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Photocatalytic Decolorization of Celestine Blue B from Industrial Wastewater Using Ni_3O_4-MgO Coupled Oxides

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This study describes the preparation of coupled oxide Ni_3O_4-MgO using co-precipitation method using their corresponding nitrates as precursor materials to prepare these coupled oxides. The prepared oxides were investigated with X-ray diffraction and Fourier transform infrared spectroscopy. The photocatalytic activity of this material was investigated by following removal of Celestine blue B dye from simulated industrial wastewaters. Different reaction conditions were undertaken to reach optimum conditions for dye removal. These conditions involve performing different catalyst loading, effect of contact time and effect of pH of reaction mixture. The remaining concentration of Celestine blue B dye over the period of reaction mixture was calculated spectroscopically by measuring the absorbance of supernatant liquid at 648 nm. From the results, it was found that the optimum conditions for dye removal in this study was 0.20 g, pH 4 and a contact time of 30 min and the dye removal percentage under these conditions was found to be 89 %.

Keywords: Celestine blue B, Coupled oxides, Industrial wastewaters, Water pollution.

INTRODUCTION

In present day, synthetic dyes are considered as a main source for pollution of water including, underlying waters, river water, lake water and drinking waters. Annually large amounts of these dyes dispose from factories into the ambient environment causing pollution of water and soil. The polluting effect of these dyes increase especially when the organic chemical structure of these dyes containing some constituents such as sulfur, nitrates, heavy metals, *etc*. [1-3]. As a result of global warming especially in the industrial states and the shortage of water, the process of treatment of polluted water becomes from essential requirements to reuse this polluted water to be reused for further uses especially for industrial processes.

In this context, different methods and techniques can be used for this purpose. These are physical methods, chemical methods and biological methods. In general, most of these methods are not sufficient effective and cost effective [4]. Recently, heterogeneous photocatalytic methods were applied as an alternative methods that can be used in treatment of polluted waters [5,6].

Many researches had been reported using phtocatalysts in heterogeneous photocatalysis systems investigating removal of polluted dyes from industrial waters. Most of these photocatalysts showed higher efficiency in dye removal besides that these photocatalysts can be cyclized to be used more than one time [4-6]. In this context, many types of semiconductors photocatalysts were applied such as TiO_2, ZnO, Cu_2O, CdS, ZnS, *etc*. in the presence of UV light and solar spectrum with hydrogen peroxide [7]. Also different modified forms of these photocatalyst include doped oxides with metals and non-metals, activated carbons/photocatalysts and coupled oxides [8,9]. On other hand, both of single MgO and Ni_3O_4 was used in treatment of polluted industrial wastewaters in heterogeneous photocatal-ysis systems and it was found that these polluted dyes in the polluted wastewaters were mineralized into CO_2, H_2O and some other volatile and inorganic materials [10,11].

The present study involves preparation of coupled oxides Ni_3O_4-MgO using co-precipitation methods. The photocatalytic activity of these materials would be investigated *via* following Celestine blue B dye removal from simulated industrial wastewaters.

EXPERIMENTAL

Coupled oxide Ni_3O_4-MgO was prepared using co-precipitation method for their corresponding nitrates, $Ni(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$ (98 %, BDH Company). To the aqueous solution of these nitrates, sodium bicarbonate (1 M) was added dropwise as a precipitating reagent with heating at 70-75 ºC with a continuous stirring under ambient atmospheric conditions. The

pH of reaction mixture was maintained around pH 9 using (pH meter 740 Inolab, WTW). This mixture was kept under heating and stirring for 2 h and the proposed precipitate of metallic carbonates filtered off, washed with de-mineralized water for several times and finally dried in oven at 120 ºC for 24 h. The obtained catalyst was calcinated at 600 ºC for 4 h using muffle furnace size tow, Gallenkamp.

Celestine blue B dye was purchased from Sigma Aldrich company and used as a polluted textile dye model. This dye has a molecular formula of $C_{17}H_{18}N_3O_4Cl$ with a molecular weight of 363.80 g mol^{-1}.

XRD patterns of each of single and composites materials were investigated using powder X-ray diffraction. XRD patterns were recorded using Simadzu-6000 X-ray diffractometer with a nickel filter using monochromatized CuKα radiation at 40 kV and operated at 30 mA.

The functional groups coupled oxides were investigated using Perkin Elmer spectrophotometer. FTIR spectrrum of Ni_3O_4-MgO are recorded in the range 4000-400 cm^{-1}.

Photocatalytic experiments were carried out using home-made photoreactor (Fig. 1). All the experiments were carried out using an aqueous solution of Celestine blue B dye (50 ppm, 30 mL) with a suspension of a required mass of the prepared Ni_3O_4-MgO catalysts. Photocatalytic reactions were carried out under irradiation with UV light from low pressure mercury lamp. In all cases, photocatalytic reactions were started after performing a dark reaction for each experiment to ensure reaching adsorption equilibrium for all experiments. Reaction was investigated by following the absorbance of supernatant liquid of Celestine blue B dye solution at 644 nm using UV-vis Shimadzu 1650 PC-UV-visible spectrometerphotometer . The percentage of dye removal was conducted using the following relationship [12]:

$$R\ (\%) = \frac{C_i - C_f}{C_i} \times 100$$

where, C_i is the initial concentration of Celestine blue B dye, C_f is the final concentration of the dye after reaction period.

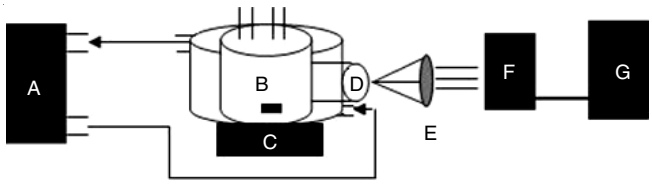

Fig.1. Photocatalytic reaction unit used in photocatalytic reactions

A study was performed to determine the best optimum of used mass of Ni_3O_4/MgO, different masses of coupled oxides were used 0.05, 0.1, 0.15, 0.20 and 0.25 g. Each of these masses were suspended in 30 mL of dye solution (50 ppm). All the experiments were carried out at a pH 4and under irradiation with UV light using mercury lamp (TQ150 Z2) Karl Kolb company. All the experiments were carried out at 293 K under atmospheric conditions.

RESULTS AND DISCUSSION

XRD patterns were used to investigate crystal structure of the prepared coupled oxide which was calcinated at 600 ºC. The peaks around at 2θ = 37.2º, 43.2º, 62.8º, 75.0º are related to pattern modes of nickel oxide (Fig. 2). The peaks around 36.9º, 42.9º and 62º are related to magnesium oxide (Fig. 2).

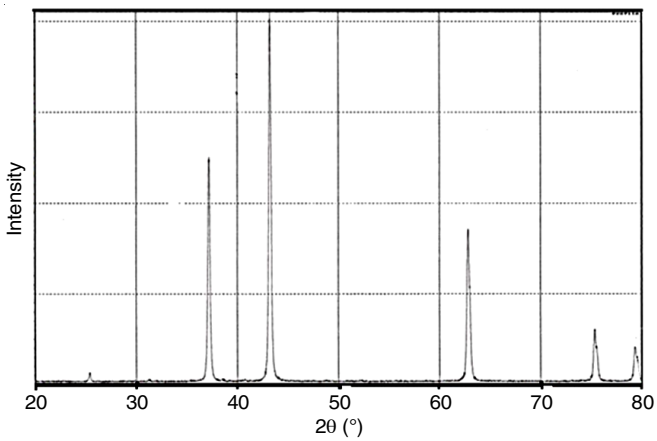

Fig. 2. XRD patterns for coupled oxides Ni_3O_4-MgO

FTIR spectra for the coupled oxide is shown in Fig. 3. These spectra show peaks around 449, 557 and 663 cm^{-1}, these peaks are corresponding to metal-oxygen bonds for both of nickel oxide and magnesium oxide. Other bands around 1500 and 433 cm^{-1} are related to surface hydroxyl group of both oxides.

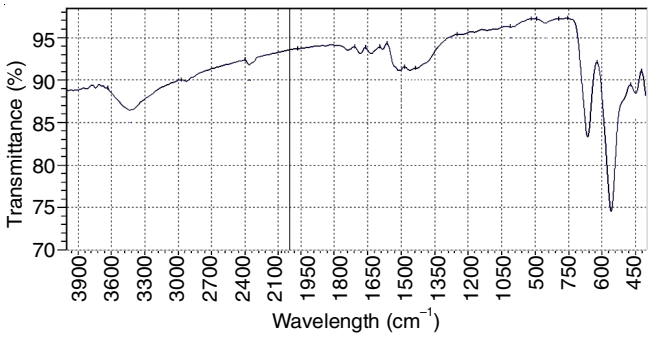

Fig. 3. FTIR spectrum for coupled oxide (Ni_3O_4-MgO)

The effect of loading of Ni_3O_4-MgO and contact time on photocatalytic removal of Celestine blue B dye was investigated in this part. A series of experiments were performed to determine the optimum load of Ni_3O_4-MgO that show high efficiency of photocatalytic removal of Celestine blue B dye under irradiation with UV light at 293 K and at pH 4. The used masses were 0.01, 0.10, 0.15, 0.20 and 0.25 g. The obtained results (Table-1) showed that 0.20 g was the optimized mass that gives higher efficiency for dye removal. The results also showed that the efficiency of dye removal was increased with increase reaction time (Fig. 4).

From the above results, it can be seen that the optimum mass of the used coupled oxides was 0.20 g, which showed high removal efficiency of dye around 85 % after 1 h of reaction time at 293 K. This arises from increase of the available active sites at the surface with increase of Ni_3O_4-MgO amount in reaction mixture. These active sites provide adsorption positions

TABLE-1
PERCENTAGE REMOVAL OF CELESTINE BLUE B DYE USING DIFFERENT AMOUNT OF Ni_3O_4-MgO AT (pH = 4)

Irradiation time (min)	Removal efficiency (%)				
	0.05 g	0.10 g	0.15 g	0.20 g	0.25 g
0	0	0	0	0	0
10	24.1	43.9	25.2	85.0	33.7
20	33.6	44.6	48.5	86.0	34.4
30	39.6	46.9	49.5	87.0	37.9
40	46.5	47.7	53.3	89.0	41.3
50	48.2	52.2	56.3	97.0	48.2
60	56.8	62.1	70.8	98.0	51.7

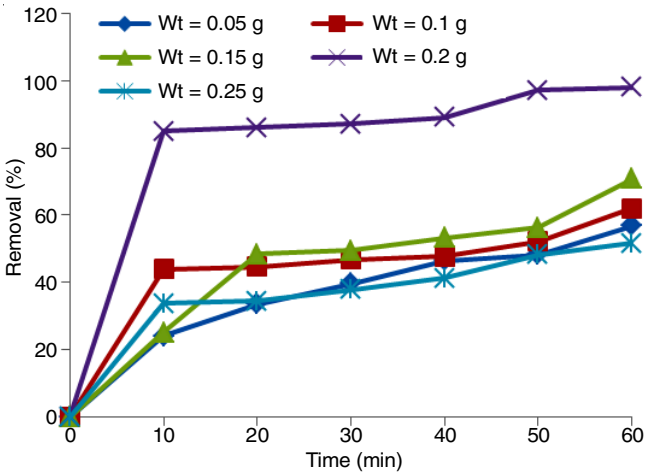

Fig. 4. Effect of contact time and mass loading of coupled oxides on photocatalytic removal of Celestine blue B dye

for dye molecules [13]. This effect can also be attributed to absorb photon of light as it according to first law of thermochemistry only adsorbed molecule would participate in photochemical processes. So that with increase of amount of catalyst, this means that high number of catalyst particles would absorb photon of light and becomes photo-excited. This would contribute in producing high concentrations of redox species such as hydroxyl radicals and oxygen superoxide. These species would contribute in dye fragmentation and producing some eco-friendly species such as CO_2 and H_2O [13,14]. In case of higher loading of coupled oxide (< 0.20 g), the efficiency of dye removal decrease to around 38 % when used the amount 0.25 g. This arises from aggregation of particles of coupled oxides with forming of inner filter in reaction mixture which prevent passing of photon of light to another side of reaction mixture as well as scattering of light out of the cell of reaction. The results of these factors lead to reduce the concentration of redox species and hence reduction the efficiency of dye removal at more dense solutions. The efficiency of dye removal increases with progress of reaction time, this arises from providing of efficient time to adsorb dye molecules at the active sites of coupled oxides [14,15].

The effect of pH of reaction mixture on the photocatalytic removal of Celestine blue B dye over suspension of MgO/Ni_3O_4 a series of experiment were performed using 50 ppm of dye solution for each run at 293 K with continuous stirring under irradiation with UV light with different four pH (3,4,7 and 9) were applied.

From these results (Table-2 and Fig. 5), the optimum removal efficiency of the dye was achieved at pH 4 and around 90 %

TABLE-2
REMOVAL EFFICIENCY OF CELESTINE BLUE B DYE BY PHOTOCATALYTIC REACTIONS OVER COUPLED OXIDES AT DIFFERENT pHs

Irradiation time (min)	Removal efficiency (%)			
	pH 3	pH 4	pH 7	pH 9
0	0	0	0	0
10	23.4	85.0	8.9	4.3
20	30.2	86.0	46.2	8.6
30	30.4	87.0	53.7	13.0
40	48.9	89.0	55.2	17.3
50	55.3	970.	64.1	21.7
60	59.5	98.0	68.6	23.4

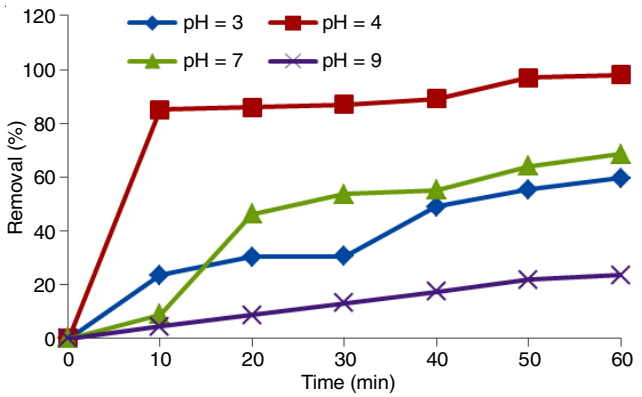

Fig. 5. Effect of pH of reaction mixture on Celestine blue B dye photocatalytic oxidation using Ni_3O_4-MgO

removal was achieved after 1 h of reaction period. This result can be related to protonation of surface of the catalyst at this acidic medium and the surface possess a net positive charge. This leads to strong attraction between negatively charged dye molecules with the surface. So that the high portions of dye molecules would adsorb at the active sites of the surface, which leads to increase the activity of photocatalytic oxidation of Celestine blue B dye under this environment [16]. At higher pH values (basic medium), the surface of catalyst exhibits a net negative charge, which lead to increase repulsion between the surface and dye molecules. Under these conditions, only few portions of dye molecules would adsorb at the surface which causes a reduction on the activity of dye removal using photocatalytic reactions [17].

Conclusion

The coupled oxide Ni_3O_4-MgO using co-precipitation method was synthesized and applied as photocatalytic material for the removal of Celestine blue B dye from the industrial wastewater. The optimum conditions for dye removal (89 %) in this study was 0.20 g of coupled oxide Ni_3O_4-MgO at pH 4 and a contact time of 30 min.

REFERENCES

1. A. Lafta, A.F. Halbus, Z.H. Athab, A.M. Kamil, A.S. Hussein, A.F. Qhat and F.H. Hussein, *Asian J. Chem.*, **26**, 119 (2014); https://doi.org/10.14233/ajchem.2014.19027.
2. F. Hussein, A. Halbus, H. Hassan and W. Hussein, *E-J. Chem.*, **7**, 540 (2010); https://doi.org/10.1155/2010/719674.
3. R. Kant, *Nat. Sci.*, **4**, 22 (2012); https://doi.org/10.4236/ns.2012.41004.

4. Z. Shi, K. He, X. Yu, Z. Yao, F. Yang, Y. Ma, R. Ma, Y. Jia and J. Zhang, *J. Environ. Sci. (China)*, **19**, 933 (2007); https://doi.org/10.1016/S1001-0742(07)60154-5.
5. A. Mills and S. Le Hunte, *J. Photochem. Photobiol. Chem.*, **108**, 1 (1997); https://doi.org/10.1016/S1010-6030(97)00118-4.
6. C. Chen, J. Chang and A. Chen, *J. Hazard. Mater.*, **185**, 430 (2011); https://doi.org/10.1016/j.jhazmat.2010.09.051.
7. O. Benhabiles, H. Mahmoudi, H. Lounici and M.F.A. Goosen, *J. Desalination Water Treat.*, **57**, 14067 (2015); https://doi.org/10.1080/19443994.2015.1061954.
8. O. Hamdaoui, *J. Hazard. Mater.*, **135**, 264 (2006); https://doi.org/10.1016/j.jhazmat.2005.11.062.
9. E. Mohammad, A. Lafta, S. Kahdem and A. Alkaim, *Int. J. Chemtech Res.*, **9**, 656 (2016).
10. E. Mohammad, A. Lafta and S. Kahdim, *Polish J. Chem. Technol.,* **18**, 10 (2016).
11. A.K. Ramasami, M.V. Reddy and G.R. Balakrishna, *Mater. Sci. Semicond. Process.*, **40**, 194 (2015); https://doi.org/10.1016/j.mssp.2015.06.017.
12. F.H. Hussein and A.F. Halbus, *Int. J. Photoenergy*, **Article ID 495435** (2012); https://doi.org/10.1155/2012/495435.
13. C. Wei, X. Tang, J. Liang and S. Tan, *J. Environ. Sci. (China)*, **19**, 90 (2007); https://doi.org/10.1016/S1001-0742(07)60015-1.
14. P. Kar, S. Verma, A. Das and H.N. Ghosh, *J. Phys. Chem. C*, **113**, 7970 (2009); https://doi.org/10.1021/jp901135n.
15. K. Mahmoudi, K. Hosni, N. Hamdi and E. Srasra, *Korean J. Chem. Eng.*, **32**, 274 (2015); https://doi.org/10.1007/s11814-014-0216-y.
16. H. Wang, C. Xie, W. Zhang, S. Cai, Z. Yang and Y. Gui, *J. Hazard. Mater.*, **141**, 645 (2007); https://doi.org/10.1016/j.jhazmat.2006.07.021.
17. D. Zhao, J. Wang, Z. Zhang and J. Zhang, *Front. Chem. Eng. China*, **3**, 206 (2009); https://doi.org/10.1007/s11705-009-0053-4.