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Synthesis of Magnesium Nanoparticles for the Removal of Lissamine green dye and its response surface Methodology using CCD method

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Abstract

In the present investigation we explore the green synthesis method of Magnesium Nanoparticles and its equilibrium studies to find the bioadsorption capacity of Mg Nps to remove the Lissamine Green dye from the aqueous effluents. The removal of the dye is observed using the UV Spectrophotometer. The optimized parameters obtained for the study as pH: 5, Agitation time: 50 min, Concentration: 20 mg/L and dosage: 2.6 g/L. At the optimized conditions the % removal of LG dye observed was 96%. CCD (Central Composite Design) is applied to evaluate the role of bioadsorption variables. Based on its excellent performance, cost-effectiveness, ease of manufacture, and large surface area, Mg Nps has great potential to produce low cost and efficient adsorbents for environmental applications.

Keywords: Bioadsorption, Lissamine green, Magnesium Nanoparticles, RSM.

1. Introduction

Dyes are the major hazardous elements which cause threat to aquatic life. These are the major pollutants that are released from different industries like textiles, food, paper and etc. These pollutants of water causes threat to aquatic life and also there is a need for the treatment of effluents in water inorder to minimize the pollution and also to make live the aquatic species So far, several methods have been developed to remove the dye, adsorption, photocatalytic destruction, electrochemical Decomposition, Fenton reaction and filtration mak. Among these purification methods, adsorption is The most attractive for removal due to its ease of operation, low Cost, high efficiency, no secondary pollution and recyclable [1-15]. Dye removal efficiency depends on physicochemical effects Characteristics of similarly developed adsorbent Internal pore structure, high specific surface area Area, pore size

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distribution, pore volume, surface charge (Surface hydrophobic and hydrophilic) and Presence of functional surface groups[16-18].Consequently, remedy of dye-infected wastewaters with decontamination approaches is important earlier than their discharge. Adsorption of dyes on less expensive and efficient strong and is one of the most effective and maximum economical strategies for disposing of dyes from wastewater.

2. Experimental procedure

2.1 Preparation of the Nanoparticle solution

Quisqualis indica plant leaves are collected from near by locality and they are washed thoroughly to remove dust and then they are boiled in distilled water to obtained the broth solution. The broth solution obtained from the leaves are mixed with 0.05M $Mg(NO_3)_2$ solution and then the mixture is heated at 60°C for 15 min then the change in colour indicates the nano particles formation.

2.2 Preparation of Dye solution

For preparation of stock solution 1g of dye powder is used for 1000 ml of distilled water which gives a dye solution of concentration 1000 ppm out of which the concentration of 20 ppm is taken for the process.

Batch equilibrium studies have been performed for the removal of LG dye to find the bioadsorption capacity.

3. Results and Discussion

3.1 Equilibrium Studies

3.1.1 Effect of Contact Time

The removal rate of lissamine green was compared to the contact time in Fig. 1 From the plot, we can see that the removal rate increases continuously in the first 50 minutes of stirring. After a contact time of 50 minutes, the change in LG dye removal rate is almost constant. Therefore, the equilibrium contact time is 50 minutes. In the current study, the contact time is 5 to 180 minutes, 50 ml of aqueous solution, 1g/L dosage are added, and the removal rate is from 16%. Up to 60% with a contact time of 5-50 minutes. The longer the contact time, the higher the removal rate, so the contact time affects the efficiency of the removal process.

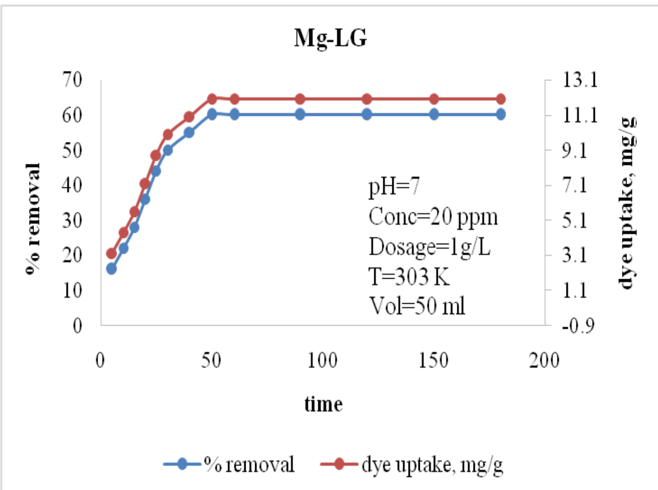

Fig. 1 Effect of Contact Time on LG dye

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3.1.2 Effect of pH

The grapH shown in Fig. 2 is plotted between % removal of Lissamine Green and pH of aqueous solution. A rapid increase in the removal rate of LG is seen as pH is increased from 2 to 5 and decrease in the removal rate is seen with further increase in pH over 5. For the current investigation of pH with 50 mL of aqueous solution, adding nanoparticle and organism, the rate of removal is increased from 60% to 74 % and dye uptake is 12 to 14.8 mg/g in the pH range from 2 to 5 and beyond the pH value of 5 it was decreased.

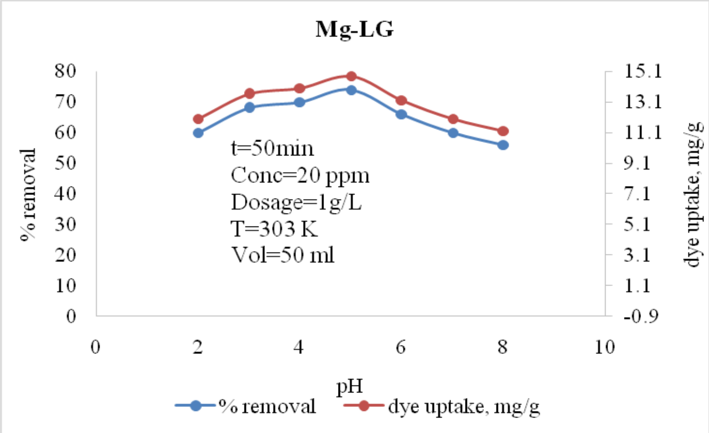

Fig. 2 Effect of pH on LG dye

3.1.3 Effect of Concentration

Fig. 3 shows the effect of the initial concentration of lissamine green in aqueous solution on the removal rate at optimal contact time. By increasing the LG dye concentration from 20 to 100 mg / l, the removal rate gradually decreases from 74% to 68.6% and the dye uptake goes from 14 mg / g to 68.6 mg/g

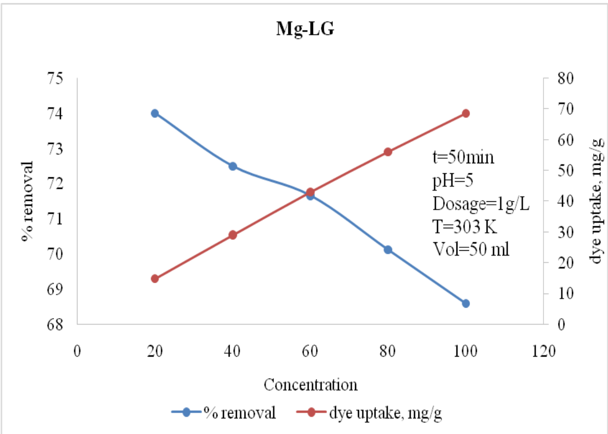

Fig. 3 Effect of concentration on LG dye

3.1.4 Effect of Dosage

Fig. 4 shows the change in the removal rate of lissamine green from aqueous solution with the biosolvent dose. Increasing the dose from 1g/L to 5 g/L increases the removal rate from 74% to 93%. Removal rate from solution increases by with increasing dose of bioadsorbent. This is because increasing the dose of bioadsorbent increases the number of active centers available for dye uptake.

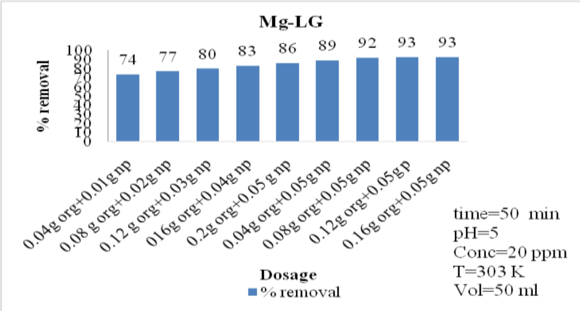

Fig. 4 Effect of Dosage on LG dye

3.1.5 Effect of temperature

The temperature effect on optimal dye absorption was important. Figure 5 shows the effect of temperature changes on the uptake of LG dyes. The results show that the QI adsorption limit of LG dyes increases with temperature. As the temperature rose from 283K to 323K, the removal rate increased from 85% to 93%. Therefore, temperature affects the removal process

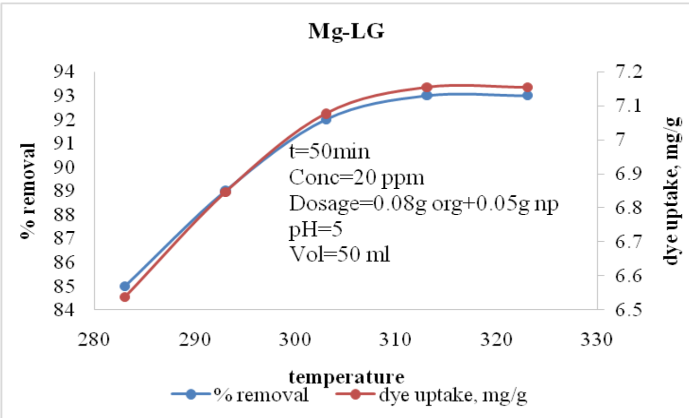

Fig. 5 Effect of Dosage on LG dye

3.2 Optimization using RSM:

3.2.1 Optimization using CCD

The parameters that have greater influence over the response are to be identified so as to find the optimum condition for the biosorption of LG dye. The quadratic model is used in the present study, to relate four independent variables and percentage biosorption of LG dye. The regression equation for is % biosorption of LG dye is function of pH (X_1), C_o (X_2), w (X_3) and T (X_4) [19].

The varieties in the relating coded estimations of four boundaries and reaction are introduced in table-.1 and their respective results were shown in table-2.

Table-.1 Levels of different process variables in coded and un-coded form for % biosorption of LG dye using *Mg Nps*

Variable	Name	Range and levels				
		-2	-1	0	1	2
X_1	pH of aqueous solution	3	4	5	6	7
X_2	Initial concentration, C_o, mg/L	10	15	20	25	30

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X_3	Biosorbent dosage, w, g/L	1	1.8	2.6	3.4	4.2
X_4	Temperature, T, K	283	293	303	313	323

The accompanying condition speaks to different relapse investigation of the test information for the biosorption of LG dye:

Table- 2 Results from CCD for LG dye biosorption by *Mg Nps*

Run no.	X_1, pH	X_2, C_o	X_3, W	X_4, T	% biosorption of CV dye	
					Experimental	Predicted
1	4	15	1.8	293	74.04	73.95
2	4	15	1.8	313	75.76	75.71
3	4	15	3.2	293	74.76	74.89
4	4	15	3.2	313	76.36	76.25
5	4	25	1.8	293	75.60	75.56
6	4	25	1.8	313	77.20	77.44
7	4	25	3.2	293	76.45	76.37
8	4	25	3.2	313	77.92	77.86
9	6	15	1.8	293	73.39	73.53
10	6	15	1.8	313	75.04	74.94
11	6	15	3.2	293	75.28	74.86
12	6	15	3.2	313	75.76	75.88
13	6	25	1.8	293	75.08	75.01
14	6	25	1.8	313	76.60	76.54
15	6	25	3.2	293	76.10	76.22
16	6	25	3.2	313	77.44	77.35
17	3	20	2.6	303	67.66	67.63
18	7	20	2.6	303	66.58	66.71
19	5	10	2.6	303	70.98	71.12
20	5	30	2.6	303	74.24	74.20
21	5	20	1	303	75.32	75.28
22	5	20	4.2	303	76.90	77.04
23	5	20	2.6	283	85.55	85.65
24	5	20	2.6	323	88.55	88.55

25	5	20	2.6	303	96.00	96.00
26	5	20	2.6	303	96.00	96.00
27	5	20	2.6	303	96.00	96.00
28	5	20	2.6	303	96.00	96.00
29	5	20	2.6	303	96.00	96.00
30	5	20	2.6	303	96.00	96.00

Experimental conditions [Coded Values] and observed response values of central composite design with 2^4 factorial runs, 6- central points and 8- axial points. Agitation time fixed at 50 min.

Table-3 represents the results obtained in CCD. Response obtained from regression in equation 1 in the form of ANOVA is presented.

Table 3- ANOVA of LG dye biosorption for entire quadratic model

Source of variation	**SS**	**Df**	**Mean square(MS)**	**F-value**	***P*> F**
Model	2421.33	14	172.952	6154.87	0.00000
Error	0.422	15	0.0281		
Total	2421.756				

df- degree of freedom; SS- sum of squares; F- factor F; *P*- probability

R^2=0.99999; R^2 (adj):0.99998:

Table-4 estimated regression coefficients for the LG dye biosorption onto *Mg Nps*

Terms	**Regression coefficient**	**Standard error of the coefficient**	**t-value**	***P*-value**
Mean/Intercept	-2596.44	32.76291	-79.249	0.000000
Dosage, w, g/L (L)	73.83	1.36398	54.127	0.000000
Dosage, w, g/L (Q)	-7.21	0.03204	-224.937	0.000000
Conc, Co, mg/L (L)	9.39	0.27124	34.616	0.000000
Conc, Co, mg/L (Q)	-0.23	0.00128	-182.102	0.000000
pH (L)	82.46	1.39713	59.018	0.000000
pH (Q)	-4.96	0.03204	-154.794	0.000000
Temperature, T, K (L)	13.67	0.19890	68.709	0.000000
Temperature, T, K (Q)	-0.02	0.00032	-69.435	0.000000

1L by 2L	-0.01	0.00839	-0.745	0.467844
1L by 3L	0.10	0.04195	2.354	0.032631
1L by 4L	-0.01	0.00420	-2.086	0.054498
2L by 3L	-0.01	0.00839	-0.745	0.467844
2L by 4L	0.00	0.00084	0.715	0.485527
3L by 4L	-0.01	0.00420	-2.384	0.030791

[a] insignificant ($P \geq 0.05$)

$$Y = -2596.44 + 73.83X_1 + 9.39X_2 + 82.46X_3 + 13.67X_4 - 7.21X_1^2 - 0.23X_2^2 - 4.96X_3^2 - 0.02 X_4^2 - 0.01 X_1X_2 + 0.10 X_1X_3 - 0.01X_1X_4 - 0.01X_2X_3 + 0.00 X_2X_4 - 0.01X_3X_4 \text{ ------ (1)}$$

In the watched reaction esteems, a proportion of the models inconstancy is given by the relationship coefficient (R2). In the current investigation, the estimation of the relapse coefficient (R2 = 0.9999) For the most part P esteems lower than 0.05 demonstrates that the model is viewed as measurably huge at 95% certainty level. The % biosorption expectation from the model is appeared in table-4

Fig.6 and Fig.7 shows pareto outline and ordinary likelihood plot (NPP) of remaining qualities. It could be seen that the trial focuses are sensibly adjusted proposing ordinary appropriation.

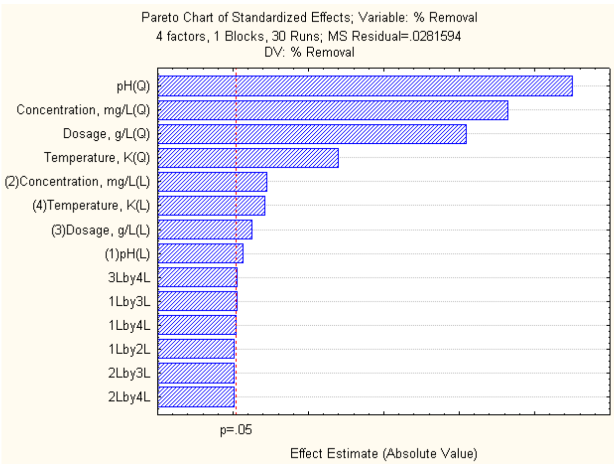

Fig.6 Pareto Chart

The optimal set of conditions for maximum percentage biosorption of LG dye is pH = 4.9821, initial LG dye concentration = 20.3324 mg/L, biosorbent dosage = 2.6332 g/L, and temperature = 304.6258 K are obtained from critical values table. The extent of biosorption of LG dye at these optimum conditions was 96.09572 %. It is evident that experimental values of % biosorption are in close agreement with that of predicted by Central Composite Design. Experiments are conducted in triplicate with the above predicted optimal set of conditions and the % biosorption of LG dye is 96 %, which is closer to the predicted % biosorption

3.2.2. Interaction effects of biosorption variables

The three-dimensional perspective on reaction surface shape plots [Fig. 8 (a) to (f)] show % biosorption as an element of for different mixes of autonomous factors. The plots are spoken

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to as a component of two factors one after another keeping different elements fixed at zero level.

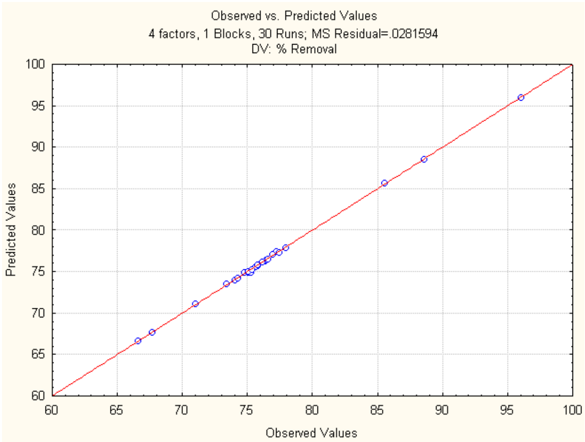

Fig. 7 Normal probability plot for % biosorption of LG dye

It is found from the reaction surface plots that the % biosorption is maximal at low and elevated levels of the info factors. Notwithstanding, there exists a district where neither an expanding nor a diminishing pattern in % biosorption is watched.

The anticipated ideal arrangement of conditions for rate biosorption of LG dye is

pH	=	4.9831
Initial CV dye concentration	=	20.3324 mg/L
Biosorbent dosage	=	2.6332 g/L
Temperature	=	304.6258 K
% biosorption of LG dye	=	96.09572

The ideal arrangement of conditions acquired with CCD is appeared in table-5 alongside trial esteems.

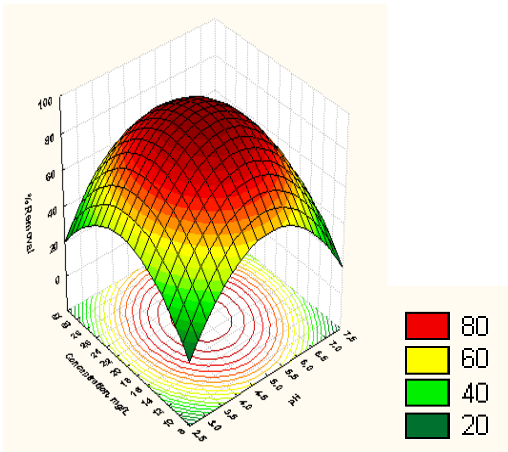

Fig. 8 (a) Surface contour plot for the effects of pH and initial LG dye concentration on % bioadsorption

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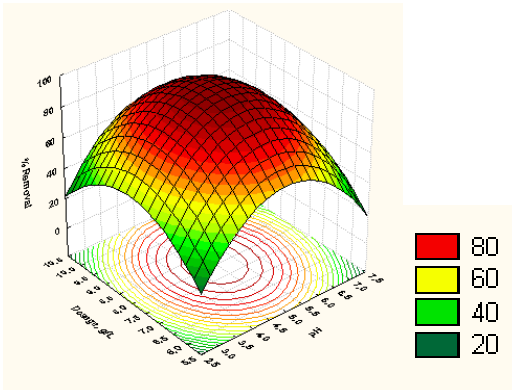

Fig. 8 (b) Surface contour plot for the effects of pH and dosage on % bioadsorption of LG dye

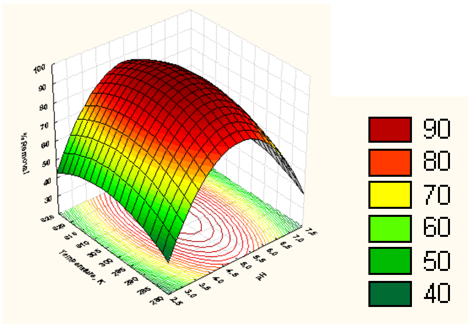

Fig.8 (c) Surface contour plot for the effects of pH and Temperature on % bioadsorption of LG dye

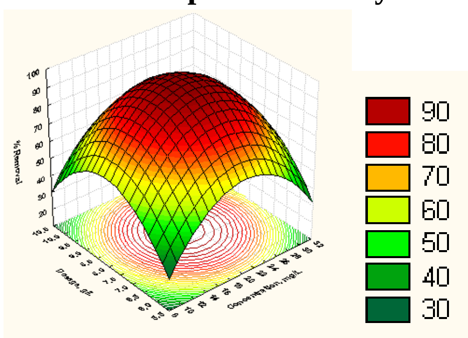

Fig. 8 (d) Surface contour plot for the effects of initial concentration and dosage on % bioadsorption of LG dye

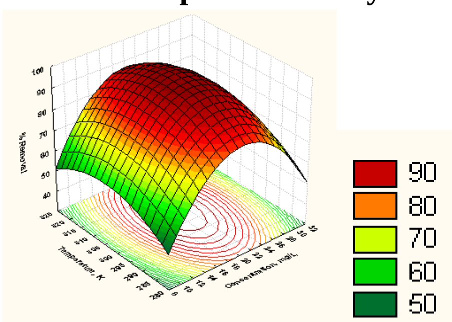

Fig. 8 (e) Surface contour plot for the effects of initial concentration and Temperature on % bioadsorption of LG dye

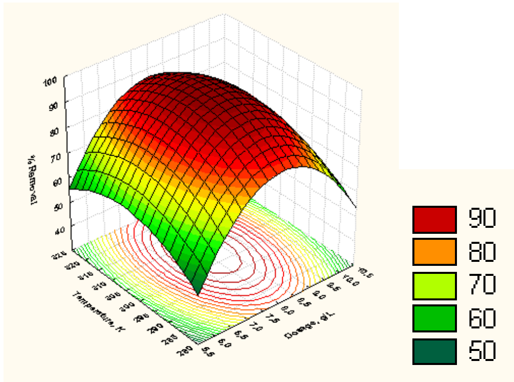

Fig. 8 (f) Surface contour plot for the effects of Dosage and Temperature on % bioadsorption of LG dye

Table 5 Comparison between optimum values from CCD and experimentation

Variable	CCD	Experimental value
pH of aqueous solution	4.9831	5
Initial LG dye concentration, mg/L	20.3324	20
Biosorption dosage, w, g/L	2.6332	2.6
Temperature, K	304.6258	303
% biosorption	94.50421	96.0

4. Conclusion

The maximum sorption of LG dye (94.504 %) onto Mg Nps is observed when the processing parameters are set as: pH = 4.9831, w = 2.6332 g/L, C_o = 20.3324 mg/L and T = 304.6258 K using CCD. The thermodynamic data show that % sorption of LG dye is increased with increase in temperature.

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Reference

[1]. Supawitch Hoijang, Sunanta Wangkarn, Pimchanok Ieamviteevanich, Supree Pinitsoontorn, Supon Anant, T. Randall Lee, Laongnuan Srisombat, " Silica-coated magnesium ferrite nanoadsorbent for selective removal of methylene blue", Colloids and Surfaces A 606 (2020) 125483

[2]. X. Hou, J. Feng, Y. Ren, Z. Fan, M. Zhang, Synthesis and adsorption properties of Sponge like porous MnFe2O4, Colloids Surf. A 363 (2010) 1–7.

[3]. T. Yao, L. Qiao, K. Du, High tough and highly porous graphene/carbon nanotubes hybrid beads enhanced by carbonized polyacrylonitrile for efficient dyes adsorption, Microporous Mesoporous Mater. 292 (2020) 1–8.

[4]. B. Safizade, S. Masoudpanah, M. Hasheminiasari, A. Ghasemi, Photocatalytic activity of BiFeO3/ZnFe2O4 nanocomposites under visible light irradiation, RSC Adv. 8 (2018) 6988–6995.

[5]. G. Fan, J. Tong, F. Li, Visible-light-induced photocatalyst based on cobalt-doped zinc ferrite nanocrystals, Ind. Eng. Chem. Res. 51 (2012) 13639–13647.

[6]. N. Singh, S. Jana, G. Singh, R. Dey, Graphene-supported TiO2: study of promotion of charge carrier in photocatalytic water splitting and methylene blue dye degradation, Adv. Compos. Hybrid Mater. 3 (2020) 127–140.

[7]. X. Liu, Q. Shao, Y. Zhang, X. Wang, J. Lin, Y. Gan, M. Dong, Z. Guo, Microwave hydrothermal synthesized ZnIn-layered double hydroxides derived ZnIn-layered double oxides for enhanced methylene blue photodegradation, Colloids Surf. A 592 (2020) 124588.

[8]. L. Sun, Q. Shao, Y. Zhang, H. Jiang, S. Ge, S. Luo, J. Lin, J. Zhang, S. Wu, M. Dong, Z. Guo, N self-doped ZnO derived from microwave hydrothermal synthesized zeolitic imidazolate framework-8 toward enhanced photocatalytic degradation of methylene blue, J. Colloid Interface Sci. 565 (2020) 142–155.

[9]. J. Kim, C. Yeom, Y. Kim, Electrochemical degradation of organic dyes with a porous gold electrode, Korean J. Chem. Eng. 33 (2016) 1855–1859.

[10]. M. Panizza, A. Barbucci, R. Ricotti, G. Cerisola, Electrochemical degradation of methylene blue, Sep. Pur. Technol. 54 (2007) 382–387.

[11]. X. Shi, C. Wang, Y. Ma, H. Liu, S. Wu, Q. Shao, Z. He, L. Guo, T. Ding, Z. Guo,Template-free microwave-assisted synthesis of FeTi coordination complex yolkshell microspheres for superior catalytic removal of arsenic and chemical degradation of methylene blue from polluted water, Powder Technol. 356 (2019) 726–734.

[12]. X. Yang, F. You, Y. Zhao, Y. Bai, L. Shao, Confinedly assembling surface nanocoating to manipulate nanofiltration membranes for highly-efficient dye removal, ES Energy Environ. 1 (2018) 106–113.

[13]. A. Onur, K. Shanmugam, A. Ng, G. Garnier, W. Batchelor, Cellulose fibre-perlite depth filters with cellulose nanofibre top coating for improved filtration performance, Colloids Surf. A 583 (2019) 123997.

[14]. M. Ayad, A. El-Nasr, Adsorption of cationic dye (methylene blue) from water using polyaniline nanotubes base, J. Phy. Chem. C 114 (2010) 14377–14383.

[15]. Y. Li, Y. Zhou, W. Nie, L. Song, P. Chen, Highly efficient methylene blue dyes removal from aqueous systems by chitosan coated magnetic mesoporous silica nanoparticles, J. Porous Mater. 22 (2015) 1383–1392.

[16]. Danial Nayeri & Seyyed Alireza Mousavi, "Dye removal from water and wastewater by nanosized metal oxides - modified activated carbon: a review on recent researches", Journal of Environmental Health Science and Engineering (2020) 18:1671–1689

[17]. Chen Q, Tang Z, Li H, Wu M, Zhao Q, Pan B. An electron-scale comparative study on the adsorption of six divalent heavy metal cations on MnFe2O4@ CAC hybrid: experimental and DFT investigations. Chem Eng J. 2020;381:122656.

[18]. Mehdizadeh S, Sadjadi S, Ahmadi SJ, Outokesh M. Removal of heavy metals from aqueous solution using platinum nanopartcles/zeolite-4A. J Environ Health Sci Eng. 2014;12(1).

[19]. *Myneni, Venkata Ratnam, Kanidarapu, Nagamalleswara Rao,"* Methylene Blue Adsorption by Magnesium Oxide Nanoparticles Immobilized with Chitosan (CS-MgONP): Response Surface Methodology, Isotherm, Kinetics and Thermodynamic Studies*",* Iran. J. Chem. Chem. Eng, Vol. 39, No. 6, 2020