Published by
NIGERIAN SOCIETY OF PHYSICAL SCIENCES
Available online @ https://journal.nsps.org.ng/index.php/jnsps

J. Nig. Soc. Phys. Sci. 4 (2022) 183–192

Journal of the Nigerian Society of Physical Sciences

Optimization by Box Behnken Design for Eosin Yellow Dye Removal from Aqueous Medium using Date Palm Seeds-Porous Carbon@TiO_2 Blend

Samsudeen Olanrewaju Azeez[a,*], Akeem Adebayo Jimoh[a], Ismaila Olalekan Saheed[a], Kabir Opeyemi Otun[a], Aliru Olajide Mustapha[a], Folahan Amoo Adekola[b]

[a]*Department of Chemistry and Industrial Chemistry, Faculty of Pure and Applied Sciences, Kwara State University, 241103, Malete, Nigeria*
[b]*Department of Industrial Chemistry, Faculty of Physical Sciences, University of Ilorin, 240003, Ilorin, Nigeria*

Abstract

Biological stains are potentially harmful compounds present in the environment, in which Eosin yellow dye (EYD) is one of the most commonly applied stains. In this research, date palm seeds-porous carbon (DPSC) and its TiO_2 blend (TiO_2-DPSC) were prepared and their efficiency on the removal of EYD from an aqueous medium was investigated. Characterization by SEM, EDX, FTIR and BET surface area was performed on the materials. The BET surface area (542.63 m^2/g) and pore diameter (2.02 nm) of TiO_2-DPSC were found to be higher than that of DPSC (332.74 m^2/g and 1.85 nm) indicating that TiO_2-DPSC is mesoporous while DPSC is microporous. The major and interactive impacts of the adsorption parameters: initial EYD concentration, pH, adsorbent dose, and time of contact were examined by Box Behnken design in response surface methodology. The high R^2 values 0.9658 and 0.9597 for DPSC and TiO_2-DPSC agreed with the adjusted R^2 values suggesting the quadratic model sufficiently interprets the adsorption data. The optimum removal efficiency of EYD onto DPSC and TiO_2-DPSC was 34.63 mg/g and 55.34 mg/g which are in agreement with the predicted removal of 34.75 mg/g and 50.11 mg/g respectively at the center point values of C_o=300 mg/L, pH 2, 362.5 min and 0.1 g adsorbent dose. The results also showed the acceptability of the Box Behnken design in response surface methodology for the optimization of EYD removal from aqueous media using DPSC and TiO_2-DPSC blends. Hence, better EYD removal reported in TiO_2-DPSC compared to DPSC was due to its improved adsorptive features.

DOI:10.46481/jnsps.2022.533

Keywords: Porous carbon, TiO_2, Adsorption, Eosin yellow dye, Box Behnken design

Article History :
Received: 21 December 2021
Received in revised form: 17 February 2022
Accepted for publication: 25 February 2022
Published: 29 May 2022

©2022 Journal of the Nigerian Society of Physical Sciences. All rights reserved.
Communicated by: E. Etim

1. Introduction

In recent years, industrial evolution has left an indelible mark on the environment. Several industrial, domestic, and laboratory activities employ dyes for coloring [1,2]. And most of these dyes are non-biodegradable, highly hazardous, toxic, and carcinogenic which poses a great risk to health [3,4]. Also, the discharge of wastewaters containing dyes into the environment aids the pollution of rivers and greatly affects both human and aquatic lives negatively [1,3,5].

Biological stains are organic dyes commonly applied for the determination of biological tissues. These stain substances have been reported as potentially carcinogenic and mutagenic com-

*Corresponding author tel. no:
Email address: samsudeen.azeez@kwasu.edu.ng (Samsudeen Olanrewaju Azeez)

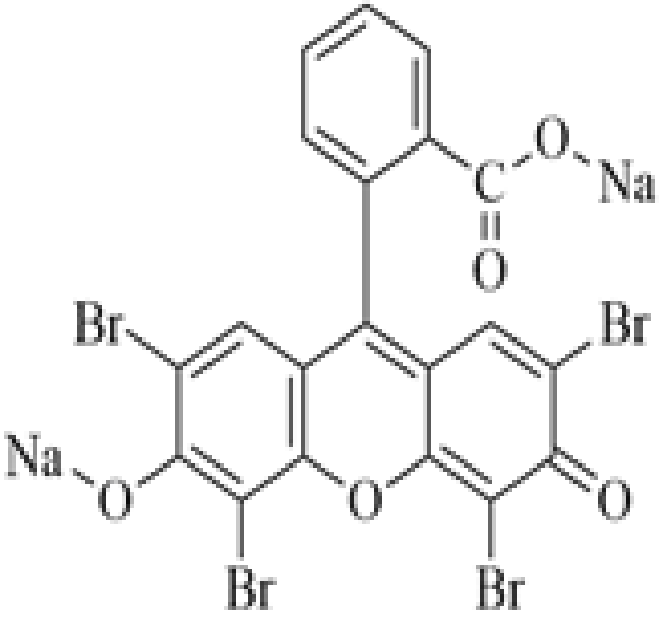

Figure 1. Structure of EYD

pounds, therefore their presence in the wastewaters being discharged into the environment is a threat to human and aquatic lives [2,4,6]. Eosin yellow dye (EYD) is a reactive, anionic water-soluble acid dye commonly used as a stain. It is heterocyclic with the molecular formula of $C_{20}H_6Br_4Na_2O_5$ and IUPAC name, 2-(2,4,5,6-Tetrabromo-6-oxido-3-oxido-3H xanthenes-9-yl) benzoate disodium salt as shown in Fig. 1. EYD is pink in color and belongs to the fluorescein class of dye with a λmax of 517 nm. It is commonly used in gram staining [4,6]. Exposure to EYD may result in severe eye and skin irritation and adversely affects vital organs such as kidney, liver, etc. It also reduces the pulmonary gas exchangeability of the lungs if inhaled [6,7].

The treatment of wastewater containing dyes before release into the environment becomes germane as a small quantity of dye in water even at part per billion level can be toxic [8]. And government policy requires that wastewater containing dye must be treated before discharge, consequently, a need to establish an effective technique that can efficiently remove these dyes from aqueous media has been the concern of the researcher. Before now, various techniques have been used to treat and remove organic pollutants in wastewater [9] which include chemical precipitation, membrane filtration, catalytic, photocatalytic oxidation methods, ion exchange, electrochemical methods, adsorption technology, etc [1,4,7,10]. The adsorption technique is widely used now for wastewater treatment due to its efficiency, cheapness, ease to handle, and simplicity of its regeneration procedure [1,10]. The search for a low-cost and effective adsorbent prepared from agricultural waste to adsorb dyes and other organics from wastewater is of interest to researchers [7,11–14]. Lately, in an attempt to fabricate an adsorbent with improved adsorptive characteristics for better removal of contaminants, research towards the development of composite materials that are more effective and of low cost to treat wastewater pollutants is increasing, Viz; date palm seeds, goethite, and their composite was used to remove acid dye from wastewater [4], novel magnetic/activated charcoal/β- cyclodextrin/alginate polymer nanocomposite was utilized in the removal of cationic [10], adsorption of organic dye by nanoporous composites of activated carbon-metal organic frameworks [8], activated carbon prepared from wild date stones was employed in the adsorption of acid dye [1], the adsorption of methyl orange by Fe-grafting sugar beet bagasse was investigated [12] and a new type of porous Zn (II) metal-organic gel was designed for effective adsorption of methyl orange [9]. TiO_2 is a non-toxic cheap and biocompatible semiconductor. It is the most commonly used photocatalyst, due to its high stability and potential in the decomposition of many organic pollutants from aqueous media [15,16]. Loading TiO_2 onto activated carbon as support has been reported [17,18]. The date palm (*Phoenix dactylifera*) is one of man's earliest plants. It originated from North Africa and the Middle East and was brought to Nigeria. It is a palm tree from the Palmae (*Arecaceae*) family that grows in the tropics [16]. Experimentally, date palm seeds were known to contain about 55-65% carbohydrate, which makes it a suitable agricultural waste precursor for the preparation of high-grade activated carbon [19].

Previously, in adsorption studies, the optimization of process variables was usually investigated individually while keeping the other parameters constant. However, this method does not give the simultaneous effect of all parameters [20]. This approach is time-wasting, requires a lot of experiments, and consumes large reagents and chemicals. These setbacks can be prevented by optimizing the independent variables concurrently employing a statistical experimental design like the Box Behnken design (BBD) under response surface methodology (RSM) [1,13]. Therefore, this research is concerned with investigating the optimization by Box Behnken design for EYD removal from aqueous medium using date palm seeds-porous carbon and TiO_2-composite.

2. Experimental

2.1. Reagents and chemicals

All the reagents used in this investigation are of analytical grade and were used with no additional purification. These include Eosin yellow dye (EYD), titanium(IV)oxide (TiO_2), phosphoric acid (H_3PO_4), ethanol (C_2H_5OH), sodium hydroxide (NaOH), and hydrochloric acid (HCl) which were purchased from Sigma Aldrich, USA. Deionized water was used to prepare all the solutions.

2.2. Sample collection and preparation of date palm seeds-porous carbon (DPSC)

The date palm fruits were gotten from Kaduna, Nigeria. The seeds were removed from the fruits, washed thoroughly with deionized water, and sundried for 2 days. The seeds were then carbonized in the furnace at 500 °C for 120 min. After which it was activated with phosphoric acid. The activation involved

immersing 100 g of the carbonized date palm seeds in 500 mL of 1 M H_3PO_4 for 48 h. It was then filtered, washed to neutral pH with hot and cold deionized water, and oven-dried at 105 °C for 2 h. Subsequently, it was reactivated for 2 h at a temperature of 300 °C then cooled, ground, and sieved with < 63 μm mesh. This product was then labeled date palm seeds-porous carbon (DPSC) [19,21].

2.3. Preparation of TiO_2-DPSC blend

The titanium (IV) oxide-date palm seeds-porous carbon (TiO_2-DPSC) was prepared by the impregnation method as follows: 10 g of DPSC was added to 100 mL of deionized water andtreatment in an autoclave at 120 °C for 2 h. The stirred for 1 h. 5 g of commercial nanoparticle TiO_2 was then added and stirred for another 2 h at 40 °C. Subsequently, a 1:1 ratio of ethanol and water was added to the resulting TiO_2-DPSC mixture and then subjected to hydrothermal treatment in an autoclave at 120 °C for 2 h. The resultant mixture was centrifuged at 4000 rpm for 15 min and the blend solid particles obtained were oven-dried at 110 °C for 1 h. It was then calcined at 400 °C for 3 h. After cooling it was ground to fine particles and stored for further use [18,22,23].

2.4. Characterization of DPSC and TiO_2-DPSC

The adsorbents were characterized using an FTIR spectrophotometer (Perkin-Elmer Spectrum GX, UK) to ascertain the functional groups present on the adsorbents. The surface morphology and elemental composition of the material were obtained with a scanning electron microscope coupled with energy dispersive spectroscopy (JEOL JSM-6510LV, Japan). The surface area of both adsorbents was determined by BET analysis via N_2 adsorption-desorption at 77 K using Micromeritics ASAP 2020 V3.02H model.

2.5. Preparation of EYD solution

A 1000 mg/L of EYD solution was prepared by dissolving 1 g of EYD in 1 L of deionized water and lower concentrations of EYD were then prepared by serial dilution [7].

2.6. Adsorption experiments

The removal of EYD by DPSC and TiO_2-DPSC blends were determined in batch mode. The initial EYD concentration, pH, contact time, and adsorbent dosage were investigated. The adsorption study involves adding 0.1 g of the adsorbents (DPSC or TiO_2-DPSC blend) to 20 mL of different initial concentrations (50 to 300) mg/L of EYD solution in a 100 mL conical flask. The flasks containing the solutions were then placed in a temperature-controlled water bath shaker and were agitated for 120 min at 30±2 °C and 200 rpm. The pH of the solutions was controlled using 0.1 M NaOH and 0.1 M HCl solutions. The samples were then centrifuged for 10 min at 4000 rpm and filtered. After which, the filtrate was analyzed for change in concentration of EYD using UV/Visible spectrophotometer (Microprocessor UV-VIS Double Beam AVI-2802) at a λmax of 517 nm. The quantity of EYD removal was calculated with Eq. (1) [1,4,24,25]:

$$q_e = \frac{(C_0 - C_e)\,V}{W} \tag{1}$$

where, q_e is the quantity of EYD removed, Co is the initial EYD concentration (mg/L), Ce is the equilibrium EYD concentration (mg/L), V is the volume of EYD solution (L) and W is the weight of adsorbent (g).

Table 1. Process parameters and their coded levels for BBD in RSM

			Range of coded values		
Parameters	Units	Factors	-1	0	+1
Initial conc	mg/L	A	50	175	300
pH		B	2	7	12
Adsorbent dose	g	C	0.1	0.3	0.5
Time	min	D	5	326.5	720

2.7. Box Behnken experimental design and statistical analysis

Optimization of the process parameters was achieved with Box Behnken design (BBD) under RSM. This was employed to determine the best interaction between the process parameters in the removal of EYD from aqueous media by DSPC and TiO_2-DPSC. The design was used to obtain sets of designed experiments by Design Expert 11.1.2.0 with four factors; initial concentration, pH, adsorbent dose, and time. To study the influence of operating variables on the quantity of EYD removal, the four variables: concentration (A), pH (B), adsorbent dose (C), and time (D) each at three levels were selected as presented in Table 2. The number of experimental runs could as well be calculated using Eq. (2):

$$N = k^2 + k + C_p \tag{2}$$

where N is the number of experimental runs, k is the number of factors and Cp is the replicate number of central points. Consequently, a total of 29 experimental runs was gotten as a function of the four factors on a three-level design, that is (-1. 0, +1) as presented in Table 1 [13,20,26].

The responses were presented as the quantity of EYD removed (mg/g) as in Table 3. The experimental data were studied and fitted well with the quadratic polynomial equation model which describes the nature of the process as expressed by Eq. (3):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{1 \le i \le j}^{k} \beta_{ij} x_i x_j + \epsilon \tag{3}$$

Where, Y is the response (quantity of EYD removed); x_i = variables; k = number of variables; β_0 = constant term; β_i = coefficients of linear parameters, β_{ij} = coefficient of the interaction parameters; β_{ii} =coefficient of the quadratic parameter; ε = residual associated to the experiments.

Table 2. Characteristics of the Adsorbents

	DPSC	TiO_2-DPSC
BET Surface area (m^2g^{-1})	332.744	542.634
Average pore volume (cm^3g^{-1})	0.188	0.271
Average pore diameter (nm)	1.853	2.015
%C	70.70	26.71
%O	29.17	44.42
%Ti	-	28.87
%Ca	0.13	-

3. Results and Discussion

3.1. Adsorbents Characterization

3.1.1. BET surface area analysis and elemental composition

The Brunauer, Emmett and Teller (BET) analysis results of both DPSC and TiO_2-DPSC are given in Table 2. The BET surface area of both adsorbents is large which are attributed to carbon materials used as a precursor and the preparation procedure utilized, but the surface area of TiO_2-DPSC is higher than DPSC. The enhancement of TiO_2-DPSC surface area is due to TiO_2 incorporated with the carbon. The result also showed that the pore volume and pore diameter of TiO_2-DPSC is greater than DPSC. According to IUPAC classification, it is perceived that TiO_2-DPSC is mesoporous and DPSC microporous [27]. This result suggests that both adsorbents are materials with a good potential for the removal of EYD. Although, TiO_2-DPSC would be a better adsorbent for removal EYD than DPSC owing to its higher surface area and mesoporous surface [21,28].

The EDX results give the elemental composition of the adsorbents. The major constituents of DPSC are carbon and oxygen with calcium as a minor element while TiO_2-DPSC exhibited a high percentage of titanium with lower percentages of carbon and oxygen as compared to DPSC (Table 2 & Fig. 2.). The relatively high weight percentage of Ti in TiO_2-DPSC indicates successful incorporation of TiO_2 into the date palm seeds-porous carbon.

3.1.2. Scanning electron microscopy (SEM)

The SEM micrograph (Fig. 3a) of DPSA showed an irregular coarse surface morphology with many micropores which exhibited a high probability for EYD to be adsorbed. Also, the SEM image of TiO_2-DPSA (Fig. 3b) revealed an improvement on the surface of the adsorbent due to agglomeration of TiO_2 particles on the surface of DSAC indicating its porous nature and supported by the increase in the BET surface area and pore diameter of TiO_2-DPSA.

3.1.3. FTIR analysis of the adsorbents

The FTIR spectra of DPSC and TiO_2-DPSC are given in Fig. 4a. The absorption bands at ~ 3400 cm^{-1} observed for both adsorbents are characteristics of O-H stretching vibrations of alcohol [5]. The band at ~ 1600 cm^{-1} shows the presence of the C=C aromatic functional group, while the peak at ~ 1233 cm^{-1} is related to the C-OH band. A band at 495.88 cm^{-1} on the TiO_2-DPSC spectrum is attributed to Ti-O-Ti bending vibrations that do not exist on DPSC. All these functional groups will take part in the adsorption process [1,4,19]. Following adsorption of EYD (Fig. 4b.), there were differences in intensities of the absorption peak indicating the involvement of the functional groups in the adsorption process as a similar observation was reported by [21].

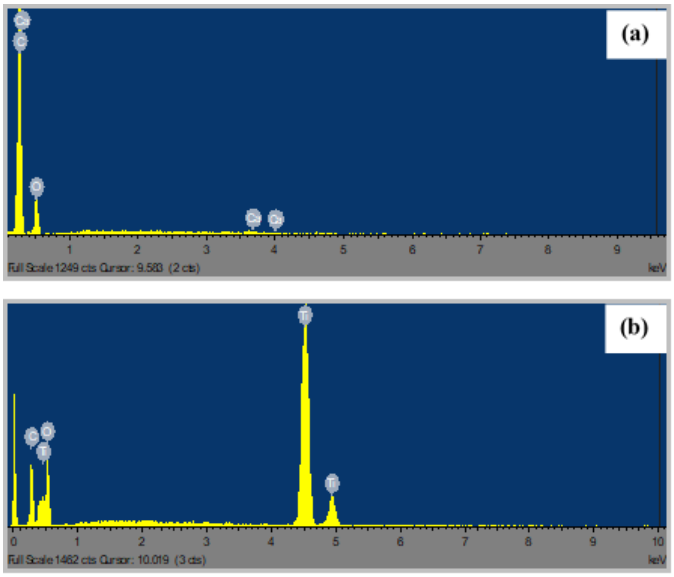

Figure 2. EDX spectra of (a) DPSC, (b)TiO_2-DPSC

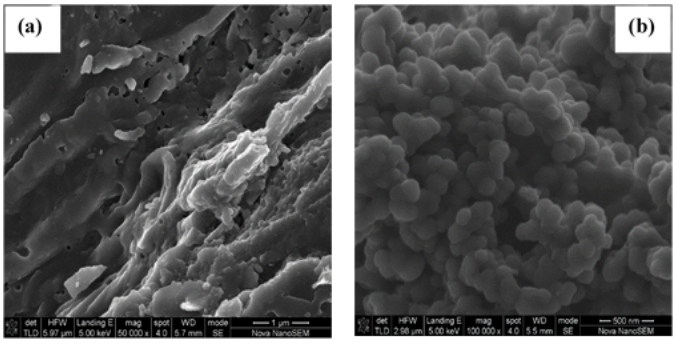

Figure 3. SEM micrograph of (a) DPSA and (b) TiO_2-DPSA

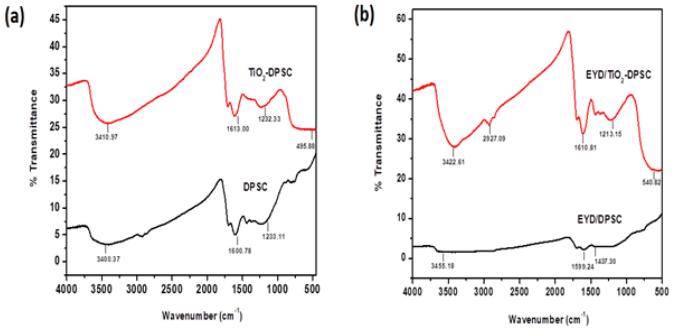

Figure 4. FTIR spectra of DSPC and TiO_2-DPSC (a) before adsorption (b) after adsorption

3.2. Optimization of EYD onto DPSC and DPSC-TiO_2 by BBD

The optimum conditions for EYD removal onto DPSC and DPSC-TiO_2 were established by BBD under RSM. The matrix of experimental design of the four process variables each at three levels with their equivalent actual and predicted responses (quantity adsorbed in mg/g) are given in Table 3. Design expert 11.1.2.0 was used to obtain the second-order polynomial equations that describe the adsorption responses (quantity adsorbed) with the four operating variables where the insignificant terms (p?0.05) are not included as given by Eq. (4) and Eq. (5) for DPSC and DPSC-TiO_2 respectively:

$$Y_{DPSC} = +2.90 + 8.38A - 5.02B - 9.41C + 1.84D - 9.21AC - 5.43BD + 4.34B^2 + 5.48C^2 + 7.77D^2 \quad (4)$$

$$Y_{TiO_2-DPSC} = +9.82 + 10.14A - 4.49B - 14.13C + 1.63D - 4.15AB - 8.64AC - 4.79BD + 7.90C^2 \quad (5)$$

Equations (4) and (5) depict how the interactive model terms impacted the removal of EYD from an aqueous solution by both adsorbents. The synergistic effect of the parameters is indicated by a positive sign while a negative sign represents an antagonistic effect [1,29].

3.2.1. ANOVA Results

The adequacy of the proposed model was analyzed using the ANOVA. The results obtained are shown in Table 4. High F-values of the models 28.20 and 23.74 for DPSC and TiO_2-DPSC respectively with their p-value less than 0.05 suggested that the quadratic models are significant. The high correlation coefficient (R^2) values of 0.965 and 0.960 with adjusted R^2 values of 0.932 and 0.919 for DPSC and TiO_2-DPSC respectively agreed with their corresponding predicted R^2 values of 0.806 and 0.785 implying that the model is adequate to describe the adsorption process. Also, the low values of percentage coefficient of variation (%CV) 29.35% and 26.80% for DPSC and TiO_2-DPSC respectively signify good reliability and high precision of the experimental values [13]. It is obvious in Table 4 that the linear terms A, B, C, and D, the interaction term AC and BD, and quadratic terms B^2, C^2, and D^2 are statistically significant ($p< 0.05$) for EYD onto DSPC while for EYD on TiO_2-DPSC, the linear term D is not significant ($p>0.05$), the interaction terms AB, AC and BD, and quadratic terms C^2 are significant. This infers that the number of experiments performed is acceptable to explain the effects of the process parameters on the amount of EYD removal from aqueous solution by both adsorbents [30–32]. Furthermore, Table 4 shows that the lack of fit (F-value = 19.25) with p-value < 0.05 indicates the lack of fit is significant for EYD removal onto DPSC while the lack of fit (F-value = 3.42) and p-value > 0.05 for EYD adsorbed by TiO_2-DPSC is not significant compared to the pure error, suggesting that the mathematical model proposed was well explained

The graph of actual versus predicted values of EYD removal onto both adsorbents is given in Fig. 5. It can be seen that the points on the plots were well grouped on the straight line; signifying a good agreement between the actual and predicted values of the responses for both adsorbents [29]. This indicates that the proposed statistical model is satisfactory for the optimization of EYD removal by both DPSC and TiO_2-DPSC [33,34].

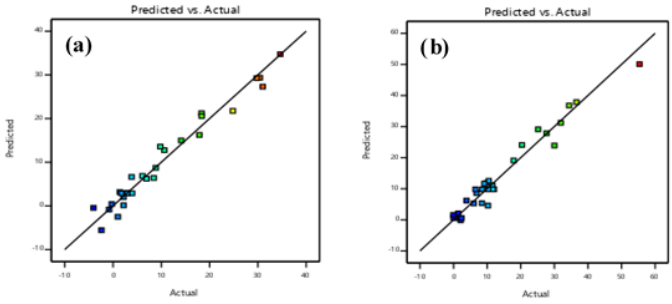

Figure 5. The plot of actual versus predicted values for EYD removal by (a) DPSC, (b)TiO_2-DPSC

DPSC: - Mean = 9.92; C.V.% = 29.35; R^2 = 0.9658; Adjusted. R^2 = 0.9315; Predicted. R^2 = 0.8057; Adeq. Precision = 19.2583

TiO_2-DPSC: - Mean = 14.19; C.V.% = 26.80; R^2 = 0.9597; Adjusted. R^2 = 0.9192; Predicted. R^2 = 0.7850; Adeq. Precision = 18.3713

3.3. Simultaneous effects of process parameters on the removal of EYD

The interactions between the process parameters on the quantity of EYD removal from aqueous solution by DPSC and TiO_2-DPSC are illustrated by 3D response surface plots (Figs. 6 – 11). These involve the simultaneous effects of any two of the process variables while keeping the other factors at the central level.

3.3.1. Simultaneous effect of initial EYD concentration and pH

The simultaneous effect of the initial EYD concentration and pH on the amount of EYD removal by DPSC and TiO_2-DPSC is given in Fig. 6. It can be seen (Fig. 6.) that increase in initial EYD concentration at low pH increases the amount of EYD removal per gram for both adsorbents. This dual interaction is not significant for EYD on DPSC but significant for EYD onto TiO_2-DPSC. The increase in the quantity of EYD adsorbed as the adsorbate concentration increases could be as a result of more EYD ions in solution as its concentration increases. At low pH, the removal of EYD was at its optimum as a result of more availability of H^+ ions in the solution. This may be due to electrostatic attraction between the anionic species of EYD in solution and the protonated surface of the adsorbents. While, at higher pH, the adsorption of EYD by the two adsorbents decreased, because more OH^- ions exist in the solution and electrostatic repulsion results between the molecules of EYD in solution and the negatively charged surface of the adsorbents. This trend corresponds to the observations reported by Mittal et al. [6], Bello et al. [21] and Abdus-Salam et al. [4].

Table 3. Box Behnken Experimental Design for EYD Removal onto DPSC & TiO_2-DPSC

Experimental run	Operating variables				Responses (mg/g) DPSA		Responses (mg/g) TiO_2-DPSA	
	Initial conc (mg/L)	pH	Adsorbent dose (g)	Time (min)	Actual quantity adsorbed	Predicted quantity adsorbed	Actual quantity adsorbed	Predicted quantity adsorbed
1	50	2	0.3	362.5	2.15	2.01	0.89	0.54
2	175	7	0.5	720	3.86	6.64	3.86	6.21
3	175	12	0.3	720	8.43	6.40	8.43	5.35
4	175	7	0.1	5	24.82	21.77	31.91	31.21
5	175	7	0.1	720	30.4	29.35	34.4	36.78
6	175	12	0.3	5	9.79	13.59	9.15	11.67
7	50	7	0.3	720	1.39	3.17	1.39	2.09
8	175	2	0.3	5	10.64	12.77	11.58	11.08
9	175	7	0.5	5	6.09	6.87	6.00	5.28
10	175	7	0.3	362.5	2.8	2.90	8.50	9.82
11	175	7	0.3	362.5	3.05	2.90	6.54	9.82
12	300	12	0.3	362.5	8.86	8.73	9.82	11.83
13	175	7	0.3	362.5	2.95	2.90	12.03	9.82
14	175	2	0.5	362.5	6.92	6.22	6.87	8.61
15	300	7	0.3	5	17.87	16.26	17.89	19.11
16	50	12	0.3	362.5	-2.39	-5.57	2.12	-0.15
17	175	12	0.5	362.5	-0.26	0.41	-0.02	0.62
18	50	7	0.1	362.5	-4.05	-0.45	10.46	12.55
19	50	7	0.3	5	2.18	0.13	2.39	0.56
20	50	7	0.5	362.5	-0.81	-0.83	-0.08	1.58
21	175	12	0.1	362.5	14.12	14.99	27.70	27.88
22	175	2	0.1	362.5	29.77	29.27	36.58	37.86
23	300	7	0.3	720	18.35	20.57	20.35	24.09
24	300	2	0.3	362.5	18.33	21.24	25.18	29.11
25	175	7	0.3	362.5	3.95	2.90	11.71	9.82
26	300	2	0.1	362.5	34.63	34.75	55.34	50.11
27	300	7	0.5	362.5	1.01	-2.50	10.24	4.57
28	175	2	0.3	720	31.01	27.31	30.01	23.91
29	175	7	0.3	362.5	1.77	2.90	10.31	9.82

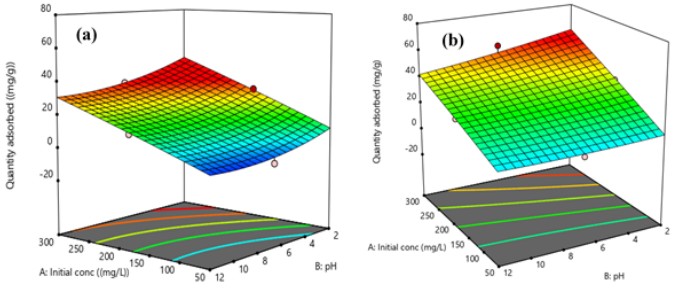

Figure 6. 3D response surface plots for the simultaneous effect of initial EYD concentration and pH at constant 0.1 g dosage and 362.5 min contact time on the quantity of EYD adsorbed onto (a) DPSC, (b) TiO_2-DPSC

3.3.2. *Simultaneous effect of initial EYD concentration and adsorbent dose*

The 3D response surface plots presented in Fig. 7 depict the simultaneous effects of initial EYD concentration and adsorbent dose on the quantity of EYD removal per gram of the adsorbents (DPSC and TiO_2-DPSC) at a fixed time of 362.5 min and pH 2. These binary interaction terms are significant in achieving the maximum amount of EYD removal by both adsorbents. The increase in initial EYD concentration greatly impacts the removal of EYD onto DPSC and TiO_2-DPSC. The uptake of EYD was at the highest at a low adsorbent dose. The vigorous adsorption of EYD observed at a lower dose could be due to many vacant adsorption sites on the adsorbents' surfaces. However, at a higher dosage, the free adsorption sites reduce because of overlapping of the active adsorption sites [4,11,31]

3.3.3. *Simultaneous effect of initial EYD concentration and time*

Fig. 8 represents the effect of combined interaction between initial EYD concentration and time of contact on the 3D response surface plots for EYD removal from an aqueous solution at constant pH and adsorbent dose. As seen from the plots, the removal of EYD increases immensely with increasing initial

Table 4. ANOVA analysis using BBD under RSM for EYD removal by DPSC & TiO_2- DPSC

Source	Sum of Squares		df	Mean Square		F-value		p-value		Remarks		%C	
	DPSC	TiO_2-DPSC		DPSC	TiO_2-DPSC	DPSC	TiO_2-DPSC	DPSC	TiO_2-DPSC	DPSC	TiO_2-DPSC	DPSC	TiO_2-DPSC
Model	3345.55	4809.09	14	238.97	343.51	28.2	23.74	< 0.0001	< 0.0001	Significant	Significant		
A-Conc	843.03	1233.23	1	843.03	1233.23	99.5	85.24	< 0.0001	< 0.0001	Significant	Significant	25.20	25.64
B-pH	302.71	242.19	1	302.71	242.19	35.73	16.74	< 0.0001	0.0011	Significant	Significant	9.05	5.04
C-Dosage	1061.82	2394.75	1	1061.82	2394.75	125.32	165.53	< 0.0001	< 0.0001	Significant	Significant	31.74	49.80
D-Time	40.52	31.75	1	40.52	31.75	4.78	2.19	0.0462	0.1606	Significant		1.21	0.66
AB	6.08	68.81	1	6.08	68.81	0.7171	4.76	0.4113	0.0467		Significant	0.18	1.43
AC	339.66	298.6	1	339.66	298.6	40.09	20.64	< 0.0001	0.0005	Significant	Significant	10.15	6.21
AD	0.4032	2.99	1	0.4032	2.99	0.0476	0.2069	0.8305	0.6562			0.01	0.06
BC	17.94	0.99	1	17.94	0.99	2.12	0.0684	0.1677	0.7974			0.54	0.02
BD	118.05	91.68	1	118.05	91.68	13.93	6.34	0.0022	0.0246	Significant	Significant	3.53	1.91
CD	15.25	5.36	1	15.25	5.36	1.8	0.3704	0.2011	0.5525			0.46	0.11
A^2	2.67	1.71	1	2.67	1.71	0.3151	0.1179	0.5834	0.7365			0.08	0.04
B^2	122.16	6.84	1	122.16	6.84	14.42	0.4731	0.002	0.5028	Significant		3.65	0.14
C^2	194.86	404.41	1	194.86	404.41	23	27.95	0.0003	0.0001	Significant	Significant	5.82	8.41
D^2	391.83	30.22	1	391.83	30.22	46.24	2.09	< 0.0001	0.1704	Significant		11.71	0.63
Residual	118.62	202.55	14	8.47	14.47								
Lack of fit	116.21	181.35	10	11.62	18.13	19.25	3.42	0.0059	0.1235	Significant	Not significant		
Pure Error	2.41	21.2	4	0.6036	5.3								
Cor Total	3464.17	5011.64	28										
Std. Dev.	2.91	3.80											

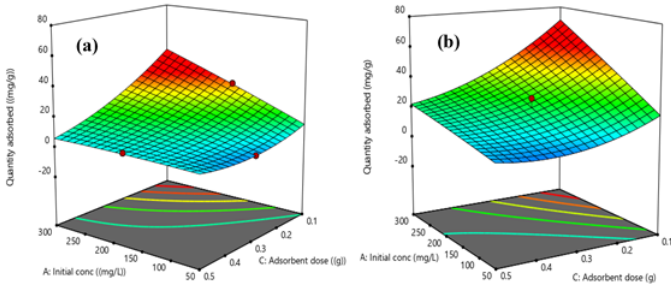

Figure 7. 3D response surface plots for the simultaneous effect of initial EYD concentration and adsorbent dose at affixed pH 2 and 362.5 min contact time on the quantity of EYD adsorbed onto (a) DPSC, (b) TiO_2-DPSC

EYD concentration. This may be due to the low pH of the solution and increase in the initial EYD concentration. However, an increase in the time of contact between the adsorbents and initial EYD concentration in solution has a small influence on the amount of EYD adsorbed at the start of the adsorption process. This low initial EYD removal result may be from several vacant active sites originally available for adsorption. Therefore, EYD molecules quickly filled the active sites. As adsorption advances, the repulsive forces between the EYD molecules on the adsorbents surfaces and in the solution becomes larger needing more time to fill the remaining vacant active sites on the adsorbents surfaces [4,21,31]. This is why there were no considerable differences in the amount of EYD removed over the time investigated.

3.3.4. Simultaneous effect of pH and adsorbent dose

The binary effect of interaction between pH and adsorbent dose on the response surface for the removal of EYD from solution at constant initial EYD concentration and time of contact is shown in Fig. 9. The optimum removal of EYD per gram was observed at low pH and low adsorbent doses indicating a synergistic effect between the parameters. The quantity of EYD removal was

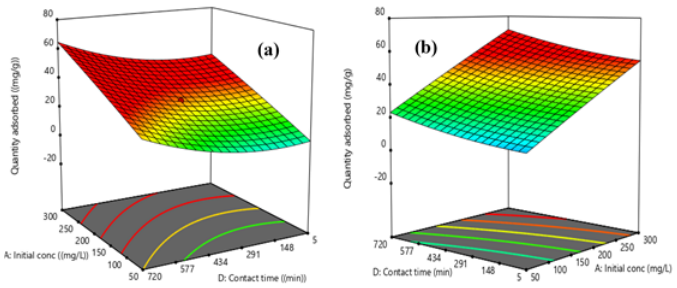

Figure 8. 3D response surface plots for the simultaneous effect of initial EYD concentration and time of contact at constant 0.1 g dosage and pH 2 on the quantity of EYD adsorbed onto (a) DPSC, (b) TiO_2-DPSC

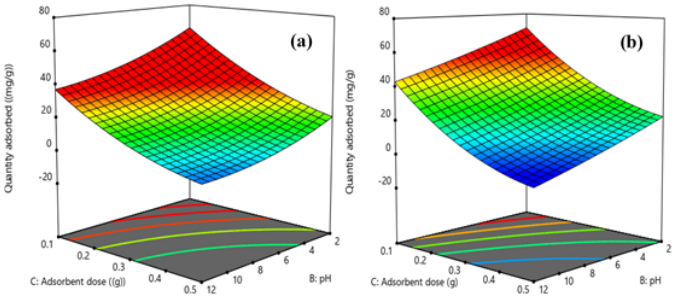

Figure 9. 3D response surface plots for the simultaneous effect of pH and adsorbent dosage at affixed 300 mg/L initial EYD concentration and 362.5 min contact time on the quantity of EYD adsorbed onto (a) DPSC, (b) TiO_2-DPSC

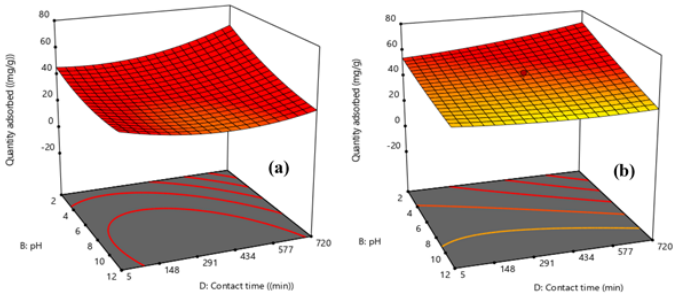

Figure 10. 3D response surface plots for the simultaneous effect of pH and contact time at constant 300 mg/L initial EYD concentration and 0.1 g dosage on the quantity of EYD adsorbed onto (a) DPSC, (b) TiO_2-DPSC

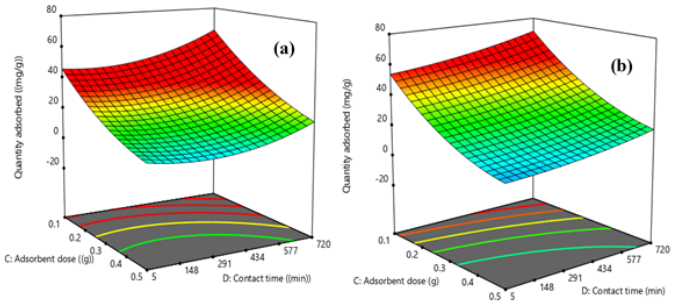

Figure 11. 3D response surface plots for the simultaneous effect of contact time and adsorbent dose at affixed 300 mg/L initial EYD concentration and pH 2 on the quantity of EYD adsorbed onto (a) DPSC, (b) TiO_2-DPSC

18.33 mg/g and 25.18 mg/g for DPSC and TiO_2-DPSC respectively.

3.3.5. Simultaneous effect of time and pH

Fig.10 illustrates the simultaneous effect of pH and time of contact on the response of EYD removal from aqueous solution at constant initial EYD concentration and adsorbents dose. The binary effect was highly significant for both adsorbents analyzed (Table 4). These dual interaction terms were used in establishing the optimum conditions for this study. According to this figure, the optimum (actual) removal of EYD was found to be 34.63 mg/g and 55.34 mg/g and predicted removal 34.75 mg/g and 50.11 mg/g for DPSC and TiO_2-DPSC respectively at the center point values of 300 mg/L initial EYD concentration, pH 2, 362.5 min time of contact and 0.1 g adsorbent dose for the two adsorbents. An additional increase in these two parameters (pH and time) resulted in a decrease in the quantity of EYD adsorbed [31,34,35].

3.3.6. Simultaneous effect of time and adsorbent dose

The simultaneous effect between the time of contact and adsorbent dose on the response surface for the amount of EYD uptake per gram by DPSC and DPSC-TiO_2 at affixed pH and initial EYD concentration is given in Fig. 11. These binary interaction terms have no significant impact on the quantity of EYD removed by both adsorbents (Table 4). It is seen that the quantity of EYD removal was at the highest at a low dose of 0.1 g for both adsorbents and very rapid at the start of the adsorption process. However, an increase in time of contact and adsorbent dose does not influence the quantity of EYD removed as the adsorption progresses. This is due to the availability of various vacant sites ready for adsorption in the early stage of the process. Thus, an increase in adsorbent doses led to a decrease in the quantity of EYD removed while an increase in time do not have a meaningful effect on the removal.

Table 5. Comparison of adsorption efficiencies of DPSC and TiO_2-DPSC with other adsorbents for EYD removal

Adsorbents	Adsorption Efficiency (mg/g)	Reference
Pineapple peels	11.76	[7]
Oil bean acid activated carbon	26.32	[36]
Teak leaf litter powder	31.64	[37]
Polyaniline saw dust	5.90	[38]
Goethite	27.78	[4]
Composite of goethite and thermally activated carbon	30.30	[4]
Chemically activated carbon	3.13	[4]
Thermally activated char-coal	1.98	[4]
DPSC	34.63	This investigation
TiO_2-DPSC	55.34	This investigation

3.4. Interactive effects of the process variables

Generally, the perturbation graph is utilized to examine the interactive influence of all factors concurrently. The response is designed by changing one of the variables while other parame-

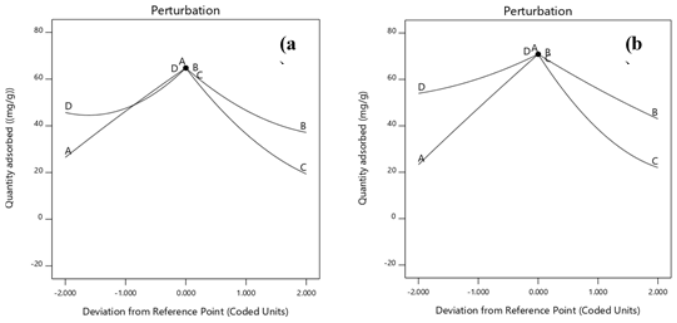

Figure 12. Perturbation graph for EYD Removal onto (a) DPSC, (b) TiO_2-DPSC

ters are kept constant at the center of the plot. Therefore, a perturbation plot is employed to determine the factor that greatly impacts the adsorption process. Fig. 12a exhibited that initial EYD concentration, pH, adsorbent dose, and time have a meaningful influence on the quantity of EYD removal per gram by DPSC due to their relatively straight line. However, the amount of EYD removal onto TiO_2-DPSC was largely influenced by three of the parameters except time due to its curvature (Fig. 12b) and this revealed that EYD removal is less sensitive to this parameter. This is following the report of Rahman &Nasir [35].

3.5. Contribution of process parameters on the response surface plots

The contribution (C) of each parameter in percentage on the response model was studied by Eq. 6 [35,39]:

$$\%C = \frac{SS_i}{SS_m} \times 100 \tag{6}$$

where SSm is the sum of squares for the model and SSi is the sum of squares for the individual parameter. The results are presented in Table 4. The results indicated that the adsorbent dose, initial EYD concentration, and pH of solution immensely contributed to EYD removal by both adsorbents with %C values of 31.74, 25.20, and 9.05 for DPSC and 49.80, 25.64 5.04 for TiO_2-DPSC respectively. The percentage contribution of a time of contact is the lowest among the individual parameters for both adsorbents in the response model. The interactive term AC gives a %C value of 10.15 and 6.21 for DPSC and TiO_2-DPSC respectively while the other dual terms have lesser contribution in EYD removal from aqueous solution.

4. Conclusion

In this research, DPSC and TiO_2-DPSC blends were successfully prepared for the removal of EYD from an aqueous medium. The surface area and pore diameter of TiO_2-DPSC is higher than DPSC. The major and interactive impacts of the adsorption parameters which include initial EYD concentration, pH, adsorbent dose, and time of contact were examined by Box Behnken design based on response surface methodology. The high R^2 values of the models are in agreement with the adjusted R^2 values. The second-order regression model sufficiently interprets the adsorption data. The adsorbent dose delivered the largest percentage contribution of 49.80% and 31.74% for TiO_2-DPSC and DPSC respectively to the response parameters while the dual interaction terms of initial EYD concentration and adsorbent dose had the highest percentage contribution of 10.15% and 6.21% for DPSC and TiO_2-DPSC respectively to EYD removal per gram compared to other interaction terms. The optimum amount of EYD removal onto DPSC and TiO_2-DPSC were discovered to be 34.63 mg/g and 55.34 mg/g respectively. The results also showed the reliability of the Box Behnken design in response surface methodology for the optimization of EYD removal from aqueous media. Based on the observed trends, it can be concluded that TiO_2-DPSC is a better adsorbent material in the removal of EYD from an aqueous solution than DPSC.

Acknowledgments

The authors are highly appreciative of Chemistry and Industrial Chemistry Department, Kwara State University, Malete, Nigeria for giving us the laboratory facilities necessary to carry out this research.

References

[1] L. Brahmi, F. Kaouah, S. Boumaza & M. Trari, "Response surface methodology for the optimization of acid dye adsorption onto activated carbon prepared from wild date stones", Appl. Water Sci. **9** (2019) 1, https://doi.org/10.1007/s13201-019-1053-2.

[2] M. S. M. Amran, D. M. Khalid, W. A. K. W. Azlina & A. Idris, "Cationic and anionic dye adsorption by agricultural solid wastes : A comprehensive review", Desalination **280** (2011) 1, https://doi.org/10.1016/j.desal.2011.07.019.

[3] I. D. Dallabona, L. Mathias, R. Maria & M. Jorge, "A new green floating photocatalyst with Brazilian bentonite into TiO 2 / alginate beads for dye removal", Colloids Surfaces A Physicochem. Eng. Asp. **627** (2021) 127159, https://doi.org/10.1016/j.colsurfa.2021.127159.

[4] N. Abdus-salam, A. V Ikudayisi-ugbe & F. A. Ugbe, "Adsorption studies of acid dye – Eosin yellow on date palm seeds , goethite and their composite", Chem. Data Collect. **31** (2021) 1, https://doi.org/10.1016/j.cdc.2020.100626.

[5] J. P. Lima, G. Alvarenga, A. C. F. Goszczynski, G. R. Rosa & T. J. Lopes, "Batch adsorption of methylene blue dye using Enterolobium contortisiliquum as bioadsorbent: experimental, mathematical modeling and simulation", J. Ind. Eng. Chem. **91** (2020) 362, https://doi.org/10.1016/j.jiec.2020.08.029.

[6] A. Mittal, D. Jhare & J. Mittal, "Adsorption of hazardous dye Eosin yellow from aqueous solution onto waste material de – Oiled S=soya: isotherm, kinetics and bulk removal", J. Mol. Liq. 179**179** (2013) 133, https://doi.org/10.1016/j.molliq.2012.11.032.

[7] F. A. Ugbe, P. O. Anebi & V. A. Ikudayisi, "Biosorption of an anionic dye ,Eosin yellow onto pineapple peels : Isotherm and Thermodynamic Study", Int. Ann. Sci. **4** (2018) 14, https://doi.org/https://doi.org/10.21467/ias.4.1.14-19 RESEARCH.

[8] M. Hasanzadeh, A. Simchi & H. Shahriyari, "Nanoporous composites of activated carbon-metal organic frameworks for organic dye adsorption : Synthesis, adsorption mechanism and kinetics studies", J. Ind. Eng. Chem. **81** (2020) 405, https://doi.org/10.1016/j.jiec.2019.09.031.

[9] M. Wang, S. Day, Z. Wu, X. Wan, X. Ye & B. Cheng, "A new type of porous Zn (II) metal-organic gel designed for effective adsorption to methyl orange dye", Colloids Surfaces A Physicochem. Eng. Asp. **628** (2021) 127335, https://doi.org/doi.org/10.1016/j.colsurfa.2021.127335.

[10] S. Yadav, A. Asthana, R. Chakraborty & B. Jain, "Cationic dye removal using novel magnetic / activated charcoal / β - cyclodextrin / alginate polymer nanocomposite", Nanomaterials **10** (2020) 1, https://doi.org/10.3390/nano10010170.

[11] S. Sadaf, H.N. Bhatti, S. Ali & K. Rehman, "Removal of Indosol Turquoise FBL dye from aqueous solution by bagasse , a low cost agricultural waste : batch and column study", Desalin. Water Treat. (2013) 1, https://doi.org/10.1080/19443994.2013.780985.

[12] F. Ghorbani & S. Kamari, "Application of response surface methodology for optimization of methyl orange adsorption by Fe-grafting sugar beet bagasse", Adsorpt. Sci. Technol. **0** (2016) 1, https://doi.org/10.1177/0263617416675625.

[13] X. Peng, G. Yang, Y. Shi, Y. Zhou, M. Zhang & S. Li, "Box – Behnken design based statistical modeling for the extraction and physicochemical properties of pectin from sunflower heads and the comparison with commercial low-methoxyl pectin", Sci. Rep. **10** (2020) 1, https://doi.org/10.1038/s41598-020-60339-1.

[14] M. Azmier, N. Azreen, A. Puad & O. Solomon, "Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by microwave-induced KOH activation", Water Resour. Ind. **6** (2014) 18, https://doi.org/10.1016/j.wri.2014.06.002.

[15] R. Rajendran, S. Vignesh, A. Sasireka & S. Suganthi, "Designing Ag2O modified g-C3N4 / TiO2 ternary nanocomposites for photocatalytic organic pollutants degradation performance under visible light : synergistic mechanism insight", Colloids Surfaces A Physicochem. Eng. Asp. **629** (2021) 127472, https://doi.org/10.1016/j.colsurfa.2021.127472.

[16] C. Orha, C. Lazau, D. Ursu & F. Manea, "Effect of TiO2 loading on powder-activated carbon in advanced drinking-water treatment", Water Soc. IV. **216** (2017) 203, https://doi.org/10.2495/WS170191.

[17] Z. Azhar, R. M. Ramli & Y. H. Noorfidza, "Photodegradation of 1-Butyl-3-methylimidazolium chloride [Bmim] Cl via synergistic effect of adsorption – photodegradation of Fe-TiO2/AC", Technologies **5** (2017) 1, https://doi.org/10.3390/technologies5040082.

[18] A. Rezaee, G. H. Pourtaghi, A. Khavanin, R. S. Mamoory, M. T. Ghaneian & H. Godini, "Photocatalytic decomposition of gaseous toluene by TiO2 nanoparticles coated on activated carbon", Iran. J. Environ. Heal. Sci. Eng. **5** (2008) 305.

[19] A. S. Nasir & V. I. Abiola, "Preparation and characterization of synthesized goethite and goethite-date palm seeds charcoal composite", Ife J. Sci. **19** (2017) 99, https://doi.org/https://dx.doi.org/10.4314/ijs.v19i1.10 Ife.

[20] Z. Anfar, H. Ait Ahsaine, M. Zbair, A. Amedlous, A. Ait El Fakir, A. Jada & N. El Alem, "Recent trends on numerical investigations of response surface methodology for pollutants adsorption onto activated carbon materials: A review", Crit. Rev. Environ. Sci. Technol. **50** (2020) 1043, https://doi.org/10.1080/10643389.2019.1642835.

[21] O. S. Bello, T. A. Fatona, F. S. Falaye, O. M. Osuolale & V. O. Njoku, "Adsorption of Eosin dye from aqueous solution using groundnut hull-based activated carbon: kinetic, equilibrium, and thermodynamic studies", Environ. Eng. Sci. **29** (2012) 186, https://doi.org/10.1089/ees.2010.0385.

[22] D. Kibanova, M. Trejo, H. Destaillats & J. Cervini-silva, "Applied clay science synthesis of hectorite – TiO2 and kaolinite – TiO2 nanocomposites with photocatalytic activity for the degradation of model air pollutants", Appl. Clay Sci. **42** (2009) 563, https://doi.org/10.1016/j.clay.2008.03.009.

[23] A. Zawawi, R. M. Ramli & N. Y. Harunl, "Synergistic effect of adsorption-photodegradation of composite TiO2/AC for degradation of 1-butyl-3-methylimidazolium chloride", Malaysian J. Anal. Sci. **22** (2018) 648, https://doi.org/https://doi.org/10.17576/mjas-2018-2204-11.

[24] S. A. Adesokan, A. A. Giwa & I. A. Bello, "Removal of trimethoprim from water using carbonized wood waste as adsorbents", J. Niger. Soc. Phys. Sci. **3** (2021) 344, https://doi.org/10.46481/jnsps.2021.320.

[25] K. O. Sodeinde, S. O. Olusanya, D. U. Momodu, V. F. Enogheghase & O. S. Lawal, "Waste glass: an excellent adsorbent for crystal violet dye, Pb2+ and Cd2+ heavy metal ions decontamination from wastewater", J. Niger. Soc. Phys. Sci. **3** (2021) 414, https://doi.org/10.46481/jnsps.2021.261.

[26] R. Elmoubarki, M. Taoufik, A. Moufti, H. Tounsadi & F. Z. Mahjoubi, "Box-Behnken experimental design for the optimization of methylene blue adsorption onto aleppo pine cones", J. Mater. Environ. Sci. **8** (2017) 2184, http://www.jmaterenvironsci.com/%0ABox-Behnken.

[27] S. O. Azeez & F. A. Adekola, "Sorption of 4-nitroaniline on activated kaolinitic clay and jatropha curcas activated carbon in aqueous solution", Jordan J. Chem. **11** (2016) 128.

[28] S. O. Azeez & F. A. Adekola, "Kinetics and thermodynamics of sorption of 4-nitrophenol on activated kaolinitic clay and jatropha curcas activated carbon from queous solution", Pak. J. Anal. Environ. Chem. **17** (2016) 93, https://doi.org/10.21743/pjaec/2016.06.014.

[29] S. O. Azeez, I. O. Saheed, F. A. Adekola, A. A. Jimoh, D. M. Aransiola & Z. A. Abdulsalam, "Box behnken design in the optimization of rhodamine B adsorption onto activated carbon pprepared from delonix regia seeds and pods", J. Turkish Chem. Soc. Sect. A Chem. **9** (2022) 205, https://doi.org/10.18596/jotcsa.893472.

[30] E. Ben Khalifa, B. Rzig, R. Chakroun, H. Nouagui & B. Hamrouni, "Application of response surface methodology for chromium removal by adsorption on low-cost biosorbent", Chemom. Intell. Lab. Syst. **189** (2019) 18, https://doi.org/10.1016/j.chemolab.2019.03.014.

[31] K. M. Oghenejoboh, "Biosorption of nickel (II) ion from synthetic wastewater on watermelon rind activated carbon using reponse surface methodology (RSM) optimization approach", Niger. J. Technol. **37** (2018) 647, https://doi.org/10.4314/njt.v37i3.13.

[32] Z. S. Alman-Abad, H. Pirkharrati & F. Asadzadeh, M. Maleki-Kakelar, "Application of response surface methodology for optimization of zinc elimination from a polluted soil using tartaric acid", Adsorpt. Sci. Technol. **38** (2020) 79, https://doi.org/10.1177/0263617420916592.

[33] F. Ghorbani & S. Kamari, "Application of response surface methodology for optimization of methyl orange adsorption by Fe-grafting sugar beet bagasse", Adsorpt. Sci. Technol. **35** (2017) 317, https://doi.org/10.1177/0263617416675625.

[34] D. Allouss, Y. Essamlali, O. Amadine, A. Chakir & M. Zahouily, "Response surface methodology for optimization of methylene blue adsorption onto carboxymethyl cellulose-based hydrogel beads: Adsorption kinetics, isotherm, thermodynamics and reusability studies", RSC Adv. **9** (2019) 3785, https://doi.org/10.1039/c9ra06450h.

[35] N. Rahman & M. Nasir, "Application of Box–Behnken design and desirability function in the optimization of Cd(II) removal from aqueous solution using poly(o-phenylenediamine)/hydrous zirconium oxide composite: equilibrium modeling, kinetic and thermodynamic studies", Environ. Sci. Pollut. Res. **25** (2018) 26114, https://doi.org/10.1007/s11356-018-2566-1.

[36] C. Okoye & D. Chime, "Removal of Eosin yellow dye from aqueous solution using oil bean seed shells based activated carbons: Equilibrium, Kinetics and thermodynamics studies", Int. J. Sci. Eng. Res. **9** (2018) 140, http://www.ijser.org.

[37] E. O. Oyelude, J. A. M. Awudza & S. K. Twumasi, "Equilibrium, kinetic and thermodynamic study of removal of Eosin yellow from aqueous solution using teak leaf litter powder", Sci. Rep. **7** (2017) 1, https://doi.org/10.1038/s41598-017-12424-1.

[38] R. Ansari & Z. Mosayebzadeh, "Removal of Eosin Y, an Anionic dye, from aqueous solutions using conducting electroactive polymers", Iran. Polym. Journa. **19** (2010) 541,. http://journal.ippi.ac.ir.

[39] F. Bandari, F. Safa & S. Shariati, "Application of response surface method for optimization of adsorptive removal of eriochrome black T using magnetic multi-wall carbon nanotube nanocomposite", Arab J Sci Eng. **40** (2015) 3363, https://doi.org/10.1007/s13369-015-1785-8.