety of natural and

synthetic materials such as activated carbon, peat, various silica, activated clay, banana pith, natural manganese

mineral, oil ash, goat hair, alum sludge, natural zeolite,

mixtures of flash, soil and mixed metal oxides have been investigated as dye adsorbents. Among the mixed metal

oxides, perovskite compounds have been proven to be of

interest due to their efficiency in adsorbing and degrading

Generally, perovskite type oxides consist of two dif-

ferent cations, each surrounded by oxygen anions. The

larger cation (A-site cation) which can be alkali, alka-

line earth, or rare earth has dodecahedral symmetry into

the framework. Whilst the smaller cation (*B*-site cation)

which can be a transition metal ion, is six coordinate.⁶ Per-

ovskite structure can tolerate significant non-stoichiometry

and partial substitution. Consequently, perovskite com-

pounds show a diversity of structural modifications and

variants. These derivatives are classified to three types:

cubic perovskites, double perovskites and layered per-

ovskites, each associated with unique physical properties.⁷

Perovskite oxides can accommodate different combina-

This work investigates the removal of Methylene blue

(MB) from aqueous solutions using the mixed metal per-

ovskite CeFe_{0.5}Cu_{0.5}O₃. The impact of the replacing of

 Fe^{3+} (4s⁰3d⁵) with Cu²⁺ (4s⁰3d⁹) has been addressed to establish the role of the *B*-site cation in controlling

the adsorption properties of the oxides. These proper-

ties can be influenced by the differences in the effec-

tive charges and the electron configurations of the *B*-site

tions of cations, so long as the crystal charge is neutral.⁸

recalcitrant organic compounds.5

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cations. The study of *B* site doping has been of interest, since the number of *d*-electrons is critical in determining the adsorption properties of perovskite oxides.^{9, 10} For example, the $CO_{(g)}$ adsorption on $LaBO_3$ reaches a maximum when $B = Fe^{3+}$, whereas $NO_{(g)}$ adsorption shows maximum for Co^{3+} and Mn^{3+} . The NO adsorption over the wide range of temperature (273–673 K) is independent of the temperature on such substrates as $LaFeO_3$ and $LaNiO_3$.¹¹

Methylene blue is a heterocyclic aromatic compound with chemical formula C₁₆H₁₆N₃SCl.¹² It can be utilized in biology and chemistry. It is solid, odourless, dark green powder at room temperature. Despites the wide range of its applications in medicine, methylene blue is a monoamine oxidase inhibitor and if infused intravenously at doses exceeding 5 mg/kg may precipitate serious serotonin toxicity.¹² Thus, the presence of such pollutant in industrial discharge water is considered to have numerous impact on the environment. The removal of industrial dyes from wastewater is a crucial process, from both economic and environmental points of view. It is thought that employing mixed metal oxides such as $CeFe_{0.5}Cu_{0.5}O_3$ in removal of organic dyes can be a good replacement with other high cost adsorbents due to its high accessibility and low cost.

2. EXPERIMENTAL DETAILS

2.1. Sample Preparation

C T T C

To prepare the samples studied in this work the Sol–Gel method was utilized. Appropriate amounts of Ce(NO₃)₃ · $6H_2O$ (99.9%, BDH), Fe(NO₃)₃ · $6H_2O$ (99.9%, MERCK) and Cu(NO₃)₂ · $6H_2O$ (99.9%, MERCK) were mixed and dissolved in 25 ml of 0.1 M nitric acid (65%, CODEX). The mixture was then added to a citric acid solution (99.7%, BDH) in the mole ratio 1:2 (oxide/acid) and heated on a hotplate at 200 °C until the gel turned into ashes. The final products were ground using a mortar and pestle techniques and heated in an alumina crucible within a commercial furnace at 250 °C for 12 hrs and then reground and heated in stages at 350 °C for 12 hrs and 1000 °C for 48 hrs.

2.2. Instrumentations

The phase composition and purity of the samples was determined from X-ray diffraction. The X-ray diffractometer used was Philips PW 1800 X-ray generator located at the Libyan Oil institution, Tripoli, Libya with a copper tube (Cu-K α_1 radiation), having a wavelength of 1.5406 Å. The operating voltage was 40 kV and the current was 30 mA. The samples were measured in flat plate mode at room temperature with a scan range of $10^{\circ} < 2\theta < 80^{\circ}$ and a scan length of 10 mins were used. Diffraction patterns obtained from the Inorganic Crystal Structure Database (ICSD) were used for the comparison with obtained products.

The absorbance of solutions was determined using ultraviolet visible spectrophotometer (UV/Vis, model Spect-21D) and (190-900 Perkin-Elmer) at maximum wavelength of absorbance (660 nm). The concentrations of solutions were estimated from the concentration dependence of absorbance fit. The pH measurements were carried out on a WTW720 pH meter model CT16 2AA (LTD. Dover Kent, UK) and equipped with a combined glass electrode.

2.3. Batch Mode

Batch mode removal studies were carried out by varying several parameters such as contact time, pH, temperature and mass of prepared oxide (adsorbent). Essentially, a 50 ml of dye solution with concentration of 10 ppm was taken in a 250 ml conical flask in which the initial pH was adjusted using HCI/NaOH. Optimized amount of adsorbent was added to the solution and stirred using magnetic stirrer for specific time.

3. RESULTS AND DISCUSSION

3.1. Characterization of Oxides

The heating regime described above produced crystalline, black coloured samples. X-ray diffraction measurements showed the CeFe_{0.5}Cu_{0.5}O₃ oxide was isostructural with undoped CeFeO₃ and have an orthorhombic (*Pnma*) structure. Figure 1 illustrates the XRD patterns of the three oxides calcined at 1000 °C. The Average Crystallite size D_p , Line broadening in radians β , Bragg angle θ , X-ray wavelength λ and lattice strain estimated from X-ray diffraction data are summarised in Table I. The crystallite size can be calculated using sheerer formula:¹³

$$D_p = 0.94\lambda/(\beta_{1/2}\cos\theta)$$

As anticipated, $CeFe_{0.5}Cu_{0.5}O_3$ displayed larger crystallite size than $CeFeO_3$. The increase in crystallite size is



Fig. 1. XRD patterns of CeFeO₃ and CeFe_{0.5}Cu_{0.5}O₃.

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Table I. Average crystallite size D_p , Line broadening in radians β , Bragg angle θ , X-ray wavelength λ , lattice strain estimated from X-ray diffraction data.

Oxide	λ (Å)	θ (°)	β	D_p (nm)	Lattice strair
CeFeO ₃	1.54056	29.048	0.1574	54.48	0.0027
CeFe _{0.5} Cu _{0.5} O ₃	1.54056	29.046	0.1181	72.61	0.0020

consistent with the relative ionic size of the Fe³⁺ (6 coordinate ionic radius, 0.55 Å) and Cu²⁺ (6 coordinate ionic radius, 0.73 Å) cations.¹⁴ Doping with a divalent cation such as Cu²⁺ is expected to impact on the overall charge of the LaFeO₃ system. Such impact possibly results in either oxygen deficiency in the lattice or partial oxidation of Ce³⁺ (12 coordinate ionic radius, 1.34 Å) to Ce⁴⁺ (12 coordinate ionic radius, 1.14 Å) required to maintain charge neutrality.¹⁴

3.2. Batch Mode

3.2.1. Effect of Contact Time

The removal percentage of dyes over the adsorbents can be calculated as: $R\% = [(C_i - C_t)/C_i] \times 100$, where R% is the removal percentage, $C_i = 10$ ppm is initial concentration of dye solutions, C_t is the concentration of dye at contact time estimated from the concentration dependence of absorbance fit. The effect of contact time on the AB removal was observed at the range of (0–150 min). Figure 2 shows the time dependence of MB removal at room temperature. The removal of dye reached equilibrium within approximate 150 min for different dye concentrations. Surprising, the removal of MB using CeFe_{0.5}Cu_{0.5}O₃ is found to be ~2.5 times higher than that using CeFeO₃. The removal of MB on the surface of



Fig. 2. The time dependence of MB removal at room temperature. The volume, concentration and pH of the MB solution are 50 ml, 10 ppm and 7 respectively. The time dependent variation of the removal is fitted as labelled on the figure.

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CeFeO₃ and CeFe_{0.5}Cu_{0.5}O₃ are 36.90 and 95.06% respectively at 150 min. This result reflects the importance of the *B*-site doping and the element composition of the oxides.

3.2.2. Effect of Adsorbent Mass

The amount of the dye adsorbed by one gram of the oxides (Q) was calculated as following: $Q (mg/g) = [(C_i - C_t) \times$ V]/W, where t = 150 min is the contact time, V = 50 ml is the volume of MB solution and W is the mass of oxides. As shown in Figure 3, Q decreases as the mass of adsorbents increased. The maximum capacity of adsorbent Q_{max} can be estimated from the intercept of the liner fit of 1/Qat Y axis. The Q_{max} of CeFeO₃ and CeFe_{0.5}Cu_{0.5}O₃ are found to be $1.70(5) \times 10^3$ and $18.8(8) \times 10^3$ mg/g respectively. Unexpectedly, the values of Q_{\max} are consistent with crystallite size of the oxides. The amount of MB adsorbed by CeFe_{0.5}Cu_{0.5}O₃ which has the larger crystallite size (72.16 nm) is higher than that adsorbed by CeFeO₃ which has the lower crystallite size (54.48 nm). The decrease in crystallite size leads to an increase in the surface area of particles.¹⁵ Thus, the removal of dye should increase as crystallite size decreases. In this case, an enhancement in the adsorption properties occurred as a result of Cu substitution.

3.2.3. Effect of pH

To study the effect of pH, experiments were carried out at various pH values, ranging from 2 to 12 for constant dye concentration (10 ppm) and adsorbent mass (0.1 g). Surprising, the two oxides displayed similar efficiency of removal at strong acidic and strong basic media. Figure 4 shows the removal of MB as a function of pH. The lowest removals of MB are found to be 37.18 and 71.06% for CeFeO₃ and CeFe_{0.5}Cu_{0.5}O₃ respectively at pH = 7.



Fig. 3. The effect of mass adsorbent on the removal of MB. The time, volume, concentration and pH of the MB solution are 150 min, 50 ml, 10 ppm and 7 respectively.



Fig. 4. The effect of pH on the removal of MB. The time, volume and concentration of the MB solution are 150 min, 50 ml and 10 ppm respectively.

The removal of MB increases as pH decreases from 7 to 2, and as pH increases from 7 to 12. The interpretation of pH effects on the efficiency of the adsorption process is a very difficult task, because of its multiple roles. It is related to the acid base property of both the metal oxide and the organic dye. The adsorption of water molecules at metal sites is followed by the dissociation of OH^- groups, leading to coverage with chemically equivalent metal hydroxyl groups (M–OH). Due to amphoteric behaviour of both the metal oxide and the organic dye, the equilibrium reactions below are considered. The electrostatic interactions between the positive catalyst surface and dye anions leading to strong adsorption of the last on the oxide support. 1. $M-OH + H^+ \leftrightarrow M-OH_2^+$.

2. M-OH \leftrightarrow M-O⁻ + H⁺.

3. Dye-OH + H⁺ \leftrightarrow Dye⁺+ H₂O.

4. H-Dye + OH⁻ \leftrightarrow Dye⁻ + H₂O.

3.2.4. Effect of Temperature

Temperature has an important impact on the adsorption process. An increase in temperature helps the reaction to compete more efficiently with e^-/H^+ recombination. The removal of MB was investigated at 25, 40, 70 and 100 °C. The obtained results are illustrated below in Figure 5. The removal of MB decreased as the temperature increased. For instance, the removal of MB using CeFeO₃ and CeFeO_{.5}Cu_{0.5}O₃ decreased respectively from 36.92 and 89.05% at 25 °C to 25.25 and 80.00% at 100 °C. The decrease in percentages of adsorption with rise in temperature may be due to desorption caused by an increase in the thermal energy. Higher temperature induces higher mobility of active sites of adsorbents.

The energy of activation (E_a) , was calculated from the Arrhenius plot of $\ln R$ versus 1000/T (Fig. 6). Arrhenius plot shows that the activation energies of the removal of



Fig. 5. The effect of temperature on the removal of MB. The time, volume and concentration of the MB solution are 150 min, 50 ml and 10 ppm respectively.

MB using CeFeO₃ and CeFe_{0.5}Cu_{0.5}O₃ are negative and equal to -4.34 ± 1 and -1.48 ± 1 kJ mol⁻¹ respectively. This result is contrary to normal expectations, and is a consequence of the competition between two effects: the increase of intrinsic kinetics with temperature, and the decrease of adsorption strength and the concentration of active intermediates with temperature.¹⁶ The adsorption of MB dye can be described as barrierless reaction, in which the reaction proceeding relies on the capture of the molecules in a potential well. Increasing the temperature leads to a reduced probability of the colliding molecules capturing one another (with more glancing collisions not leading to reaction as the higher momentum carries the colliding particles out of the potential well), expressed as a reaction cross section that decreases with increasing



Fig. 6. Arrhenius plot of lnR% versus 1000/T (K)

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temperature. Such a situation no longer leads itself to direct interpretations as the height of a potential spot. $^{\rm 17}$

4. CONCLUSION

The removal of Methylene blue from aqueous solution using the mixed metal perovskite $CeFe_{0.5}Cu_{0.5}O_3$ has been reported. In general, the amount of MB adsorbed by the *B* site doped oxide $CeFe_{0.5}Cu_{0.5}O_3$ is about two times higher than that adsorbed by the undoped oxide $CeFeO_3$. The study showed no finite time for the MB removal up to 150 min. The adsorption of MB was mass, temperature and pH dependent. The two oxides showed maximum removal efficiency of dye at 25 °C and pH = 2.0 and 12. The oxides showed minimum removal efficiency of dye at 100 °C and pH = 7. The adsorption capacity of MB from water was $1.70(5) \times 10^3$ and $18.8(8) \times 10^3$ mg/g using $CeCrO_3$ and $CeFe_{0.5}Cu_{0.5}O_3$ respectively. This study indicated that doping with Cu^{2+} into $CeFeO_3$ can successfully enhance the adsorption properties of the oxide.

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