

Preparation of Adsorbents Containing CdS Quantum Dots from the Orange Peel for the Sewage Treatment

Mandanipour, Valiollah*⁺

Department of applied chemistry, University of Gonabad, Gonabad, I.R. IRAN

Sadeghi-Maleki, Mohammad-Rasool

Department of applied chemistry, University of Gonabad, Gonabad, I.R. IRAN

Pasandideh-Nadamani, Mohammad

Faculty of Chemistry, University of Mazandaran, Babolsar, I.R. IRAN

ABSTRACT: Photocatalytic degradation of pollutants using the semiconductor Quantum Dots (QDs) can be applied to water treatment processes. In this paper, first, the Orange Peel (OP) and the Activated Carbon (AC) were prepared from the orange peel wastes. Second, CdS quantum dot-loaded adsorbents were prepared from these adsorbents and they were labeled as CdS@OP and CdS@AC, respectively. This new photocatalyst was characterized using FT-IR, FESEM, and UV-Vis. Then, the adsorption properties of these prepared adsorbents for the removal of alizarin, as an organic pollutant, were studied, and AC was selected as a better adsorbent for this purpose. Afterward, the photocatalytic properties of these adsorbents were also studied for the degradation of alizarin, under sunlight irradiation. A factorial design method was used to achieve the optimal condition and the best photocatalyst was selected. Finally, CdS@AC nanocomposite was selected as a more effective photocatalyst with the degradation efficiency of 82% of dye solution, under 2h sunlight irradiation.

KEYWORDS: Orange peel; Adsorbent; Activated carbon; Nanocomposite; Photodegradation.

INTRODUCTION

Production of a large amount of wastewater- due to industrialization, population growth, and urbanization became serious environmental problems in many countries. Therefore, different techniques were investigated and developed for the treatment and removal of contaminants from wastewaters [1,2]. A large proportion of these contaminants are organic compounds; and dyestuffs are one of the most harmful of them, that could

result in various problems through poisoning and absorbing the oxygen of the waters [3]. As a result, many strategies were used for the removal/or degradation of the dye materials from wastewaters, including adsorption [4], flocculation [5], filtration [6], oxidation, and electrolysis [7]. However, the photocatalytic degradation of pollutants by the Advanced Oxidation Processes (AOPs), is one of the new strategies that is used in wastewater purification

* To whom correspondence should be addressed.

+ E-mail: valimandanipour@yahoo.com ; valimandanipour@gonabad.ac.ir

1021-9986/2021/3/704-714

11/\$/6.01

methods. In AOPs, strong oxidizing species, mainly including $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals are formed in situ; and these oxidizing species break down the dye molecules into small less-harmful substances [8]. In these AOPs, the organic pollutants are usually completely mineralized to nontoxic and safe materials such as CO_2 and water [8].

So far, the application of different nanoparticles, such as TiO_2 [9–11] and quantum dots [12,13], for the photocatalytic degradation of pollutants in AOPs has been extensively investigated. Although these nanoparticles have a high potential for photocatalytic degradation, their free use has some practical limitations, such as difficulties in reusability, agglomeration and the loss of performance. Therefore, various modification and functionalization processes are done to improve the pollutant removal properties of these nanoparticles [14]. The preparation of the composites containing these nanoparticles is one of the strategies that has been extensively investigated and used [14,15]. The preparation of mesoporous SBA-15, embedded with CdS quantum dots and its photocatalytic properties for the degradation of *alizarin* were previously reported [14]. In this article, we study the preparation of CdS quantum dots containing activated carbon from agricultural residues, as an inexpensive and more applicable nanocomposite for the practical applications was studied. These activated carbon compounds and the other affordable adsorbents were mostly prepared from natural wastes such as the agricultural residues [16,17]. Furthermore, the application of the different nanomaterials for the oxidation processes in wastewater treatment has gained great attention for wastewater treatments, in recent years [18]. Quantum Dots (QDs) are a group of nanomaterials that have been used extensively for the photocatalytic degradation of dyes and the other organic pollutants [19]. However, application of free QDs was associated with some difficulties, such as oxidation and agglomeration of QDs and difficulties in separation. So, in this article, the preparation and application of some inexpensive CdS QDs containing nanocomposites from the orange peel wastes for the removal and photocatalytic degradation of *alizarin* - as an example of the organic pollutant of wastewaters - were studied.

EXPERIMENTAL SECTION

Materials and apparatuses

All chemical compounds were used as they were received without further purification. Na_2S , CdCl_2 , and Alizarin

($\text{C}_{14}\text{H}_8\text{O}_4$) were purchased from Merck chemical company (Germany). The orange peel wastes were obtained from a local juice shop.

The FT-IR spectra were recorded by FT-IR spectrophotometer (Tensor 27- Bruker) and the N_2 adsorption/desorption analysis was done by Belsorp II (Japan) instrument and SEM images were recorded by MIRA 3 TESCAN digital scanning electron microscope.

The COD analysis was done by DR-5000-HACH instrument and the absorption spectra were recorded at the room temperature by PG Instruments T90+.

Method

Preparation of adsorbents

The obtained orange peel wastes were washed with distilled water and they were dried in a drier for 2 h, at 105°C , until a constant weight was reached. Then, the dried product was ground in a ball mill and it was sieved to obtain particles in sizes ranging from 0.3 to 0.6 mm. These obtained materials were divided into two parts. The first part was stored directly and it was labeled as OP. The second part was soaked in nitric acid solution (10 wt. %) for 24 h. Then, the obtained samples were decanted and they were dried in an oven at 105°C . Finally, these materials were carbonized in a muffle furnace for 1 h at 500°C in the absence of air, to the obtain activated carbon and it was labeled as AC.

Preparation of CdS QDs modified adsorbents

About 300 mg of the previously prepared biosorbent (i.e. OP or AC) were dispersed in 50 mL of aqueous solution containing 500 mg CdCl_2 , under the magnetic stirring for 24 h. Then, 10 ml of aqueous solution containing 500 mg Na_2S was added to the mixture. After 6 h, the obtained CdS QDs modified nanocomposites were filtrated, they were washed with distilled water, and they were dried. The prepared nanocomposites from OP and AC were labeled as CdS@OP and CdS@AC, respectively.

Adsorption experiment

To examine the adsorption activity of the prepared materials, 100 mg of each material (i.e. OP, AC, CdS@OP or CdS@AC) was dispersed in 24 mL double distilled water. Then 6 mL of alizarin aqueous solution (100 ppm) was added to the mixture and it was stirred in a dark place. At the specified time intervals, the concentration of dye

in the supernatant was determined by UV–vis absorption spectroscopy at the $\lambda_{\max}=480$ nm. The percentage of dye removal was calculated using the following relationship:

$$\% \text{ of dye removal} = \frac{C_0 - C_t}{C_0} \times 100 = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

Where C_0 and C_t (mg L^{-1}) are the initial dye concentration and the concentration of dye at time t , and A_0 and A_t are the absorbance of the initial dye solution and the absorbance of dye at time t , respectively.

Photocatalytic dye-degradation

To examine the photocatalytic activity of the prepared materials, 100 mg of each material (i.e. OP, AC, CdS@OP or CdS@AC) was dispersed in 24 mL double distilled water. Then 6 mL of alizarin aqueous solution (250 ppm) was added and it was stirred in a dark place for 24 h to attain an adsorption/desorption equilibrium. Afterwards, the suspension was irradiated by the visible light irradiation (sunlight) for the photocatalytic experiment under the moderate stirring. At specified time intervals, the concentration of dye in the supernatant was determined by UV–Vis absorption spectroscopy at the $\lambda_{\max}=480$ nm [13]. The percentage of the dye degradation was calculated using the following relationship:

$$\% \text{ of dye degradation} = \frac{C_0 - C_t}{C_0} \times 100 = \frac{A_0 - A_t}{A_0} \times 100 \quad (2)$$

Where C_0 , C_t , A_0 and A_t terms are defined similar to the previous section. However, it must be mention that A_0 refers to the absorbance of solution after achieving equilibrium condition in a dark place.

RESULTS AND DISCUSSION

In this section of the paper, we firstly characterizing the produced materials; then the adsorption and photocatalytic properties of these prepared materials will be studied over alizarin removal in aqueous medium.

The FT-IR spectra of the prepared materials were shown in Fig. 1. The most intense peak at 3432 cm^{-1} in Fig.1 (a) & (b) is related to the antisymmetric stretching vibration of –OH groups of the carbohydrates and belongs to lignin compounds in the orange peels [20]. The peak at 2921 is related to stretching vibrations of C–H groups in –CH₃ and –CH₂; and the peaks around 1732 – 2250 cm^{-1} were related to the stretching of carbonyl (C=O) groups.

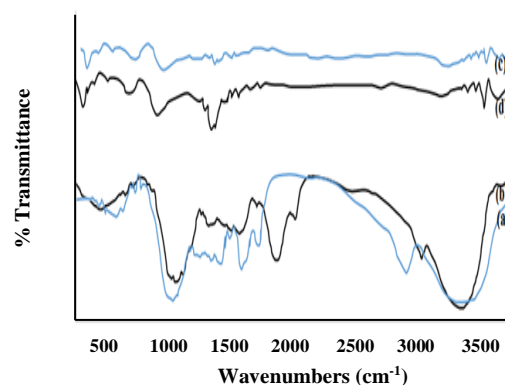


Fig. 1: FT-IR spectra of prepared (a) OP, (b) AC, (c) CdS@OP and (d) CdS@AC adsorbents.

Also, the intense band around 1015 cm^{-1} relates to the C–O–R bands while the distinct band around 1265 cm^{-1} was related to aliphatic chains (–CH₂– and –CH₃) forming the basic structure of this lignocellulosic materials. Moreover, the peaks at 3532 cm^{-1} and 3750 cm^{-1} in Fig.1 (c) & (d) are related to the stretching vibration of –OH groups; and the peak at 1840 cm^{-1} is related to the vibration of C=O groups, that indicated the prepared active carbon contains hydroxyl, carbonyl, methoxy, and lactones groups [21]. In total, the differences in the FT-IR spectra of prepared activated carbon and orange peels demonstrated changes in the structure of components during carbonizing process and the lack of structural changes at the nanoparticle formation stage on the adsorbents indicates that the composite formation did not lead to structural changes in the adsorbent substrate.

The SEM images of the prepared materials were shown in Fig. 2. The SEM image of prepared raw materials (OP) in Fig.2 (a) demonstrated fine flake-like structures. These fine structure were disappeared in the prepared activated carbons (AC), instead, the thick structures with different sizes and shapes were appeared in Fig.2 (b). A similar phenomena, but with less structural changes, can be observed for the preparation of CdS QDs modified OP-biosorbent nanocomposites (CdS@OP) in Fig.2(c). Finally, the SEM image of the prepared CdS@AC in Fig.2 (d) shows more smooth and thick structures, as a result of reaction with acidic solvent and pyrolysis processes.

In our previous similar works [12,13], the size and morphology of prepared CdS QDs was studied in detail; and the size of prepared QDs in this article was determined

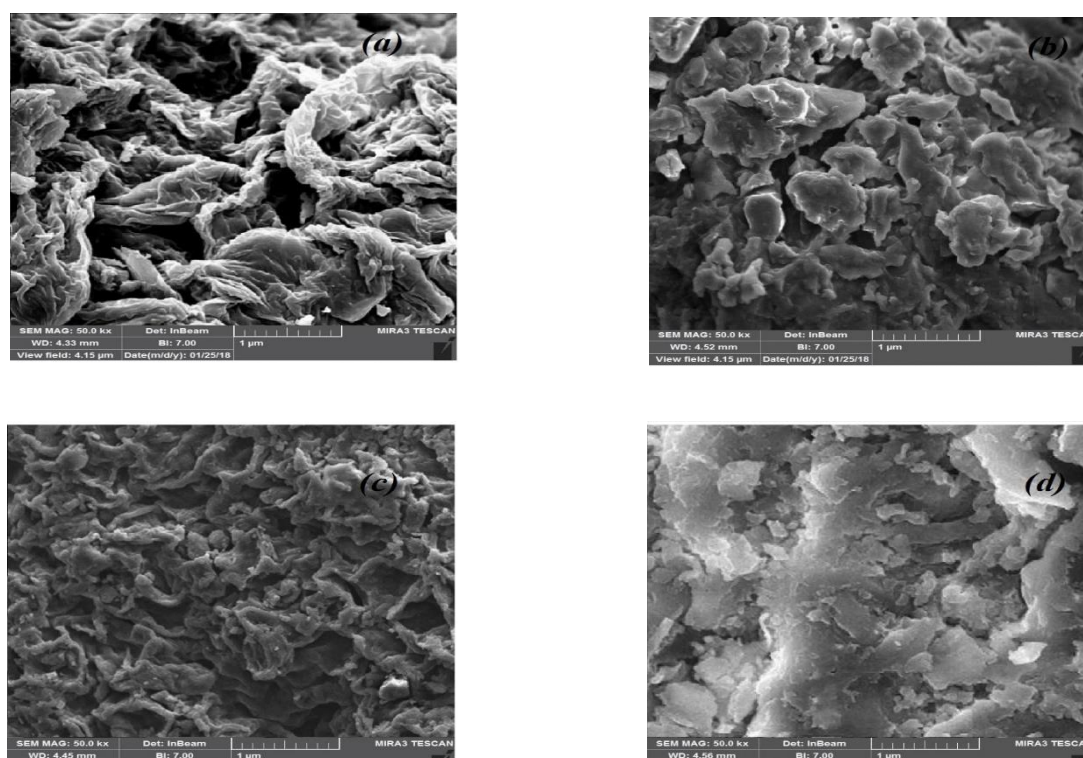


Fig. 2: SEM images of prepared (a) OP, (b) AC, (c) CdS@OP and (d) CdS@AC adsorbents.

using absorption UV-Vis spectroscopy. Fig. 3 demonstrates the UV spectra from some of the different synthesized catalysts. The peaks are moved vertically in order to overlap and fit the peaks for comparison. Normally, the absorption is high for activated carbon containing materials and they absorb almost all of the emitted light. The peaks around 340 nm in Fig. (3) and (d) demonstrate the formation of CdS QDs, with the size of about 2.9 nm using Peng method (ref samadi), in the CdS@OP and (d) CdS@AC catalysts.

N₂ adsorption-desorption isotherms of prepared materials were also studied by Brunauer-Emmett-Teller (BET) surface area analysis and Barrett-Joyner-Halenda (BJH) pore size and volume analysis, and their results were shown in Fig. 4, and Table 1. As it was shown, the surface area, pore volume and pore diameter of prepared nanocomposites are smaller than their adsorbent source; which demonstrated that the pores of adsorbent were filled by CdS QDs.

Dye removal studies

Adsorption of the dye molecules from solution onto the surface of catalyst is the key process in the dye removal.

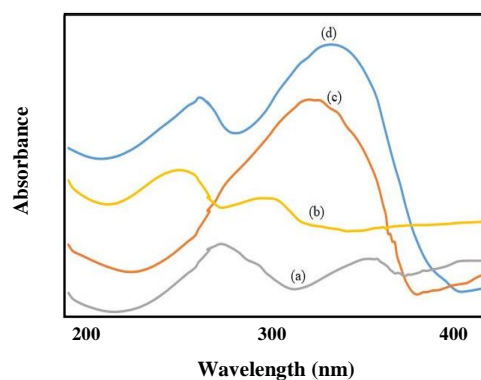


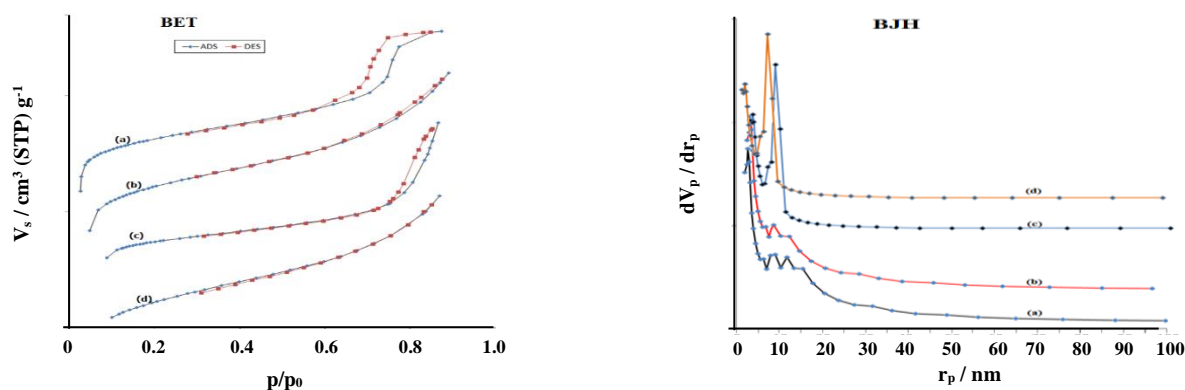
Fig. 3: UV-Vis spectra of prepared (a) OP, (b) AC, (c) CdS@OP and (d) CdS@AC adsorbents..

Several parameters could affect this adsorption process including: type of adsorbent, amount of dye, time, temperature and pH of solution. These parameters would be explained in the following paragraphs.

Fig. 5(I) demonstrates the effects of the type of adsorbent type and also the effect of the contact time on alizarin removal. To study the influence of the contact time

Table 1: Pore structure parameters of: (a) OP, (b) AC, (c) CdS@OP and (d) CdS@AC adsorbents.

Sample	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
OP	327	0.2586	9.87
AC	458	0.5451	10.13
CdS@OP	107	0.036	7.23
CdS@AC	214	0.031	9.67

**Fig. 4: BET and BJH diagrams of prepared (a) OP, (b) AC, (c) CdS@OP and (d) CdS@AC adsorbents.**

on the adsorption of alizarin, experiments were done with 100 mg of each adsorbent and 6 mL of alizarin solution (100 ppm) in 24 mL of water at 298 K at the different contact times. As it can be seen, the dye materials were quickly adsorbed in the first contact times. Then the adsorption rate declined slowly and reached equilibrium at about 60 min. At first, the dye molecules were adsorbed on the surface of the nanocomposite and the adsorption rate was fast. However, when the sites of the exterior surface were saturated, the dye ions entered onto the remaining pores of the nanocomposite particles and they were adsorbed by the inside sites of the particles. This process took a relatively longer contact time and therefore, the adsorption rate decreased [14]. Furthermore, as mentioned above, Fig. 5 (I) also demonstrates the effect of the adsorbent type on the dye removal. As can be seen, among the different adsorbents including (a) OP, (b) AC, (c) CdS@OP, (d) CdS@AC & (e) no adsorbent, the activated carbon (AC) materials had better removal efficiency. Based on these phenomena, it can be concluded that the carbonizing process during the preparation of AC could result in the activation of the adsorption sites in the adsorbent materials. However, during the preparation of CdS QDs containing adsorbent, most of these activated

sites were occupied and the adsorption efficiency of the prepared nanocomposites (i.e. CdS@OP & CdS@ACs) was decreased in comparison with their adsorbent sources.

Fig. 5 (II) shows the change of dye removal with increasing initial dye concentration. To investigate the influence of the initial dye concentration on the adsorption of alizarin, experiments were done with 100 mg of adsorbent (i.e. (a) OP, (b) AC, (c) CdS@OP or (d) CdS@AC) and 6 mL of alizarin solution with different concentrations in 24 mL of water at 298 K for 60 min. As it can be seen, the percentage of the dye removal was increased by increasing the initial dye concentration up to 100 ppm. In these conditions, a powerful driving force that was created by the initial dye concentration overcomes the mass transfer resistance between the liquid and the nanocomposite materials[22]. But, in higher concentration, filling the active sites of the nanocomposite resulted in the decrease in the percentage of the dye removal [14].

The influence of pH on the adsorption was shown in Fig. 5 (III). The pH of the solution is an important parameter that greatly affects the adsorption process. To investigate the impact of pH on the adsorption of alizarin, experiments at the different pH values were done with 100 mg of each adsorbent and 6 mL of alizarin solution (100 ppm)

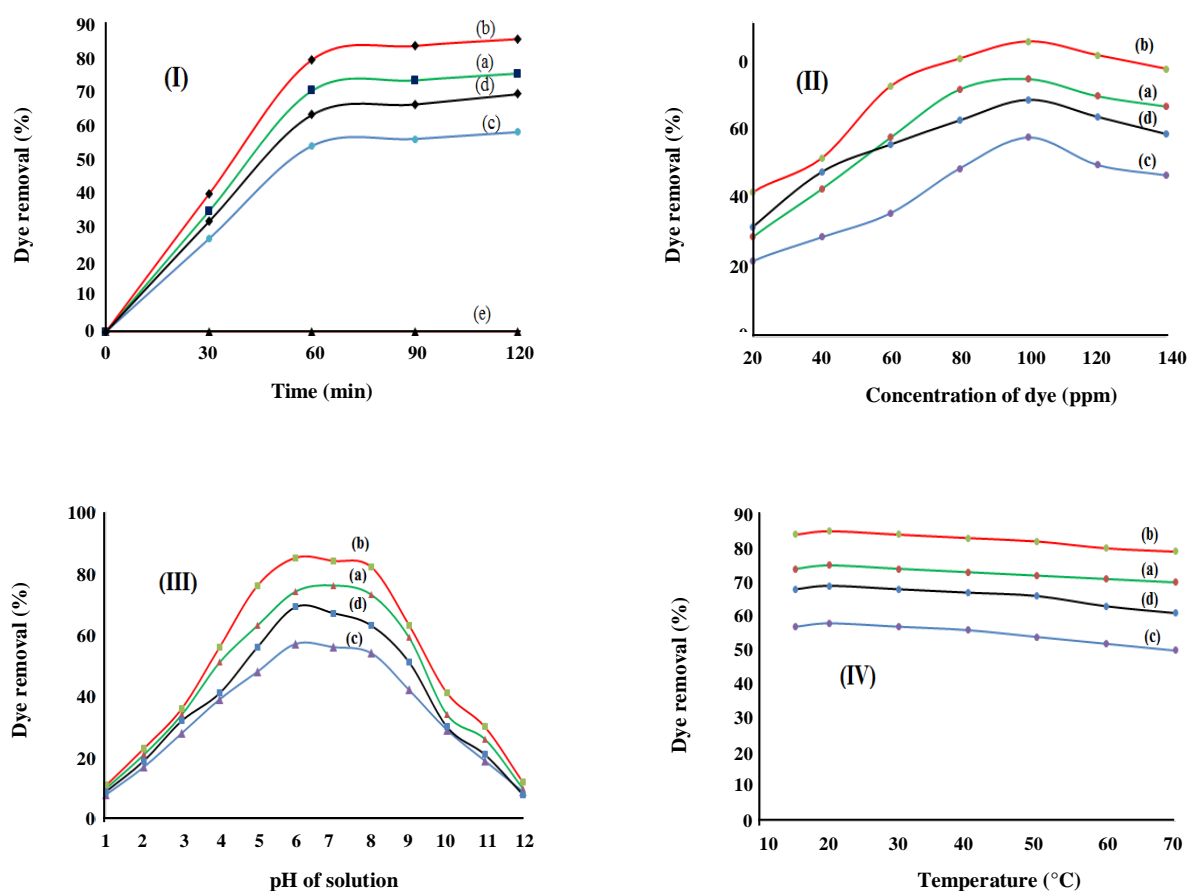


Fig. 5: Effects of: (I) type of adsorbent & contact time, (II) dye concentration, (III) pH and (IV) temperature on dye removal process [(a) OP, (b) AC, (c) CdS@OP, (d) CdS@AC & (e) no adsorbent].

in 24 mL of water at 298 K for 60 min. The pH was adjusted by HCl and NaOH solutions. Because of the impact of pH on the UV-vis spectrum of alizarin, the pH of sample solutions were adjusted to pH=7 and then UV-Vis absorption spectroscopy measurement was done at the $\lambda_{\max}=435$ nm. The results of Fig. 5(III) demonstrates that the molecular form of the dye is favored to be adsorbed, while the anionic form is the second option for the acidic solutions, much better than for the basic media.

The effect of temperature on the adsorption of alizarin by nanocomposites was also studied and the results were shown in Fig. 5 (IV). To study the impact of the temperature on the adsorption of alizarin, experiments were done with 100 mg of each adsorbent and 6 mL of alizarin solution (100 ppm) in 24 mL of water at adjusted pH=7 for 60 min, at different temperatures. The results showed that the adsorption was slightly

decreasing with temperature, which demonstrated that the adsorption process was exothermic. Furthermore, this very small change in adsorption by the temperature suggests that the heat of adsorption of alizarin onto adsorbents was so low that the temperature variation could not change the thermodynamics of the adsorption process. This approved that the adsorption procedure was physical, not chemical. These results showed that the temperature had no effect on the diffusion rate of the alizarin onto the surface and the internal pore of the adsorbent particles [14,23].

Photocatalytic degradation studies

At this stage, photocatalytic properties of the prepared adsorbent were studied using an experimental design approach. The advantage of using the experimental design approach in comparison with the usual One-Factor-at-a-Time (OFAT) optimization methods is that, the OFAT

Table 2: Factors and their levels in the experimental design.

Factors		levels			
(A)	Kind of adsorbent	OP	AC	CdS@OP	CdS@AC
(B)	Amount of adsorbent (mg)	100			300
(C)	pH	5	8	10	
(D)	time of photodegradation (h)	1			2

methods are time consuming and more expensive. Also, they neglect the effect of the interaction among the factors, and lead to the incorrect optimization results [24,25]. Therefore, a mixed factorial design approach with experimental nature was used for obtaining the correct values of the optimization. The selected factors and their levels are presented in Table 2.

Data was analyzed using Design-Expert Version 7.0 statistical software. The selected experiments and the obtained responses were shown in Table 3. The applied response is the dye degradation percentage (D %) that was calculated according to equation (2).

Analysis of the variance (ANOVA) was used for the analysis of the model and its results were shown in Table 4. The Main effects and two-factor interactions were used in the designed model, and the model accuracy was analyzed using diagnostic tools (i.e. the normal plot or residuals, residual vs. predicted plot, residuals vs. run plot and the predicted vs. actual plot) using the software. Finally the obtained equations for each adsorbent was obtained and written in the following:

For *OP* adsorbent:

$$D\% = -8.26571 - 3.94121 \times 10^{-3} B + 3.23269 C + 2.88133 D - 6.87961 B.C + 0.040568 B.D - 1.41390 C.D \quad (3)$$

For *AC* adsorbent:

$$D\% = -8.89407 - 6.13909 \times 10^{-3} B + 3.33448 C + 2.99924 D - 6.87961 B.C + 0.040568 B.D - 1.41390 C.D \quad (4)$$

For *CdS@OP* adsorbent:

$$D\% = 15.90947 + 0.076103 B + 1.07560 C + 15.22924 D - 6.87961 \times 10^{-3} B.C + 0.040568 B.D - 1.41390 C.D \quad (5)$$

For *CdS@AC* adsorbent:

$$D\% = 18.27624 + 0.074348 B + 1.02966 C + 16.90174 D - 6.87961 \times 10^{-3} B.C + 0.040568 B.D - 1.41390 C.D \quad (6)$$

In these equations, D% refers to the percent of dye degradation, and B, C, and D parameters refers to Amount of adsorbent (mg), pH and time of photodegradation (h), respectively.

Findings showed that the calculated R-squared was 0.9654, very close to 1, which implies that more than 96% of the variability in the data could be explained by the model.-Adequate precision, which is a criterion of S/N (signal to noise ratio) was very greater than 4, which indicates that the model discrimination is adequate [13]. As it is seen in the table, the effect of the block was a significant one. The block effect in this study was the effect of the sunlight irradiation condition on the different days. The significance of the block effect shows that the changes in the state of sunlight in the different days could affect the photodegradation efficiency.

Finally, the optimization conditions were found using the desirability plot (Fig. 6). The optimal values to achieve the maximum dye photodegradation within the test range are as follows: 300 mg of CdS@AC at pH=5 and the irradiation time of 2 h, which predicted to result in 82.41% of degradation. The obtained actual amount of degradation for these conditions was 82%, which shows that the model's prediction has been confirmed in reality.

Complementary studies

The mechanism of photodegradation of the organic molecules by quantum dots has already been suggested [26,27]. In brief, when a photon with higher amount of energy than the QDs' band gap is absorbed, it excites electrons from the valence band (vb) to the conduction band (cb) and this subsequently leads to the creation

Table 3: Designed experimental for selected factorial design.

STD	Run	Block	Factor (A)	Factor (B)	Factor (C)	Factor (D)	Response (D %)
7	1	Day1	CdS@OP	300	5	1	52
23	2	Day1	CdS@OP	300	10	1	34
10	3	Day1	AC	100	8	1	4
31	4	Day1	CdS@OP	300	5	2	76
28	5	Day1	CdS@AC	100	5	2	48
30	6	Day1	AC	300	5	2	5
40	7	Day1	CdS@AC	300	8	2	76
26	8	Day1	AC	100	5	2	4
48	9	Day1	CdS@AC	300	10	2	49
47	10	Day1	CdS@OP	300	10	2	47
22	11	Day1	AC	300	10	1	4
9	12	Day1	OP	100	8	1	3
4	13	Day1	CdS@AC	100	5	1	39
12	14	Day1	CdS@AC	100	8	1	40
5	15	Day1	OP	300	5	1	5
20	16	Day1	CdS@AC	100	10	1	36
32	17	Day1	CdS@AC	300	5	2	82
36	18	Day1	CdS@AC	100	8	2	54
44	19	Day1	CdS@AC	100	10	2	32
21	20	Day1	OP	300	10	1	5
34	21	Day1	AC	100	8	2	4
14	22	Day1	AC	300	8	1	5
35	23	Day1	CdS@OP	100	8	2	33
1	24	Day1	OP	100	5	1	3
13	25	Day2	OP	300	8	1	6
16	26	Day2	CdS@AC	300	8	1	53
27	27	Day2	CdS@OP	100	5	2	45
24	28	Day2	CdS@AC	300	10	1	49
37	29	Day2	OP	300	8	2	8
17	30	Day2	OP	100	10	1	6
2	31	Day2	AC	100	5	1	7
15	32	Day2	CdS@OP	300	8	1	48
18	33	Day2	AC	100	10	1	6
3	34	Day2	CdS@OP	100	5	1	40
42	35	Day2	AC	100	8	2	6
19	36	Day2	CdS@OP	100	10	1	35
41	37	Day2	OP	100	10	2	7
46	38	Day2	AC	300	10	2	6
8	39	Day2	CdS@AC	300	5	1	51
39	40	Day2	CdS@OP	300	8	2	75
45	41	Day2	OP	300	10	2	6
43	42	Day2	CdS@OP	100	10	2	47
33	43	Day2	OP	100	8	2	7
38	44	Day2	AC	300	8	2	8
6	45	Day2	AC	300	5	1	5
25	46	Day2	OP	100	5	2	8
11	47	Day2	CdS@OP	100	8	1	43
29	48	Day2	OP	300	5	2	9

Table 4: ANOVA results.

Source	Sum of Squares	df	Mean Square	significance
Model	25922.45	21	1234.40	significant
block	526.69	1	526.69	significant
Residual	1182.86	25	47.31	not significant
Cor. Total	27631.98	47		R-Squared = 0.9654 Adj R-Squared = 0.9197 Adeq Precision = 15.343

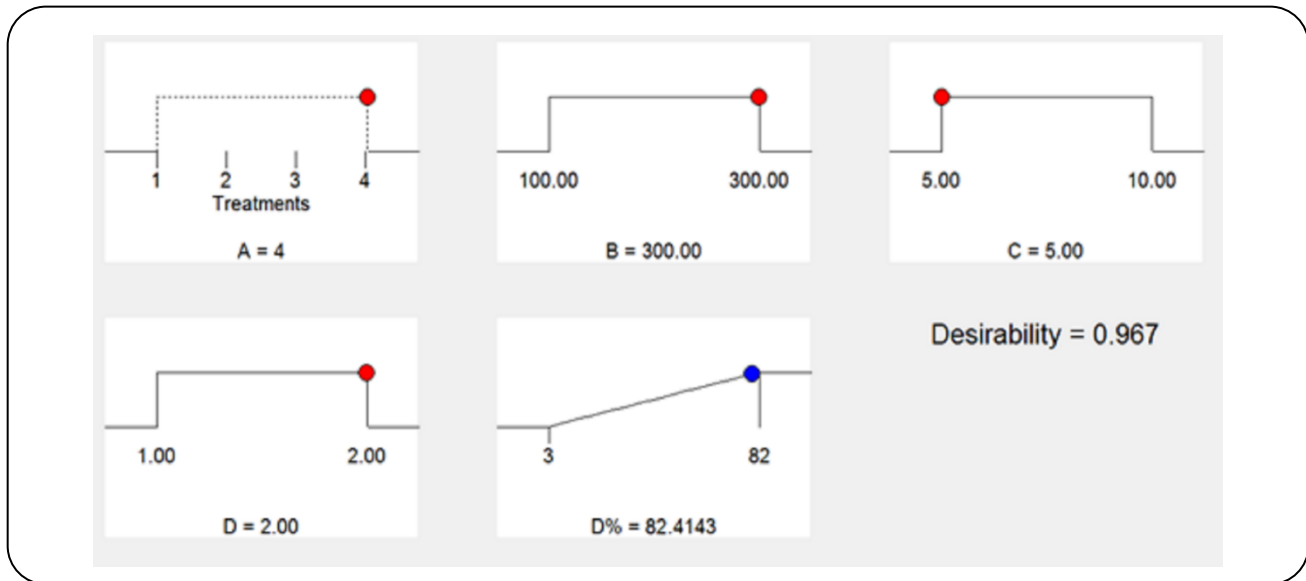
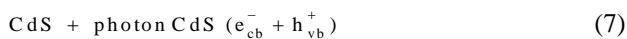


Fig. 6: Desirability plot for optimization of degradation process.

of a pair of electron-hole (h_{vb}^+ & e_{cb}^-) in the valence band and conduction band, respectively. (Eq. (7)) [27].



Next, the h_{vb}^+ and e_{cb}^- can react with the dissolved oxygen, water or hydroxyl groups and this can generate different radical groups. These radical production reactions are shown in the following equations [26,27]:



The role of the proposed reactive hydroxyl and oxygen species on photodegradation process was investigated and

proved in our previous article [14], by adding selective radical scavengers to photodegradation medium. Then, these formed radical groups attack to the adsorbed dye molecules on the surfaces of proofed adsorbent and decompose and degrade them.

Afterward, in order to examine the photodegradation of the organic molecules by the prepared nanocomposite, the chemical oxygen demand (COD) of the supernatant solution of alizarin dye by a DR-5000-HACH instrument was analyzed before and after the photodegradation process. The results indicated that the COD amount of solution decreased from 450 mg/L to 79 and 75 mg/L, using CdS@OP and CdS@AC, respectively. These results demonstrate that the organic compounds were degraded and no significant amounts of organic species were remained in the solution at the end of the photodegradation process.

The stability of the prepared nanocomposite was also studied under the same circumstances. The results

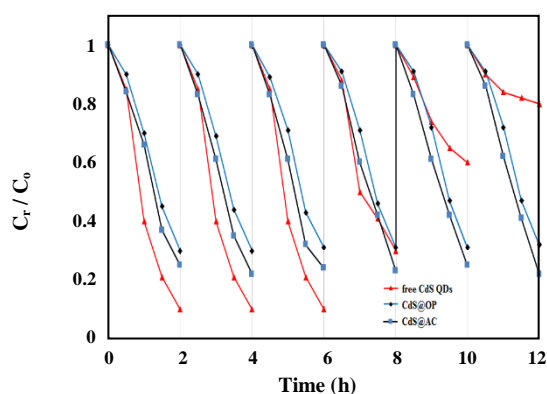


Fig. 7: The reusability of free CdS QDs, CdS@OP, and CdS@AC nanocomposites for photocatalytic degradation of alizarin.

indicated that although in the early cycles, the free CdS QDs showed better degradation efficiency than the prepared nanocomposites; but in the next cycles (in the fourth cycle and the after one) the prepared nanocomposites (i.e. CdS@OP and CdS@AC) had considerably better efficiencies than the free CdS QDs (Fig. 7). This is important probably due to the photo-corrosion of the CdS QDs. This phenomenon also indicates that the nanocomposites can protect the CdS QDs from the surrounding environment and they could also prevent photo-leaching and/or photo-corrosion of the QDs which is an advantage of the application of the prepared nanocomposites in the photodegradation process.

Overall, these experiments show that cheap and stable adsorbent and photocatalyst materials for removal and photocatalytic degradation of dye and other organic molecules could be produced using orange peel waste, for application in wastewater refinement methods.

CONCLUSIONS

In this study, preparation of the different adsorbents from the orange peel waste was studied, in order to achieve some cheap and stable materials for the removal of the dye and other organic molecules from wastewaters. Then, the adsorption and photocatalytic degradation properties of the prepared adsorbent were studied over the removal and degradation of alizarin. Results demonstrated that the prepared OP, AC, CdS@OP, and CdS@AC have good adsorption properties for the alizarin removal. Moreover, the prepared CdS@OP and CdS@AC showed both the adsorption and photocatalytic degradation properties. These prepared nanocomposites (CdS@OP and

CdS@AC) were much more stable against oxidation, agglomeration, and photo-corrosion than free quantum dots, which make them suitable for long-term applications. The effects of the different factors on the photodegradation process were examined by a factorial design method. The results showed that the pH, the type and amount of nanocomposite, the time of the photodegradation process and the sunlight irradiation conditions were factors, influential on the photodegradation process.

Acknowledgments

We thank the Central lab of the University of Gonabad for financial support.

Received : Apr. 19, 2019 ; Accepted : Jan. 13, 2020

REFERENCES

- [1] Ahmed M.B., Zhou J.L., Ngo H.H., Guo W., Thomaidis N.S., Xu J., *Progress in the Biological And Chemical Treatment Technologies for Emerging Contaminant Removal from Wastewater: A Critical Review*, *J. Hazard. Mater.*, **323**:274-298 (2017).
- [2] Gogate P.R., Pandit A.B., *A Review of Imperative Technologies for Wastewater Treatment I: Oxidation Technologies at Ambient Conditions*, *Adv. Environ. Res.*, **8**:501-551(2004).
- [3] Vakili M., Rafatullah M., Salamatinia B., Abdullah A.Z., Ibrahim M.H., Tan K.B., Gholami Z., Amouzgar P., *Application of Chitosan and its Derivatives as Adsorbents for Dye Removal from Water and Wastewater: A Review*, *Carbohydr. Polym.*, **113**: 115-130 (2014).
- [4] Seow T.W., Lim CK., *Removal of dye by Adsorption: A Review*, *Int. J. Appl. Eng.*, **11**(4): 2675-2679 (2016).
- [5] Yue Q.Y., Gao B.Y., Wang Y., Zhang H., Sun X., Wang S.G., Gu R.R., *Synthesis of Polyamine Flocculants and their Potential Use in Treating Dye Wastewater*, *J. Hazard. Mater.*, **152**: 221-227 (2008).
- [6] Wu J., Eiteman M.A., Law S.E., *Evaluation of Membrane Filtration and Ozonation Processes for Treatment of Reactive-Dye Wastewater*, *J. Environ. Eng.*, **124**:272-277 (1998).
- [7] Alizadeh M., Ghahramani E., Zarrabi M., Hashemi S., *Efficient De-Colorization of Methylene Blue by Electro-Coagulation Method: Comparison of Iron and Aluminum Electrode*, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **34**(1): 39-47 (2015).

- [8] Kansal S.K., Lamba R., Mehta S.K., Umar A., Photocatalytic Degradation of Alizarin Red S Using Simply Synthesized ZnO Nanoparticles, *Mater. Lett.*, **106**:385–389(2013).
- [9] Reddy K.R., Hassan M., Gomes V.G., Hybrid Nanostructures Based on Titanium Dioxide for Enhanced Photocatalysis, *Appl. Catal. A Gen.*, **489**: 1–16 (2015).
- [10] Reddy K.R., Nakata K., Ochiai T., Murakami T., Tryk D.A., Fujishima A., Facile Fabrication and Photocatalytic Application of Ag Nanoparticles-TiO₂ Nanofiber Composites, *J. Nanosci. Nanotechnol.*, **11**: 3692–3695 (2011).
- [11] Kachbouri S., Elaloui E., Moussaoui Y., The effect of Surfactant Chain Length and Type on the Photocatalytic Activity of Mesoporous TiO₂ Nanoparticles Obtained Via Modified Sol-Gel Process. *Iran. J. Chem. Chem. Eng. (IJCCE)*, **38(1)**:17-26 (2019).
- [12] Samadi-Maybodi A., Abbasi F., Akhoondi R., Aqueous Synthesis and Characterization of CdS Quantum Dots Capped with Some Amino Acids and Investigations of their Photocatalytic Activities, *Colloids Surfaces A Physicochem. Eng. Asp.*, **447**: 111–119 (2014).
- [13] Samadi-Maybodi A., Sadeghi-Maleki M.-R., In-Situ Synthesis of High Stable CdS Quantum Dots and Their Application For Photocatalytic Degradation of Dyes, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, **152**: 156–164 (2015).
- [14] Samadi-Maybodi A., Sadeghi-Maleki M.-R., Preparation of Mesoporous SBA-15 Supported CdS Quantum Dots and Its Application for Photocatalytic Degradation of Organic Pollutants in Aqueous Media, *J. Inorg. Organomet. Polym. Mater.*, **6**:1–13(2018).
- [15] Morales-Flores N., Pal U., Mora E.S., Photocatalytic Behavior of ZnO and Pt-Incorporated ZnO Nanoparticles in Phenol Degradation, *Appl. Catal. A Gen.*, **394**: 269–275 (2011).
- [16] Ioannidou O., Zabaniotou A., Agricultural Residues as Precursors for Activated Carbon Production—A Review, *Renew. Sustain. Energy Rev.*, **11**: 1966–2005 (2007).
- [17] Rafatullah M., Sulaiman O., Hashim R., Ahmad A., Adsorption of Methylene Blue on Low-Cost Adsorbents: A Review, *J. Hazard. Mater.*, **177**: 70–80 (2010).
- [18] Qu X., Alvarez P.J.J., Li Q., Applications of Nanotechnology in Water and Wastewater Treatment, *Water Res.*, **47**: 3931–3946 (2013).
- [19] Ullah R., Dutta J., Photocatalytic Degradation of Organic Dyes with Manganese-Doped ZnO Nanoparticles, *J. Hazard. Mater.*, **156**: 194–200 (2008).
- [20] Zapata B., Balmaseda J., Fregoso-Israel E., Torres-Garcia E., Thermo-Kinetics Study of Orange Peel In Air, *J. Therm. Anal. Calorim.*, **98**: 309–315 (2009).
- [21] Xie Z., Guan W., Ji F., Song Z., Zhao Y., Production of biologically Activated Carbon from Orange Peel and Landfill Leachate Subsequent Treatment Technology, *J. Chem.*, **2014**: 1-10 (2014).
- [22] Tsai W.-T., Hsien K.-J., Hsu H.-C., Adsorption of Organic Compounds from Aqueous Solution onto the Synthesized Zeolite, *J. Hazard. Mater.*, **166**: 635–641 (2009).
- [23] Dong Y., Lu B., Zang S., Zhao J., Wang X., Cai Q., Removal of Methylene Blue from Coloured Effluents b Adsorption onto SBA-15, *J. Chem. Technol. Biotechnol.*, **86**: 616–619 (2011).
- [24] Rahmanian B., Pakizeh M., Mansoori S.A.A., Abedini R., Application of Experimental Design Approach and Artificial Neural Network (ANN) for the Determination of Potential Micellar-Enhanced Ultrafiltration Process, *J. Hazard. Mater.*, **187**: 67–74 (2011).
- [25] Protière M., Nerambourg N., Renard O., Reiss P., Rational Design of the Gram-Scale Synthesis of Nearly Monodisperse Semiconductor Nanocrystals, *Nanoscale Res. Lett.*, **6**: 472–486 (2011).
- [26] Daneshvar N., Salari D., Khataee A.R., Photocatalytic Degradation of Azo Dye Acid Red 14 in Water: Investigation of the Effect of Operational Parameters, *J. Photochem. Photobiol. A Chem.*, **157**: 111–116 (2003).
- [27] Guo Y., Jiang L., Wang L., Shi X., Fang Q., Yang L., Dong F., Shan C., Facile Synthesis of Stable Cadmium Sulfide Quantum Dots with Good Photocatalytic Activities under Stabilization of Hydrophobic Amino Acids, *Mater. Lett.*, **74**: 26–29 (2012).