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Ultrasonic Assisted Removal of Methyl Paraben (MP) on Ultrasonically Synthesized $Zn(OH)_2$-NPs-AC: Experimental Design Methodology

Amir Abbas Ghazali*

Department of Chemistry, Omidiyeh Branch, Islamic Azad University, Omidiyeh, Iran

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ABSTRACT

$Zn(OH)_2$ nanoparticles ($Zn(OH)_2$-NPs) were sonochemically synthesized. Very low amount of $Zn(OH)_2$-NPs was loaded on activated carbon with weight ratio of 1:10 followed by the characterization using FT-IR, XRD and SEM. $Zn(OH)_2$ nanoparticle-loaded activated carbon ($Zn(OH)_2$-NP-AC) as safe, green and cost-effective adsorbents were used for the removal of methyl paraben (MP). Also, the impacts of variables including initial MP dye concentration (X_1), pH (X_2), adsorbent dosage (X_3), sonication time (X_4) came under scrutiny using central composite design (CCD) under response surface methodology (RSM). The experiments have been designed utilizing response surface methodology. In this current article the values of 12 mgL^{-1}, 0.03 g, 7.0, 4.0 min were considered as the ideal values for MP dye concentration, adsorbent mass, pH value and contact time respectively. The rapid adsorption process at neutral pH using very small amount of the adsorbent makes it promising for the wastewater treatment applications. More than 99.5% of methyl paraben was removed with maximum adsorption capacities 100 mgg^{-1} for MP. The kinetics and isotherm studies showed that the second-order and Langmuir models apply for the kinetics and isotherm of the adsorption of MP dye on the adsorbent used here. The adsorbent was shown to be well regenerable for several times. The short-time adsorption process, high adsorption capacity and the well regenerability of the safe, green and cost-effective $Zn(OH)_2$-NP-AC make it advantageous and promising for the aqueous solutions.

Keywords: Methyl Paraben (MP), $Zn(OH)_2$ nanoparticles-loaded activated carbon, Response Surface Methodology, Central Composite Design

1. INTRODUCTION

Dyes are mainly non-biodegradable in the ecosystem due to their synthetic natures and complicated aromatic molecular structures [1]. Due to the toxic nature of some dyes, mutagenic impacts of them, and skin disorders (irritation and allergies) related to them, the potential pollution of dyes and their intermediates has drawn the attention of many researchers. In addition, microbial

*Corresponding author: ghazaliamirabbas@gmail.com

degradation of synthetic dyes due to carcinogenic impact of benzidine and other aromatic compounds has been a matter of health concern [2].

Parabens are esters of p-hydroxybenzoic acid and are used as preservatives and antimicrobial in many personal care products (PCPs), as well as in pharmaceutical preparations [3], food commodities, beverages and industrial products. Parabens are found in sunscreen creams, toothpastes, cosmetics, glues, fats and oils. Their broad use in consumer products [4] is due to their antibacterial and antifungal properties as well as their favourable human safety profile. A potential relationship has been found between daily use of parabens containing PCPs and breast cancer as well as melanoma in younger people [5]. The four widely used preservatives in daily-use products include Butylparaben (BP), ethylparaben (EP), methylparaben (MP), and propylparaben (PP),) which are either used singly or in combination [6]. Some published studies have also reported that the high concentrations of parabens are able to cause male reproductive disorders. Due to all the above applications of parabens, they routed to wastewater treatment plants. Parabens are removed in a considerable extension during some wastewater treatment technologies. Nevertheless, they have been identified in river water samples at the low ng L^{-1} level. Moreover, parabens have been detected in soil and sediment samples [7]. Therefore, it is necessary to remove toxic dyes from industrial wastewater before discharging. Coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques, ozonation and biosorption are available for dye removal from aqueous media [8–14]. The fate of the pollutants in the environment and especially in the water is controlled by a series of physical, chemical and biological processes. Ultrasound irradiation is well known to accelerate chemical process due to the phenomenon of acoustic cavitation, that is, the formation, growth and collapse of micrometrical bubbles, formed by the propagation of a pressure wave through a liquid [15]. Adsorption has been a particular attention among the worldwide researchers due to its high efficiency, lower operation cost and simple operation process [16,17]. Finding new adsorbent materials to improve removal efficiency has always been the important issue in adsorption [18]. Nanomaterials based adsorbent following the loading on porous, non-toxic and large number of functional groups adsorbents like activated carbon led to combination of unique above features with distinct properties concern to metallic nanoparticles make possible them at best recognizing material for trapping and accumulation of pollutants like dyes [19–21]. The offer mentioned AC functional groups like hydroxyl, carbonyl, carboxylic and amide groups and presence of high surface area [22,23]. Application of ultrasound irradiation accelerates chemical processes via the production of acoustic cavitations achieved by the propagation of pressure wave through a liquid [24]. Ultrasound energy improves the mass transfer through convection pathway and probable activation of reactive surface that is emerged from physical phenomena such as micro-streaming and turbulence, acoustic (or shock) waves and microjets [25]. Shock waves have the potential of creating microscopic turbulence within interfacial films surrounding neighbor solid particles. Ultrasonic radiation as a powerful tool intensifies the mass transfer (adsorption and desorption) process by various known and probable mechanisms [26,27].

In this work, $Zn(OH)_2$-NPs-AC were sonochemically synthesized. Very low amount of the Zn(OH)2-NPs was loaded

on AC with weight ratio of 1:10. FTIR, XRD and SEM were used for their characterization Zn(OH)2 nanoparticle-loaded AC (Zn(OH)2-NP-AC) were used as safe, green and cost-effective adsorbents for the removal of methyl paraben (MP) dye. Response surface methodology (RSM) as a cost-effective and time-saving method was applied to model and optimize the removal of MP while adsorbent mass, pH, initial MP concentration and sonication time were considered as variables. RSM was also applied to investigate the possible interaction between the variables involved. The optimum conditions were predicted. The isotherm and kinetics of the adsorption were also studied. The regenerability of Zn(OH)2-NPs was investigated.

2. EXPERIMENTAL

2.1. Materials and apparatus

All chemicals (with analytical reagent grade) including Zinc acetate dehydrate (98.0%), Carbon Active (AC) and Methyl Paraben (MP) (99.9%), sodium hydroxide, hydrochloric acid, They were supplied from Merck (Darmstadt, Germany). A multiwave ultrasonic generator (UP 200S, Hielscher, Germany) with a titanium horn of 7 mm in diameter operating at 20 kHz with a maximum power output of 200 W was used for the ultrasonic irradiation during the synthesis of $Zn(OH)_2$ nanoparticles. X-ray powder diffraction (XRD) spectrum was taken using an X'pert diffractometer of Philips Company (Netherlands) with mono chromatized Cu kα radiation. The pH measurements were carried out using pH/ion meter model-686 (Metrohm, Switzerland, Swiss). Ultrasonic Homogenizer (UHP-400) (made in Ultrasonic Technology Development company-Iran) was used for the ultrasound-assisted adsorption. Absorbance spectra of MP were acquired using a UV–Vis Array spectrophotometer teif sanj pishro pajohesh (Laboratory Industrial and Research System- made in Iran). The morphology of adsorbent was characterized using scanning electron microscope (SEM, KYKY-EM3200, China). FTIR spectra were recorded using JASCO-FTIR680 (Japan) instrument over the range 4000–400 cm^{-1}. An Avantes instrument (Avaspec-2048-TEC, Anglia Instruments Ltd., UK) was used for taking diffuse reflectance spectrum from Zn(OH)2-NP powder for its band gap measurement.

2.2. Methods

The stock solution (100 mg/L) of methyl paraben (MP) was prepared by dissolving 10 mg of methyl paraben in100 mL distilled water. All working solutions with desired concentrations were daily prepared by diluting the stock solution with double distilled water. The adsorption experiments were performed in a batch mode while the solution was ultrasonicated at conditions designed under RSM. The adsorbent Zn(OH)2-NP-AC was separated by the centrifugation for 15 min. The dilute phase was analyzed for the determination of methyl paraben (MP) concentration using UV–Vis spectrophotometer at wavelength of 284 nm (Fig. 1).

2.3. Synthesis of $Zn(OH)_2$ –NPs

To synthesize zinc hydroxide nanoparticles (Zn(OH)2-NPs), 50 mL aqueous solution of NaOH (0.2 M) was added to the aqueous solution of Zn(CH3COO)2.2H2O (0.1 M) with rate of 1mL/min under ultrasonic irradiation using a probe directly immersed into the solution.

2.4. Preparation of $Zn(OH)_2$-NP-AC

The reaction solution for synthesis, Activated carbon was powdered and sieved with sieve mesh of 100. The zinc hydroxide nanoparticles (Zn $(OH)_2$-NPs)

were loaded on AC with weight ratio 1:10 as follows: first 2.0 g AC was thoroughly dispersed in 150 mL water under the sonication for 20 min. 0.2g $Zn(OH)_2$-NP was dispersed in 50 mL water for 20 min. Then, both solutions were intermixed and sonicated for 15 min and then it was stirred for 15 h at 300 rpm. $Zn(OH)_2$-NP-AC was separated by the centrifugation and it was dried at 80°C for 18 hours and finally characterized and used as an absorbent for adsorptions experiments.

2.5. Central composite design (CCD)

Central composite design (CCD) is a method to reduce the number of experiments and cost, and to investigate the effects of parameters by designing experimental runs [28–30]. In present work, design expert software (version 7.0) was used for analysis of the CCD results. The considered parameters were initial MP concentrations (X1), pH (X2), adsorbent mass (X3) and contact time (X4). The number of experiments were 31 at 5 levels (-α (-2), low (-1), center (0), high (+1) and +α (+2)) (Table 1). Analysis of variance (ANOVA) was studied to evaluate the significance and adequacy of the developed model by assessing the lack of fit, regression coefficient (R^2) and the Fisher test value (F-value) [31,32]. Continuously, the mathematical relationship between the five independent parameters was obtained by a second-order polynomial response equation [33].

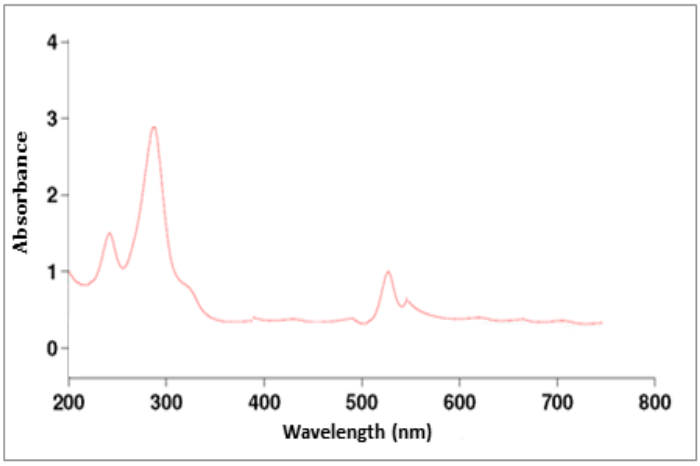

Fig. 1: Sorption spectra adsorption of Zn(OH)2-NPs nanoparticles loaded on activated carbon**.**

Table 1. Experimental factors, levels and matrix of CCD.

Factors	**levels**			**Star pointα = 2.0**	
	Low (-1)	**Central (0)**	**High(+1)**	**-α**	**+α**
(X_1) methyl paraben (MP) Concentration (mg L^{-1})	10	15	20	5	25
(X_2) pH	5.0	6.0	7.0	4.0	8.0
(X_3) Adsorbent mass (g)	0.0150	0.0225	0.0350	0.005	0.045
(X_4) Sonication time (min)	3.0	4.0	5.0	2.0	6.0

Run	**X_1**	**X_2**	**X_3**	**X_4**	**R% methyl paraben (MP)**
1	20	6	0.025	4	92.63
2	30	7	0.015	3	55.0
3	10	5	0.015	5	95.0
4	20	6	0.025	4	92.5

Run	X_1	X_2	X_3	X_4	R% methyl paraben (MP)
5	30	5	0.015	3	73.0
6	10	7	0.035	3	99.2
7	20	4	0.025	4	96.0
8	20	6	0.025	6	93.0
9	30	5	0.035	3	80.0
10	30	5	0.015	5	90.0
11	20	6	0.025	4	93.2
12	30	7	0.015	5	70.76
13	30	7	0.035	5	80.4
14	10	7	0.015	3	95.0
15	20	6	0.025	4	93.0
16	30	5	0.035	5	93.5
17	20	6	0.025	4	93.12
18	10	5	0.015	3	93.66
19	10	7	0.015	5	97.66
20	10	5	0.035	5	95.0
21	10	7	0.035	5	100.0
22	40	6	0.025	4	58.73
23	30	7	0.035	3	65.0
24	20	6	0.025	4	93.62
25	20	6	0.025	4	93.52
26	20	6	0.005	4	90.0
27	20	6	0.025	2	75.0
28	20	8	0.025	4	82.0
29	10	5	0.035	3	95.0
30	20	6	0.045	4	100.0

3. RESULTS AND DISCUSSION

3.1. Characterization

3.1.1. FTIR analysis

The characteristic functional groups of $Zn(OH)_2$-NPs, $Zn(OH)_2$-NP-AC and AC were investigated using FTIR spectra (Fig. 2). A peak appeared around 500 cm^{-1} corresponds to the stretching mode of Zn–O bonds in the spectra of $Zn(OH)_2$-NPs and $Zn(OH)_2$-NP-AC. The broad band around 3426 cm^{-1} was assigned to the the symmetric and asymmetric O–H stretching vibrations of water present in $Zn(OH)_2$-NPs and/or AC functional group. The peak appeared at 1500 cm^{-1} is due to H–O–H bending. In other words, the observed peaks in the range of 1500-3500 cm^{-1} are probably attributed to the absorbed water molecules in the KBr matrix or the prepared nanostructures or their probable interaction. The observed peak around 1100 cm^{-1} is due to single C-C bond stretching mode of acetate solution used [34].

3.1.2. XRD analysis

The XRD pattern of the $Zn(OH)_2$-NPs nanoparticles is shown in Fig.3. The synthesized nanoparticles are found to be polycrystalline in nature. All detectable peaks corresponding to (100), (101), (102), (300) and (200) planes belong to the

$Zn(OH)_2$-NPs nanoparticles (JCPDS no. 36–2280) [35].

3.1.3. Surface morphology

The graph in Fig.4: shows the morphological features and particle size distribution of the $Zn(OH)_2$ nanoparticles using SEM micrograph. It has been seen that the particles were mostly spherical with a various size distribution as they form agglomerates. From the particle size distribution, we obtain the average particle size in the range of 44-57 nm very close to those determined by XRD analysis [36].

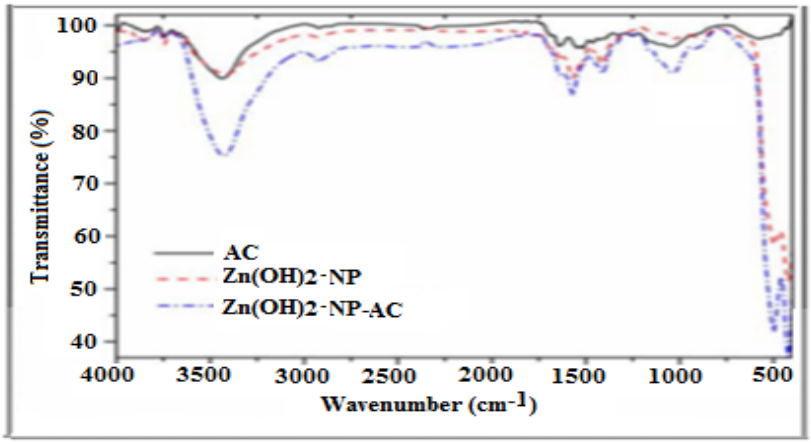

Fig. 2: FT-IR spectra of AC, Zn(OH)2-NP and Zn(OH)2-NP-AC.

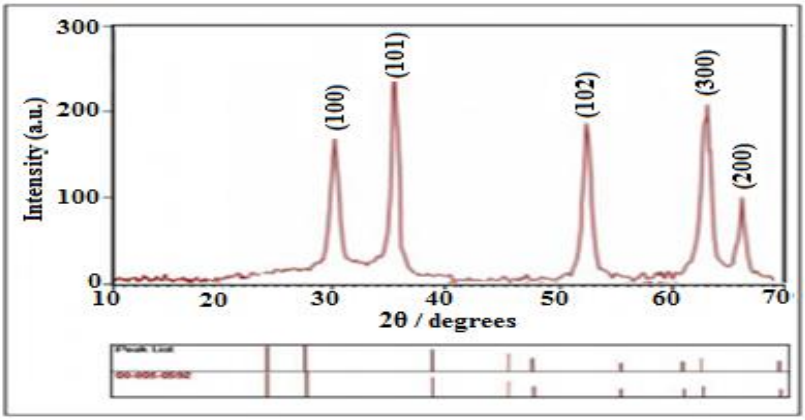

Fig. 3: The XRD patterns of Zn(OH)2 nanoparticles prepared by the sonochemical process.

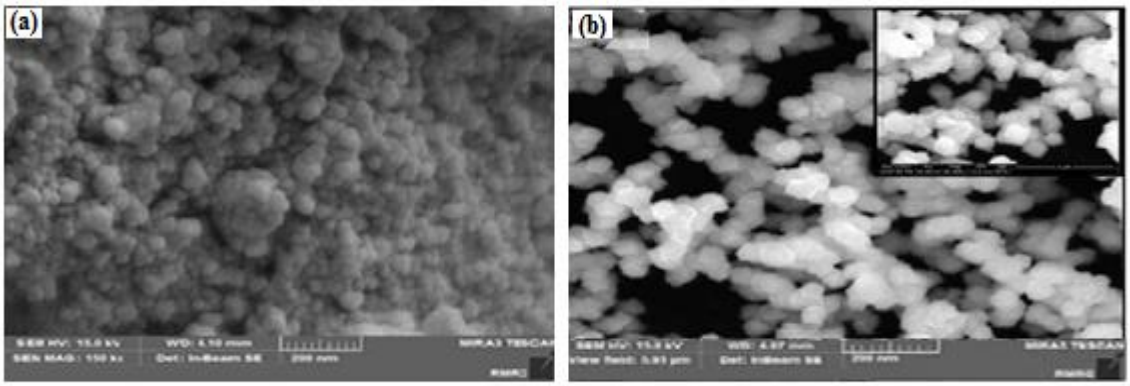

Fig. 4: (a) The (SEM) image of the Zn(OH)2 nanoparticles (b) The (SEM) image of the Zn(OH)2-NP-AC.

3.2. Desirability function

Desirability function (DF) creates a function for each individual response leading to final output of global function (D), maximum value of which supports the achievement of optimum value. The principle and application of desirability function for the best predication of real behavior of adsorption system was pointed out previously [37]. The desirability profiles indicate the predicted levels of variables, which produce the most desirable responses.

3.3. Modeling the process and statistical analysis

Table 2, presents the variance analysis of all the linear, quadratic, and interaction effects of the three planning factors with regard to R% of methyl paraben (MP) dye according to the F-value and p-value (<0.05), the model in removal of dyes was highly significant in the polynomial equation within 95% confidence interval [38]. The value of the determination coefficient for removal of dye indicates that the response surface quadratic model is the most appropriate one for predicting the performance of dye adsorption on $Zn(OH)_2$-NPs-AC. The plots of experimental removal % versus those calculated from equations indicated a good fit. The codified values for the quadratic equations after excluding the insignificant terms are shown in equation (1):

$$R\%_{MP} = 93/084 - 10/093X_1 - 3/340X_2 + 2/4167X_3 + 4/2700X_4 - 4/9075X_1X_2 - 1/3925X_1X_3 + 3/5525X_1X_4 + 0/89500X_2X_3 - 0/17500X_2X_4 - 0/44000X_3X_4 - 3/7119X_1^2 - 1/1059X_2^2 + 0/39410X_3^2 - 2/3559X_4^2 \quad (2)$$

where Y is the predicted response (R% of dye), and X_1, X_2, X_3 and X_4 are the coded values of initial MP concentrations, pH, adsorbent mass and ultrasound time, respectively. The X_1, X_2, X_4, X_5, X_1X_3, X_1X_4 and all quadratic effects were significant for R% of methyl paraben (MP).

Table 2: Indicates that the predicted values of dye adsorption efficiency obtained from the model and the experimental data were in a good agreement.

Table 2. Analysis of Variance for full quadratic model

			methyl paraben (MP)		
Source of variation	**Df**	**Sum of square**	**Mean square**	**F-value**	**P-value**
Model	14	4353.1	310.93	751.23	< 0.0001
X_1	1	1746.2	1746.2	4218.9	< 0.0001
X_2	1	267.73	267.73	646.86	< 0.0001
X_3	1	140.17	140.17	338.65	< 0.0001
X_4	1	437.59	437.59	1057.2	< 0.0001
X_1X_2	1	385.34	385.34	930.99	< 0.0001
X_1X_3	1	31.025	31.025	74.957	< 0.0001
X_1X_4	1	201.92	201.92	487.86	< 0.0001
X_2X_3	1	12.816	12.816	30.965	< 0.0001
X_2X_4	1	0.49	0.49	1.1839	0.29375
X_3X_4	1	3.0976	3.0976	7.4839	0.015321
X_3X_5	1	225.83	225.83	545.61	< 0.0001
X_1^2	1	33.962	33.962	82.053	< 0.0001
X_2^2	1	4.3128	4.3128	10.42	0.0056318
X_3^2	1	154.12	154.12	372.37	< 0.0001
X_4^2	15	6.2085	0.4139	751.23	< 0.0001
Residual	9	5.1621	0.57357		
Lack of Fit	6	1.0464	0.1744	3.2889	0.080484
Pure Error	29	4359.3			
Cor Total					

3.3. Optimization of CCD by DF for Extraction Procedure

The profile for desirable option with predicted values in the STATISTICA 10.0 software was used for the optimization of the process (Fig. 5). The desirability in the range of 0.0 (undesirable) to 1.0 (very desirable) was used to obtain a global function (*D*) that is the base of optimization. The CCD design matrix results were obtained as maximum (100 %) for methyl paraben (MP), respectively. According to these values, DF settings for either of dependent variables of removal percentages were depicted on the right hand side of (fig. 5).

3.4. Response Surface Plots

The 3D RSM surfaces corresponding to R% methyl paraben (MP) was depicted and considered to optimize the significant factors and to give useful information about the possible interaction of variables. As also seen from (fig. 6), the effects of significant interaction terms on the curvature of the surfaces are observed as expected the RSM plot (fig. 6), that the dye removal percentage changes versus the adsorbent dosage [39]. The positive increase in the dye removal percentage with increase in adsorbent mass is seen. Significant diminish in removal percentage at lower amount of $Zn(OH)_2$-NPs-AC is attribute to higher ratio of dye molecules to the vacant sites of the adsorbent. The maximum MP dye deletion of 100%, the optimum conditions were as follows: pH of 7.0, ultrasound time of 4 min, adsorbent mass of (0.03 g) and initial MP dye equal to 12 mgL^{-1} for MP dye. Additionally, to

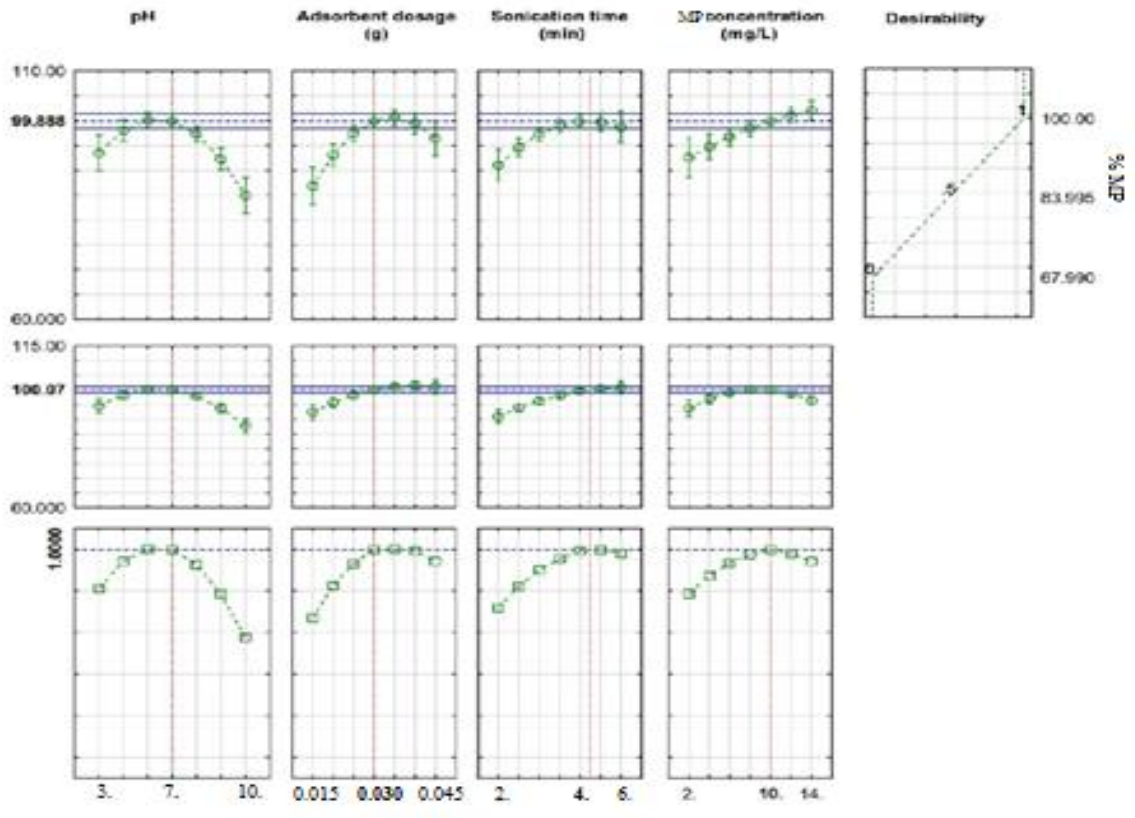

Fig. 5: Profiles for predicated values and esirability function for removal percentage of methyl paraben (MP) line indicates current values after optimization.

examine the optimum conditions experimentally, eleven experiments under the same conditions at 25^0C was conducted. Based on the great conformity between the experimental and prediction data, it was confirmed that the central composite design could be utilized successfully for the evaluation and optimization of the influences of the adsorption independent variables on the removal efficiency of MP dye from aqueous media with the help of $Zn(OH)_2$-NPs-AC.

3.5. Adsorption equilibrium study

An adsorption isotherm expresses the fraction of adsorbate molecules which are divided up between liquid and solid phases at equilibrium. With a help of four adsorption isotherms: 1-Langmuir, 2-Freundlich, 3-Temkin, and 4-Dubinin - Radushkevich isotherms, adsorption of methyl paraben (MP) onto Zn(OH)2 -NPs-AC nanoparticles was displayed [40].

The design of the adsorption equilibrium isotherm was done using mathematical relation of the quantity of adsorbed target of sorbent (q_e(mg/g)) to the equilibrium non-adsorbed quantity of dyes in solution (C_e (mg/L) at distinct temperature [41,42]. Approved models of Langmuir, Freundlich, Temkin and Dubinin–Radushkevich based on desired conditions were used for isotherm studies. Langmuir model as the most frequent one by ensuing equation (2), was used [43]:

$$q_e = \frac{\mathbf{Q_m K_l C_e}}{\mathbf{1 + K_l C_e}} \quad (2)$$

Where C_e, represents the concentration of adsorbate at equilibrium (mg/L), Q_m refers to the highest monolayer sorption capacity (mg/g) and K_L shows Langmuir constant (L/mg). C_e/q_e was plotted against

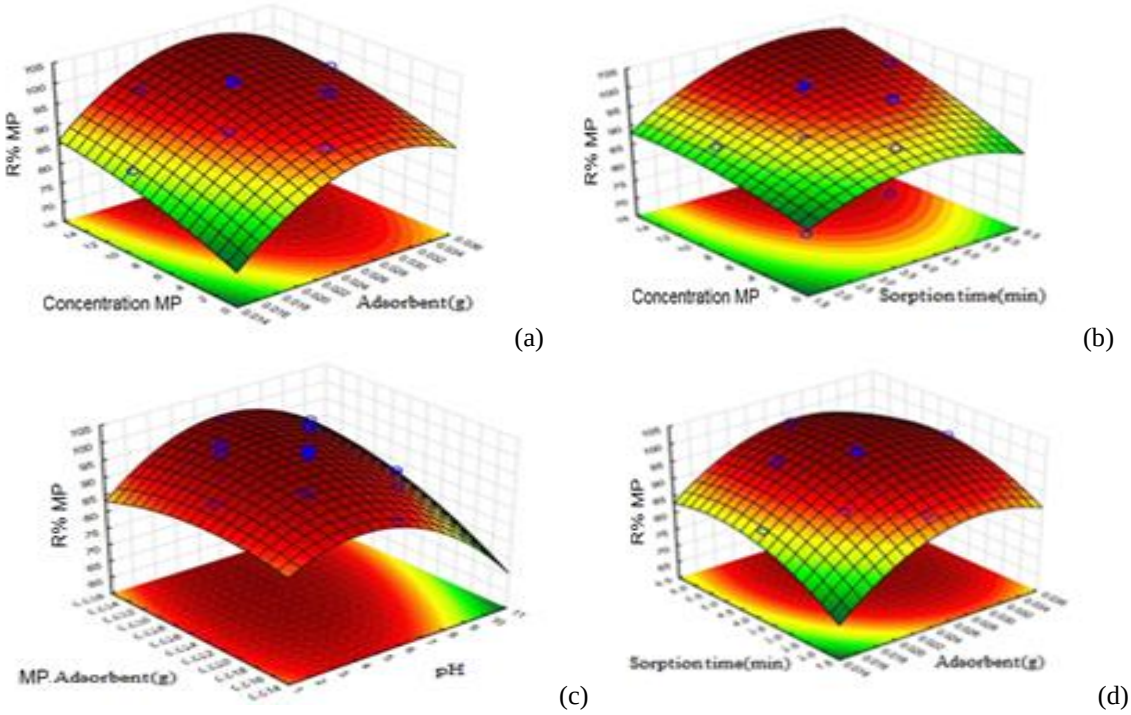

Fig. 6: Response surfaces for the dyes removal: (a) initial MP concentration–adsorbent dosage (b) initial MP concentration-contact time (c) initial MP concentration- pH (d) contact time, adsorbent dosage.

C_e. The calculation of parameters of Q_m, K_L, and R^2 was performed based on the slope and intercept of such lines and exhibited in (Table. 3). From the intercept and slope of the plot of C_e/q_e versus C_e, the values of Q_m (theoretical max sorption capacity (mg/g)) and K_a (the Langmuir adsorption constant (L/mg)) were acquired. For the interpretation of the experimental data over the whole concentration range, Langmuir model was proven to be the best since it provided high correlation coefficient at all adsorbent masses. The rise in the quantity of sorbent led to a remarkable boost in the quantity of adsorbed ions. The calculation of K_F and the capacity of the adsorption (parameters of Freundlich isotherm model) were done from the intercept and slope of the linear plot of $\ln q_e$ versus $\ln C_e$. Temkin isotherm model was used for the evaluation of the heat of the adsorption and the adsorbent–adsorbate interaction. In the aforementioned model, B refers to the Temkin constant, t shows heat of the adsorption (J/mol), T stands for the absolute temperature(K), R represents the universal gas constant (8.314J/mol. K) and K is the equilibrium binding constant(L/mg). For estimating the porosity, apparent free energy, and the properties of adsorption, D–R model was employed [44]. Fitting the experimental data to these isotherm models and considering the higher values of correlation coefficients (R^2 = 0.99) for methyl paraben (MP), it was concluded that the Langmuir isotherm is the best model to explain the methyl paraben adsorption onto Zn(OH)2 -NPs-AC, which quantitatively describes the formation of a monolayer of adsorbate on the outer surface of the Zn(OH)2-NPs-AC nanoparticles. It also shows the equilibrium distribution of methyl paraben (MP) between the solid and liquid phase.

3.7. Kinetic study

Values of the kinetic parameters of pseudo-first-order and second-order [45,46] models are presented in (Table. 4), along with qe,cal, qe,exp. and R^2. The correlation coefficient for the pseudo-second-order equation was (0.99) for the adsorption of MP onto Zn(OH)2-NPs-AC. The calculated qe,cal value also agrees very well with the experimental data. This strongly suggests that the adsorption of

Table 3: Various isotherm constants and their correlation coefficients calculated for the adsorption of methyl paraben (MP) onto Zn(OH)2-NPs-AC nanoparticles.

Isotherm	**Equation**	**parameters**	**Value of parameters For Methyl paraben (MP)**
Langmuir	$q_e=q_m bC_e/(1+bC_e)$	Q_m (mg g^{-1})	100.0
		K_a (L mg^{-1})	73.0
		R^2	0.99
Freundlich	$\ln q_e = \ln K_F + (1/n) \ln C_e$	1/n	0.217
		K_F (L mg^{-1})	35.48
		R^2	0.951
Tempkin	$q_e = B_1 \ln K_T + B_1 \ln C_e$	B_1	6.8
		K_T (L mg^{-1})	64.105
		R^2	0.973
Dubinin-Radushkevich (DR)	$\ln q_e = \ln Q_s - B\varepsilon^2$	Q_s (mg g^{-1})	100.0
		$B\times 10^{-7}$	73.0
		E (kJ mol^{-1})	0.99
		R^2	0.217

methyl paraben (MP) onto Zn(OH)2-NPs-AC is most appropriately represented by a pseudo second-order rate process. The close to unity value of R^2 indicated good fitness of film diffusion model. However, the straight lines did not pass through the origin, there by suggesting that resistance or film diffusion might not be the sole rate-limiting step. The Elovich constants could be computed from the plots of qt versus lnt [47]. The low values of correlation coefficient (R^2) ascertained the unsuitability of this model for the adsorption of MP onto Zn(OH)2-NPs-AC adsorbents (Table. 4).

3.8. Regeneration of adsorbent

Based on the optimal condition, 10 mL solution of 12 mg/L methyl paraben (MP) and 0.03 g of Zn(OH)2-NPs-AC were mixed and sonicated for 4.0 min. Subsequently, the mixture was centrifuged for 15 min and the removal percentage of MP was found to be 99.8 %. Then, the regeneration of adsorbent was investigated by using different solvents (ethanol, methanol, acetone, acetonitrile, N, N, di methyl formamide, benzene and water). High efficiency was found for methanol for the well regeneration of Zn(OH)2-NPs-AC. The MP dye adsorbed by the adsorbent was extracted by using 10 mL methanol at pH 7.0 by a three-stage washing procedure. Then, the pH of extracted solution was adjusted to 4.5 for reading the adsorption of MP. The MP extraction percentages from the adsorbent were found to be 87, 90, 92, 91 and 75 % for the first to fifth regeneration, respectively, showing very good regeneration of the adsorbent.

3.9. Comparison maximum adsorption capacity for the Methyl Paraben with other Parabens and different adsorbents

Table. 5, demonstrates the max adsorption capacities of varied adsorbents for the deletion of Parabens comparatively. The type and density of active sites in adsorbents which are responsible for adsorption of parabens from the solution result in the variation in ($q_{max)}$ values. The outcomes of the table clearly show that the sorption capacity of utilized sorbent in the current study is significantly high. In general, morphology, particle size and distribution, and surface structure of this sorbent were effective in its successful outcomes.

Table. 4: Kinetic parameters for the adsorption of methyl paraben (MP) onto Zn(OH)2 -NPs-AC.

Model	parameters	Value of parameters for MP
pseudo-First-orderkinetic	k_1 (min^{-1})	0.54
	qe (mg g^{-1})	47.8
	R^2	0.697
pseudo-Second-order kinetic	k_2 (min^{-1})	0.092
	q_e (mg g^{-1})	1.36
	R^2	0.999
Intraparticle diffusion	K_d (mg g^{-1} $min^{-1/2}$)	3.62
	C (mg g^{-1})	37.27
	R^2	0.964
Elovich	β (g mg^{-1})	0.345
	α (mg g^{-1} min^{-1})	63
	R^2	0.942

Table. 5: Juxtaposition of the adsorption capacities of different adsorbents for the adsorption of Parabens onto nano sorbent

Parabens	Adsorbent	Dosage sorbent (g)	Adsorption capacity (mg g^{-1})	References
Methyl Paraben and Propyl Paraben	(ß-CD) toluene-2,6-diisocyanate.	0.4	0.1019 and 0.2551	[1]
Methyl Paraben	Activated carbon (AC)	0.1	7.52	[4]
Methyl Paraben and Propyl Paraben	Surfactant Triton X-114	-	152.16 and 180.21	[7]
Methyl Paraben and Propyl Paraben	MWTACC	0.1	85.9 and 90.0	[9]
Propyl Paraben	TiO_2NPs-AC	0.025	120.0	[16]
Benzyl Paraben	Mn-doped PbS	0.1	145.0	[48]
Methyl Paraben	Zn $(OH)_2$-NPs-AC	0.03	100.0	Present study

4. CONCLUSION

The sonochemically synthesized $Zn(OH)_2$ nanoparticles were loaded on AC and used as efficient and regenerable adsorbent. The adsorbent was successfully used for the ultrasound assisted removal of the methyl paraben (MP) within a short time (4.0 min). The experiments were designed by response surface methodology and quadratic model was used to prediction of the variables. The influence of process variables (MP concentration, pH, adsorbent mass and contact time) on adsorption of MP was investigated by central composite design (CCD) of RSM. The adsorption of MP onto Zn $(OH)_2$-NPs-AC was found to be 99.2% at pH: 7.0, MP concentration: 12.0 mg L^{-1}, adsorbent mass: 0.03 and sonication time: 4.0 min. At optimum adsorption conditions, the experimental removal efficiency of Zn $(OH)_2$-NPs-AC reached 98.7 for MP. Equilibrium adsorption showed that system followed both Langmuir model. The maximum adsorption capacity value of methyl paraben (MP) with Zn $(OH)_2$-NPs-AC was 100 mgg^{-1}. The kinetics scrutiny decided that methyl paraben (MP) dye deletion followed pseudo second-order rate equation. In addition the possibility of recycling the adsorbent was well proved by desorption studies. Based on the results from the linear regression-based analysis, it was revealed that the derived empirical models represented a passable prediction of performance onto Zn $(OH)_2$-NPs-AC nanoparticles with significant determination coefficients (R^2= 0.994). Additionally, the statistical outcomes guaranteed that the recommended equations could favourably be employed for the adsorption of methyl paraben (MP) dye from aqueous solutions. Further investigations on the suitability of this adsorbent for the deletion of other materials have been suggested. Also it was suggested to investigate on the suitability of this adsorbent in industrial application. The findings proved the appropriateness of the present precedure for the successful deletion of Pollutants from aqueous solution.

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مجله شیمی فیزیک و شیمی نظری
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حذف رنگ متیل پارابن به استفاده از التراسونیک و روش پاسخ سطح و طراحی کامپوزیت مرکزی با کمک نانو جاذب سنتزی هیدروکسید روی بر روی کربن فعال: مقایسه روش طراحی تجربی

امیرعباس غزالی*

دانشگاه آزاد اسلامی واحد امیدیه، گروه شیمی، امیدیه، ایران

چکیده

نانو ذرات هیدروکسید روی تثبیت شده بر روی کربن فعال به روش سونوشیمیایی سنتز شدند. مقدار بسیار کمی از نانو ذرات هیدروکسید روی بر روی کربن فعال با نسبت وزنی ۱:۱۰ بارگیری شد و سپس با استفاده از FT-IR، XRD و SEM مشخصه‌بندی شد. نانو ذرات هیدروکسید روی تثبیت شده بر روی کربن فعال به عنوان جاذب ایمن، سبز و مقرون به صرفه برای حذف رنگ متیل پارابن استفاده شد. همچنین، تأثیر متغیرها از جمله غلظت اولیه رنگ متیل پارابن(X1)، pH (X2)، دوز جاذب (X3)، زمان فراصوت (X4)، با استفاده از طراحی کامپوزیت مرکزی (CCD) تحت روش سطح پاسخ (RSM) مورد بررسی قرار گرفت. آزمایشات با استفاده از روش سطح پاسخ طراحی شده است. در این مقاله کنونی مقادیر ۱۲ میلی‌گرم در لیتر، 0.03 گرم، ۷,۰ ، ٤,۰ دقیقه به ترتیب مقادیر ایده آل برای غلظت رنگ MP ، جرم جاذب، مقدار pH و زمان تماس در نظر گرفته شد. فرآیند جذب سریع در pH خنثی با استفاده از مقدار بسیار کمی از جاذب، آن را برای کاربردهای تصفیه فاضلاب امیدوار کننده می‌کند. بیش از ۹۹,۵٪ متیل پارابن با حداکثر ظرفیت جذب ۱۰۰ میلی‌گرم در گرم رنگ متیل پارابن حذف شد. مطالعات سینتیک و ایزوترم نشان داد که مدل‌های درجه دوم و لانگمویر برای سینتیک و ایزوترم جذب رنگ متیل پارابن در جاذب مورد استفاده در اینجا کاربرد دارند. نشان داده شد که جاذب برای چندین بار به خوبی بازسازی می‌شود. فرآیند جذب کوتاه مدت، ظرفیت جذب بالا و بازآفرینی خوب، نانو ذرات هیدروکسید روی تثبیت شده بر روی کربن فعال ایمن، سبز و مقرون به صرفه ، آن را برای محلول‌های آبی سودمند و امیدوار کننده می‌کند.

کلید واژه‌ها: متیل پارابن، نانو ذرات هیدروکسید روی بر کربن فعال، روش پاسخ سطح، طراحی کامپوزیت مرکزی

* مسئول مکاتبات: ghazaliamirabbas@gmail.com