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Valorization of walnut husks as a natural coagulant for optimized water decolorization

Ali Zourif [*], Asmaa Benbiyi [**], Salma Kouniba, Mohamed EL Guendouzi

Laboratory of Physical-Chemistry, Materials and Catalysis, Faculty of Sciences Ben M'Sik, Hassan II, University of Casablanca, Morocco

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A B S T R A C T

Coagulation-flocculation is an essential wastewater treatment and decolorization process. This study investigates walnut husks, an abundant agricultural waste, as a biocoagulant. The aim is to evaluate the coagulation efficacy of walnut husk powder (WHP) for removing methylene blue (MB) and turbidity (TUR) from water. WHP was prepared and characterized using Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM-EDX), and X-ray fluorescence spectrometry (XRF) techniques. Jar tests were conducted in varying doses, granulation, and the initial pH. Box Behnken Design based on the response surface method (BBD-RSM). Predicted MB and TUR eliminations matched experimental values. Under optimal conditions at pH 9, 89.48 % MB and 96.59 % TUR removal were attained at 900 mg. L^{-1} and 1000 mg. L^{-1} doses. Results prove that WHP shows promise as an efficient biocoagulant for the removal of dyes and turbidity from wastewater.

1. Introduction

Each year, more than seven million tons of dye are produced worldwide. Various industries use these dyes, including paper, plastics, food, and cosmetics; the most important is the textile industry (Afkhami and Moosavi, 2010). Color is the primary contaminant recognized in wastewater. A quantity contaminated with these dyes, even at low concentrations, leads to a potential risk to human health and the ecosystem, as the colored effluents would interfere with photosynthesis (Gita et al., 2017). The byproducts of the degradation of these dyes also have a dangerous impact on the environment as they contain toxic aromatic amino compounds (Konstantinou and Albanis, 2004). Among these dyes, methylene blue (MB) is the industry's most classical and widely used dye (Domga et al., 2022). It is a basic dye used in mouthwash to reduce the viral load in the mouth and is a component of sunscreens (Arakeri and Rao US, 2021). It is also applied to colored textile products such as silk, linen, cotton, wool, and jute (Khan et al., 2022). MB is highly toxic and poses several health risks to humans upon exposure, including nausea, vomiting, eye injuries, and the development of methemoglobinemia (Khomri et al., 2022).

Therefore, it is important to develop innovative, low-cost processes by which dye molecules treated. Many techniques have recently been employed to remove hazardous dyes from industrial effluents to mitigate damage to the aquatic environment and improve the quality of discharged water, such as electrochemical and biological treatments (Qu and Liang, 2022) (Khalil and Liu, 2021), solvent extraction (Zhang et al., 2022), oxidation (Hodges et al., 2018), adsorption (Rashid et al., 2021), and coagulation-flocculation (Zhao et al., 2021; Benbiyi et al., 2022). However, the coagulation-flocculation technique is the most preferred method of wastewater treatment (Teh et al., 2016), due to its simplicity, rapidity, high efficiency, and availability of coagulants-flocculants (Zhang et al., 2018a, 2018b). The most common coagulants-flocculants used in the treatment of industrial effluents are aluminum sulfate (Zhou et al., 2008), ferric chloride (Farajnezhad and Gharbani, 2012), polyacrylamide (PAM) (Huang et al., 2016), and poly aluminum chloride (PAC) (Zhang et al., 2018a, 2018b). These coagulant-flocculants give a very interesting yield that can remove up to 100 % of a pollutant.

Despite the advantages of these last compounds, they present several disadvantages that limit their use such as toxicity, high costs, and the fact that they generate a lot of sludge (Verma et al., 2012). Biocoagulants-flocculants represent a significant advance in wastewater treatment, offering innovative solutions to the drawbacks associated with traditional chemical coagulants and flocculants. These substances

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[*] Corresponding author.

[**] Corresponding author.

E-mail addresses: zourifali@gmail.com (A. Zourif), a.benbiyi@gmail.com (A. Benbiyi).

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are mainly derived from agricultural waste. Agricultural waste used as biocoagulants and flocculants often comes from renewable natural sources, such as fruit, vegetables, and plants. In this context, materials such as banana peels (Priyatharishini et al., 2019), Moringa oleifera pits (Landázuri et al., 2018), cassava peels (Mohd-Asharuddin et al. 2018), and Aloe vera (Benalia et al., 2022) are particularly valuable. These materials are generally considered to be by-products or waste products of the agricultural industry, which makes them abundantly available and inexpensive.

The efficiency of pollutant removal is strongly influenced by the active components of these biocoagulants. These active substances are responsible for coagulation, for example, cellulose, lignin, proteins, tannins, polyphenols, polysaccharides, and starches (Kurniawan et al., 2022). It is worth noting that these biocoagulants can be used directly in their natural (Mohd-Asharuddin et al. 2018) form or through the extraction of their active compounds for example, extraction of tannins from Acacia catechu bark (Azreen et al., 2021).

Currently, Morocco ranks twentieth in the world for the production of walnuts (Juglans regia L), with 7702 ha and more than 12,467 tons of nuts annually (Houmanat et al., 2021). Walnut husks are fruit wastes that disposed of after consumption in uncontrolled landfills. Nevertheless, they have proven an excellent capacity in the removal of heavy metal ions (Pehlivan and Altun, 2008), organic compounds (Gallo-Cordova et al., 2017), and dyes (Miyah et al., 2018) in the treatment of polluted water.

While walnut husks have demonstrated promising adsorption capacity for removing various pollutants, their potential as a coagulating agent has not yet been explored to date. However, given their composition rich in tannins and polyphenols (Kabiri et al. 2019), walnut husks are likely to exhibit similar coagulation properties as other natural biomaterials such as Moringa oleifera. The functional groups present on their surface could destabilize charged colloids through charge neutralization and inter-particle bridging. Moreover, walnut husks represent an abundant bio-sourced waste material in Morocco (Houmanat et al., 2021). Their valorization as a natural, eco-responsible coagulant for water treatment would enable more sustainable management of this bioresource. For these reasons, we have undertaken to evaluate for the first time the coagulation potential of walnut husks, thereby opening up new possibilities for this promising agent.

The main objective of this research project is to investigate the effectiveness of WHP in removing pollutants from contaminated water using the coagulation-flocculation process. To accomplish this goal, WHP powder was prepared and characterized using various analytical techniques, including FTIR, XRD, and XRF. In order to determine the optimal conditions for pollutant removal, the study employed the Box-Behnken design and Response Surface Methodology (BBD-RSM). Specifically, the effects of several parameters (dose, granulation, and initial pH) and their interactions examined concerning the removal of two specific pollutants, namely MB and TUR. The results of this study could provide valuable insights into the use of WHP as a coagulant or flocculant in the treatment of polluted water. By identifying the optimal conditions for pollutant removal, this research could help to improve the efficiency of the coagulation-flocculation process and contribute to the development of more effective, sustainable, and cost-effective solutions for the treatment of polluted waters.

2. Materials and methods

2.1. Reagents

MB is also known as base blue 9 (CAS number 61-73-4, chemical formula $C_{16}H_{18}ClN_3S$, molecular weight 319.9 g. mol^{-1} and $\lambda_{max} = 662$ nm) was used as a dye. Hydrochloric acid (HCl) (Sigma-Aldrich 37 %, CAS number 7647-01-0) and Sodium hydroxide (NaOH) (Solvachim 99 %, CAS number 1310-73-2) are used to adjust the initial pH of the pollutant solution.

2.2. Preparation and characterization of biocoagulant WHP

Walnut husks were collected from a local region near Ouarzazate (Skoura 31° 4′ 2″ N, 6° 33′ 55″ W), Morocco. They were selected as a natural coagulant due to their demonstrated effectiveness, economic feasibility, and abundant availability. The Walnut husks were thoroughly washed with distilled water to eliminate dirt, dust, and other surface contaminants. After cleaning, the Walnut husks were crushed using a mill, the powder was washed with distilled water and dried at 105 °C (Arulmathi et al., 2019). The powder obtained was then sieved through sieves with fractions between 112 and 63 μm. The obtained powder was stored in a dry place to avoid any possible alteration.

Different techniques were used to evaluate the WHP before and after the coagulation process. The mineralogy of WHP was undertaken by a Burker D8 ADVANCE X-ray diffractometer with a Cu $\lambda(CuK_\alpha) = 1.5418$ Å anticathode, the data were recorded by Xpert software. FT-IR spectra were obtained using a Bruker Tensor 27 FTIR spectrometer operating in the 4000–400 cm^{-1} range. Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) analysis of WHP was performed by Hirox microscopy to determine the morphology and elements present in the powder before and after coagulation. The chemical composition of WHP was determined by XRF using an epsilon 4 X-ray fluorescence spectrometer (Malvern Panalytical Company).

2.3. Experimental procedure

A precisely dosed amount of dye was dissolved in distilled water to prepare the mother solution. The solution (50 mg. L^{-1}) was prepared by diluting the mother solution with distilled water. A turbid water solution at a concentration of 2.5 g. L^{-1} was prepared by stirring kaolin in distilled water at 50 Rpm for 2 h. After stirring, the solution was allowed to stand for 24 h for complete hydration of the kaolin.

WHP was added to colored or turbid water samples in doses of 300, 700, and 1000 mg. L^{-1} defined by the experimental design. The initial pH of each solution was adjusted using 0.1 M HCl and NaOH before testing. The solutions underwent rapid mixing by jar test (VELP Scientifica JLT 4 Flocculator) at 300 Rpm for 3 min, followed by slow agitation at 60 Rpm for 20 min. Flocculation was then allowed by sedimentation for one hour. The clarified supernatant was collected and analyzed. Settled particles (sludge) were also recovered by filtration for analysis.

2.4. Pollutants reduction percentage calculation

The percentage removal of MB after coagulant treatment was calculated using Equation (Eq.1) using the UV- 6300 PC and the percentage removal of TUR is determined by Equation (Eq.2) using a VELP turbidimeter:

$$\text{Pollutant removal }(\%) = \frac{Ci - Cf}{Ci} \times 100 \tag{1}$$

$$\text{Turbidity removal }(\%) = \frac{To - Tf}{To} \times 100 \tag{2}$$

where:

C_i: Initial reading of parameter before treatment.
C_f: Final reading of parameter after treatment.
T_o: Initial turbidity value.
T_f: Final turbidity value at each measurement point.

2.5. Box-Benhken design (BBD)

The traditional method uses single-factor experiments by changing one variable at a time. However, this method makes it difficult to study the optimization effect between variables (Ölmez, 2009). Therefore, the BBD-RSM was used to improve the study. RSM is a set of techniques that relate experimental factors to responses according to one or more criteria (Amini et al., 2008).

The advantages of the Box Behnken planes include that they are all spherical and only require the use of three factors. These planes are also rotatable and provide orthogonal locking (Watson et al., 2015). This design is not fully functional but provides minimal effort and accurate results. This optimization process consists of three steps. First is performing an ANOVA, which is a statistical technique that decomposes the total variance of a data set into fractions associated with specific sources of variance to test hypotheses about the model parameters. The second is estimating the coefficient of the mathematical model. The third is predicting the response and verification of the model fit (Ferreira et al., 2007).

The performance of the coagulation-flocculation process can depend on several parameters. The factors at three levels were varied to study the optimization of biocoagulation-flocculation parameters, such as dose (X_1), initial pH (X_2), and granulation (X_3). The choice of these factors is not arbitrary and depends on the specific application and the type of pollutants present in the water. Two types of pollutants are MB and TUR, and they are influenced by the dose of the coagulant, the initial pH, and the granulation of the coagulant.

It is important to note that there is a range of optimal doses for each coagulant employed. If the dose is too low, particles will not be removed effectively, while if it is too high, the water may become excessively cloudy and may also be toxic. Therefore, the dose optimal of the coagulant used plays a critical role in the effectiveness of the process. The charge and structure of different polymeric coagulants change as a function of the pH because their functional groups accept protons or dissociate, depending on the pH value, such as organic coagulants (chitosan, banana peels, Moringa oleifera) or synthetic coagulants based on polyacrylamide. Therefore, the initial pH is a very influential factor in the coagulation-flocculation process (Naceradska et al., 2019). The granulation or size distribution of coagulants had a distinct influence on the mechanism of the coagulation-flocculation process. Nanoparticles cause self-aggregation due to Brownian motion, while microparticles are affected mainly by two physical processes, interception and sedimentation, because they are more stable and disperse easily (Sun et al., 2019).

The quadratic equation (Eq.3) explains the performance of the system:

$$Y = \beta o + \sum_{i=1}^{k} \beta_i xi + \sum_{i=1}^{k} \beta_{ii} xi^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij}\, xixj + \varepsilon \tag{3}$$

Y is the process response, k is the number of patterns, i and j are the index numbers for the pattern, βo is the free term, x_1, x_2…, x_k are the independent variables, β_i is the first order effect, β_{ii} is the quadratic effect, β_{ij} is the interaction effect, and ε is the random error between the predicted and experimental values.

3. Results and discussion

3.1. Characterization of biocoagulant

The XRD pattern of the WHP shows a semi-crystalline structure in Fig. 1. The amorphous region can be attributed to the lignin content of the biomass, and the crystalline peaks can be attributed to the cellulose fraction (Okolo et al., 2021). Moreover, it indicates that there is no significant change in the semi-crystalline structure of the WHP after coagulation of the MB dye. Therefore, the crystallinity is not affected by the dye molecule (Basu et al., 2017). The following bands are observed in the FTIR spectrum (Fig. 2), a strong band at 3400 cm^{-1} which is attributed to the O—H group; a clear band at 2935 cm^{-1} is attributed to the C—H stretching (Mashkoor et al., 2018); two bands at 1737 cm^{-1} and 1615 cm^{-1} correspond to the carbonyl groups (—COOH, —$COOCH_3$) of the carboxylic acid, a small band at 1396 cm^{-1} is assigned to OH bending; 1046 cm^{-1} is attributed to the C—O stretching of cellulose; the significant band at 609 cm^{-1} belongs to the yellow pigment of the nut husks (Uddin and Nasar, 2020).

During the flocculation coagulation process, different functional groups are involved, which is demonstrated by the changes in intensity and position of the peaks in the WHP after the process. Fig. 2 shows a shift in peaks after flocculation coagulation, indicating the involvement of different functional groups in the process. Specifically, the involvement of alcoholic and carboxylic groups that have negative centers is

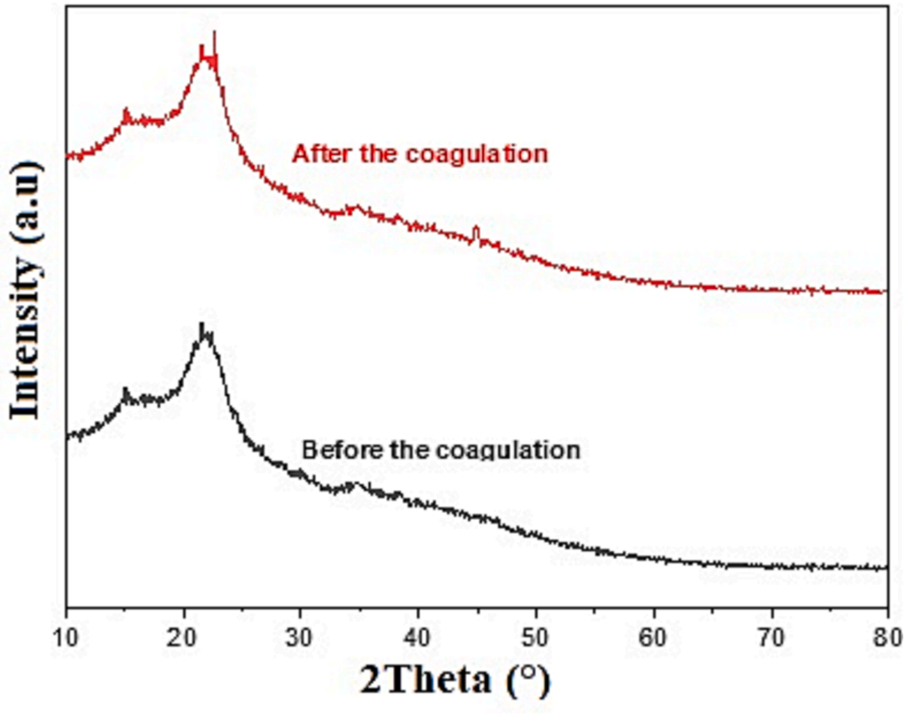

Fig. 1. XRD pattern of WHP before and after the coagulation.

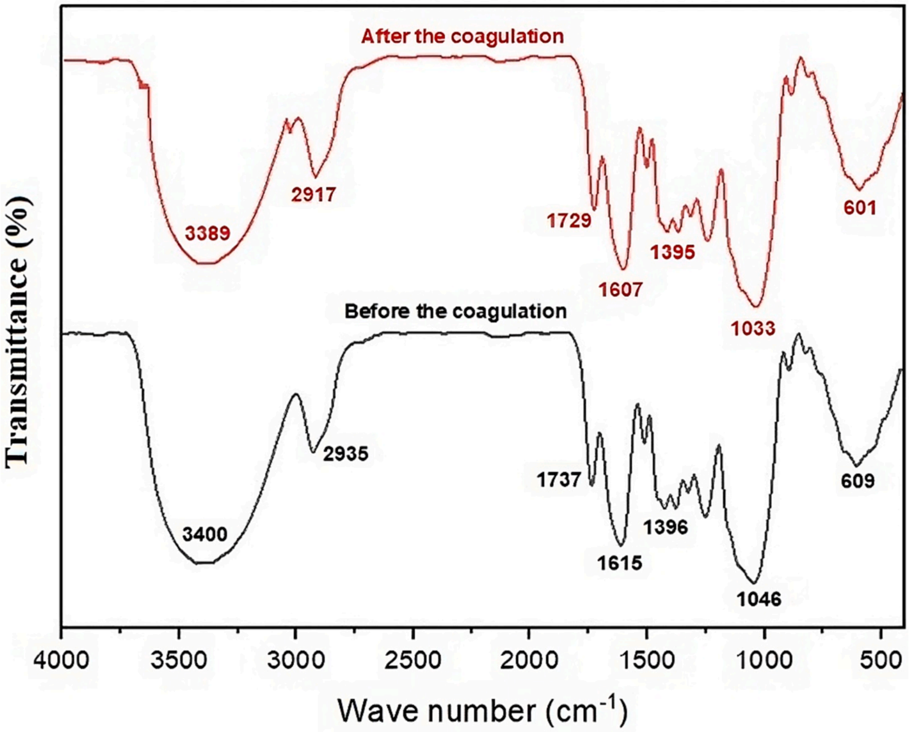

Fig. 2. FTIR of WHP before and after the coagulation.

evident in the coagulation-flocculation of MB by WHP. These functional groups have strong attractive forces with the positive centers of the MB dye, which are cationic. Therefore, they play an active role in the process, resulting in a shift in the peaks observed in WHP. Overall, the changes in the WHP peaks provide valuable insights into the involvement of different functional groups during flocculation coagulation, which can help optimize the process for the efficient removal of cationic dyes from wastewater.

SEM showed that the powder consists of small particles with sizes of about 20 µm and a homogeneous texture. The particles have different shapes and are distant from each other (Fig. 3). EDX analysis of the WHP before and after coagulation-flocculation was performed to judge the adhesion of MB molecules to the coagulant. The EDX results presented in Table 1 show that the percentage of Ca, Fe, Al, and Si elements present in the WHP decreases after coagulation-flocculation therefore, it is suggested that these elements have the power to destabilize the polluted water. Changes in the weight of C and O atoms were also observed, and clearly due to the adsorption of the dye molecule (Mashkoor et al., 2018). Chemical analysis by XRF showed that the WHP contains mainly

Table 1
Elemental composition of WHP before and after the coagulation.

Element	Weight (%) before	Weight (%) After
C	66.15	68.85
O	27.63	28.03
Ca	2.65	1.44
Fe	1.54	0.58
Al	0.93	0.31
Si	0.48	0.30
K	0.42	0.27
Mg	0.10	0.06
S	0.10	0.06

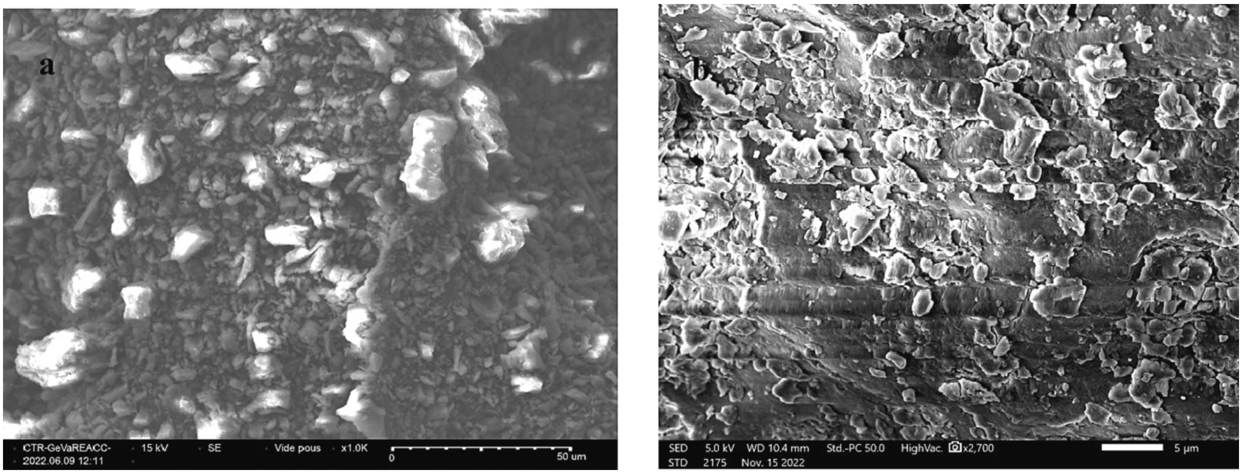

Fig. 3. SEM of WHP before (a) and after (b) the coagulation.

organic matter (88.348 wt%), with a high content of CaO (5.653 wt%) and Fe_2O_3 (2.523 wt%) and the other minerals are trace elements (Table 2). This analysis confirms and coheres well with the EDX analysis.

3.2. BBD-RSM statistical analysis

WHP was used as a coagulant for MB and TUR polluted water. Each experiment was repeated three times to observe reproducibility, and the result was subjected to a three-step process. Table 3 gives the experimental range and levels of the independent variables in this study. The independent variables were coded as −1 (low), 0 (medium), and +1 (high).

Table 4 shows the experimental results of the two responses and the predicted results by the JMP Pro 16 software using the BBD-RSM.

The relationship between the observed values of MB and TUR removal and the values predicted by the fitted regression models (Fig. 4) shows that the clustering of points around the diagonal line indicates a good correlation between the values obtained in the experiment and the values predicted by the models (Sharma and Simsek, 2020).

3.2.1. Analysis of variance (ANOVA)

The results of the ANOVA for each MB and TUR removal are presented in Table 5. A large F-value indicates that most of the response changes can be explained by the regression equation. The associated probability value (P-value) is used to estimate whether the F-value is large enough to indicate statistical significance. A P-value $>$ F-value, less than 0.05 indicates that the model is considered statistically significant (Kumar et al., 2007). This means that at least one term in the regression equation is closely related to the response variable. The model chosen to explain the relationship between the factors and the responses is valid (Ravikumar et al., 2006).

The ANOVA showed a linear relationship between the main effects, quadratic effects, and interaction effects of inputs on the removal of MB (Y_1; Eq.4) and TUR (Y_2; Eq.5):

$$Y_1 = 113.2501 - 0.0819X_1 - 9.0001X_2 + 4.1963X_1X_2 \tag{4}$$

$$Y_2 = 72.8310 + 0.0317X_1 + 0.3836X_3 - 2.53\text{x}10^{-4}X_1X_3 \tag{5}$$

ANOVA was used to quantify the significance of the developed model based on the P-value and corresponding F-value. When WHP was used as a coagulant, the F-value statistical values for MB and TUR were 7.2922 and 15.9609 in Table 5, respectively. The low probability value (P model < 0.05) proves this model is significant. The high F-value and lack of significant fit indicate that the experimental data obtained have a good fit with the model. The R^2 values obtained for MB and TUR were 0.9292 and 0.9663, respectively. The correlation coefficient (R^2) value obtained was very high and much closer to 1, indicating a good fit for the statistical model (Henseler and Sarstedt, 2013).

3.2.2. Response surface plots

Fig. 5 shows the three-dimensional response surface plot of MB removal with the interactive effect of X_1 coagulant dose, X_2 pH of the initial solution, and X_3 coagulant granulation set to the central code (0) 80 μm. While the TUR with the interactive effect of X_1 the coagulant dose, X_3 the coagulant granulation (μm), and X_2 pH of the initial solution that was set to the central code (0) 6. The elliptical shape of the three-dimensional surface curves shows a good interaction between the two variables. The three-dimensional surface curves provide an accurate geometric representation and give the appropriate statistics, such as the optimal range for different values of the test variables within the experimental design (Nair et al., 2014).

Table 3
BBD-RSM code matrix.

Independent variables	Factor Code	Range and levels		
		−1	0	+1
Dose (mg. L^{-1})	X_1	300	700	1000
initial pH	X_2	3	6	9
Granulation (μm)	X_3	63	80	112

Table 4
Experimental and predicted values of MB, and TUR removal.

N°	Factors			Experimental values		Predicted values	
	X_1	X_2	X_3	MB removal % (Y_1)	TUR removal % (Y_2)	MB removal % (Y'_1)	TUR removal % (Y'_2)
1	300	3	80	83.17	85.08	79.92	85.52
2	300	9	80	76.06	86.07	75.92	86.72
3	1000	3	80	76.93	90.96	76.54	90.27
4	1000	9	80	95.88	92.36	99.65	91.94
5	300	6	63	76.07	89.13	77.42	88.87
6	300	6	112	75.46	86.12	77.72	86.61
7	1000	6	63	92.05	92.83	88.66	92.25
8	1000	6	112	89.93	84.16	89.68	84.49
9	700	3	63	74.73	85.87	77.80	85.49
10	700	3	112	87.01	92.29	85.95	93.48
11	700	9	63	74.83	86.18	75.13	85.44
12	700	9	112	91.46	84.84	89.12	84.75
13	700	6	80	74.56	89.31	75.01	89.39
14	700	6	80	74.70	89.47	75.01	89.39
15	700	6	80	75.80	89.42	75.01	89.39

WHP showed a maximum MB removal of 99.59 % under the basic condition of initial pH 9 with a dose of 900 mg. L^{-1} and granulation of 112 μm. Fig. 6 shows that pH has a critical role in color removal as it strongly influences the solubility and hydrolysis of dyes (Dao et al., 2016).

The combined effect of the dose and initial pH of the solution of the coagulation process on MB removal is shown in the same figure. It was observed that the percentage of dye removal increases with the dose but decreases with the increase in the initial pH of the solution. This means that higher values of dye removal can be obtained by simultaneously increasing the dose and keeping the pH of the initial solution in the range of 7–9. This is due to the decrease in charge density of the solution that changes with the initial solution pH (Arulmathi et al., 2019). It can be suggested that the mechanism of coagulation between MB and WHP is adsorption and charge neutralization. The binding between the adsorption sites of WHP and methylene blue (cationic) is chemical in nature, specifically an electrostatic interaction between the opposite charges. The adsorption sites of WHP are negatively charged because it is rich in alcoholic and carboxylic groups, while methylene blue is positively charged due to the presence of nitrogen atoms that have gained an electron. This electrostatic interaction attracts the methylene blue to the adsorption sites and keeps it bound to the WHP surface.

Particle destabilization and charge neutralization occur in coagulation due to the addition of positively charged ions of metal salt or polyelectrolyte. Fig. 7 shows the effects of the mutual interaction between pH and coagulant dose on TUR removal. After coagulation-flocculation, dissolved/suspended particulate matter can be

Table 2
Chemical composition of WHP (wt.%) before and after the coagulation.

Sample	MgO	Al_2O_3	SiO_2	Fe_2O_3	P_2O_5	CaO	K_2O	SO_3	Cr_2O_3	Traces
Before	0.240	0.176	0.576	2.523	0.390	5.653	1.332	0.139	0.186	0.438
After	0.015	0.094	0.277	0.894	0.357	2.789	1.007	0.084	0.180	0.431

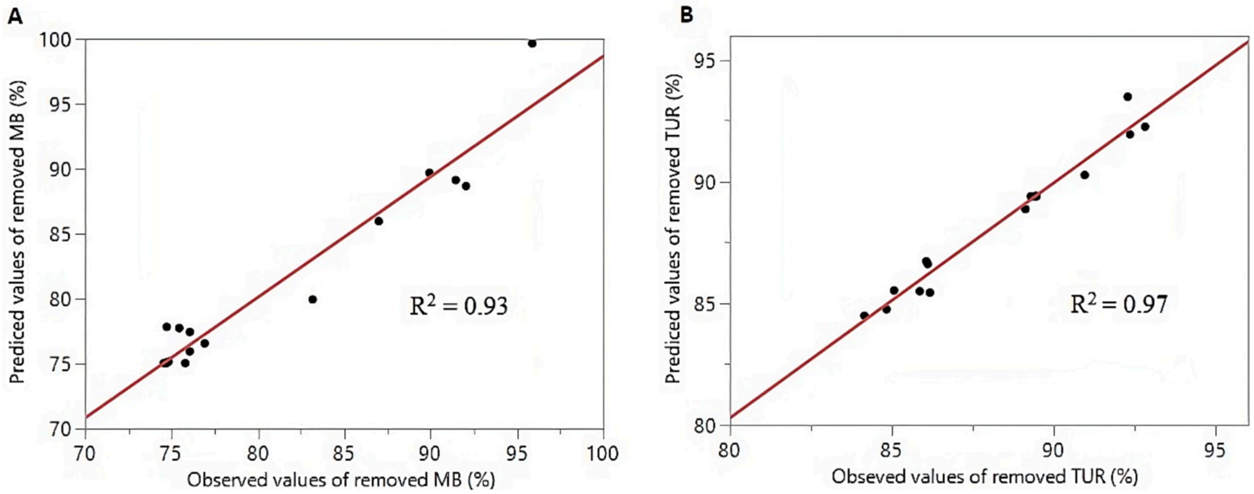

Fig. 4. MB and TUR values removed obtained experimentally versus predicted values by the models.

Table 5
ANOVA results for quadratic models of MB and TUR removal.

Source	MB removal		TUR removal	
	F-value	P-value	F-value	P-value
Model	7.2922	0.0207*	15.9609	0.0036*
X_1	2.1550	0.0070*	2.9720	0.0026*
X_2	1.9500	0.0123*	0.3680	0.4112
X_3	0.0340	0.9242	2.9720	0.0010*
X_1X_2	1.9500	0.0112*	0.0940	0.8051
X_1X_3	0.3700	0.4267	2.3430	0.0454*
X_2X_3	0.0360	0.9200	1.5630	0,0273
X_1^2	1.1220	0.0754	0.4250	0.3758
X_2^2	1.3000	0.0501	0.0270	0.9395
X_3^2	0.9640	0.1087	0.5790	0.2634
Lack of fit	43.0178	0.0228*	177.5109	0.0056*
R^2	0.9292	———	0.9663	———
Adjusted R^2	0.8178	———	0.9058	———

* Significant.

precipitated and removed by gravity, resulting in the formation of a clear supernatant liquid (due to the removal of dissolved matter, there will be considerable TUR removal) (Verma et al., 2010). From the experimental results, it is suggested that the elimination of TUR occurred by the neutralization of the particle load in the solution and that the mechanism of entrapment floc formation occurred when the coagulant was neutralized by the metal salts based mainly on iron and aluminum, as they showed their presence in EDX and XRF (Fig. 8). The WHP showed a maximum TUR removal of 95.31 % in the basic condition of pH 9, a dose of 1000 mg of coagulant, and granulation of 63 μm.

3.3. *Comparison with previous works*

The WHP biocaogulant achieved 99.59 % MB dye removal under optimal pellet conditions of 112 μm, initial pH of 9, and 1 g.L^{-1} using the BBD-RSM. The experiments under the optimum conditions were replicated three times to ensure data reliability (Table 6).

Biocoagulation-flocculation and bioadsorption are wastewater treatment processes that use waste to remove pollutants. Biocoagulation-flocculation consists of using waste (in its native form)

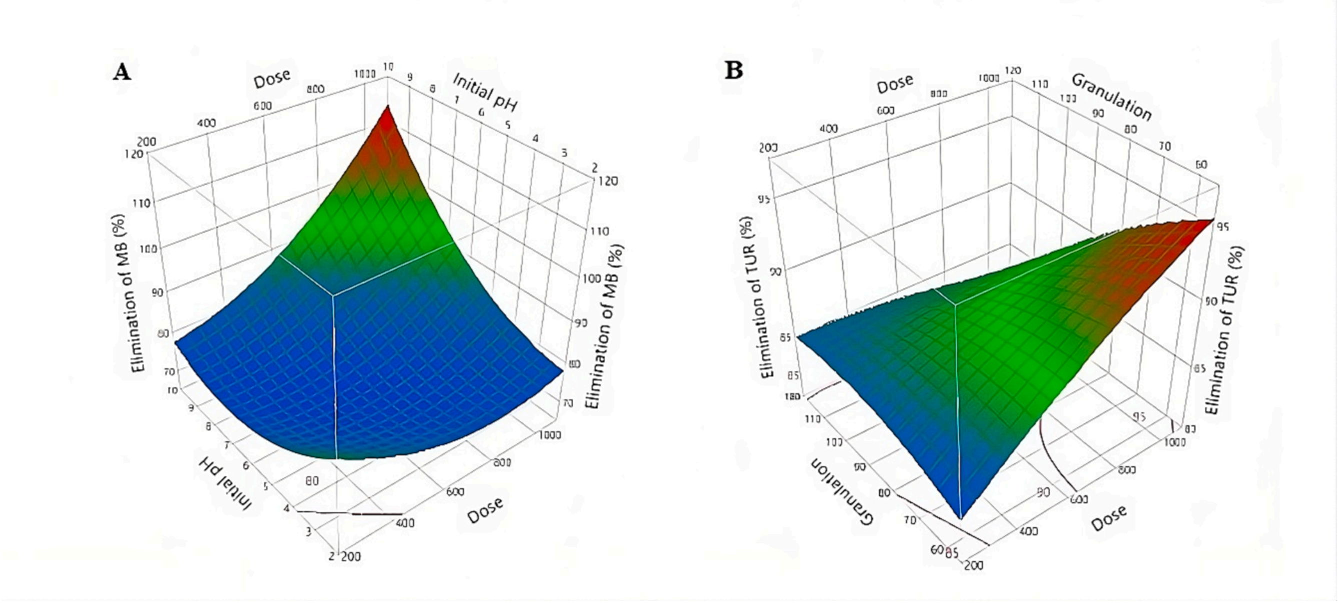

Fig. 5. Three-dimensional response surface plot of MB (A), and TUR (B) removal.

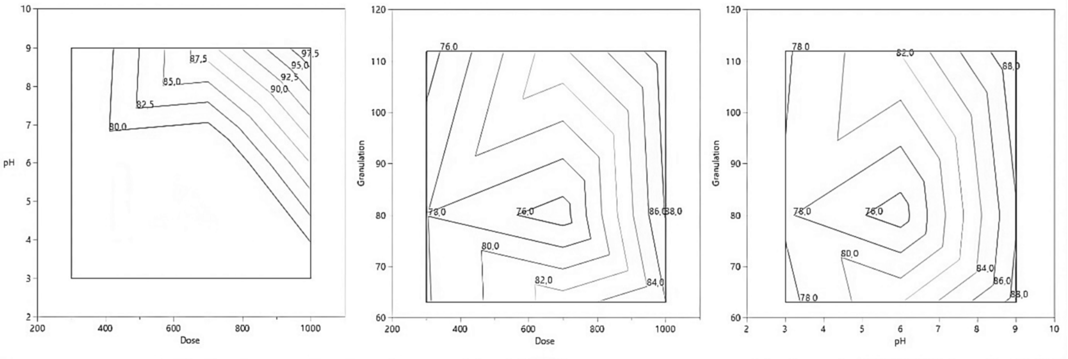

Fig. 6. The interaction between dose, initial pH, and granulation in the elimination of MB.

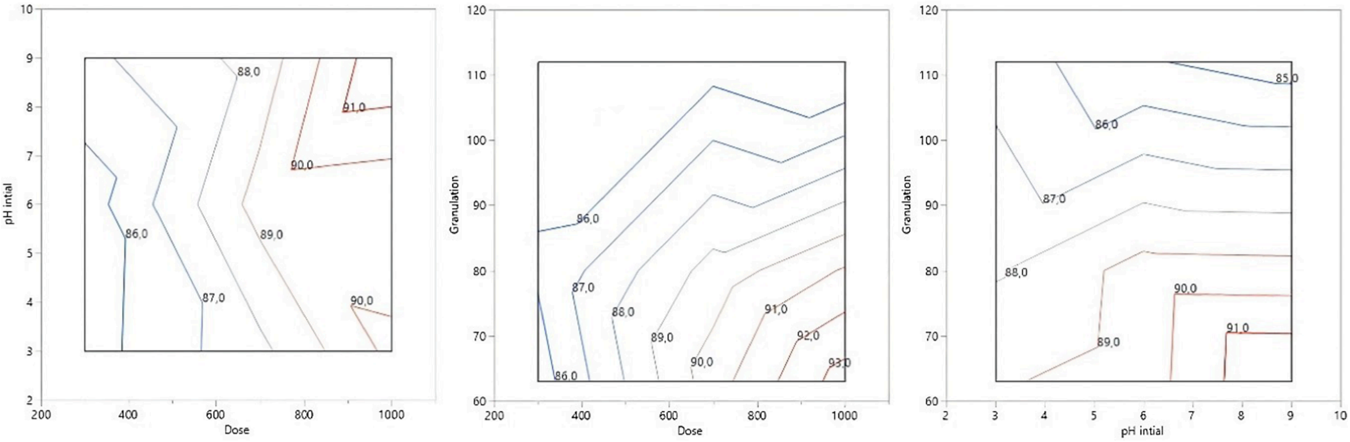

Fig. 7. The interaction between dose, initial pH, and granulation in the elimination of TUR.

to coagulate and flocculate particles in suspension in water, forming agglomerates that can be more easily separated. Bioadsorption uses waste (mainly transformed into carbon) to adsorb pollutants on its surface, thus retaining them in the treatment system. This results in a higher cost for the preparation of the adsorbents (Verma et al., 2012).

Table 7 summarizes some previous studies on MB removal with the processes of biocoagulation-flocculation and bioadsorption Various biomasses have been tested as bio-coagulants or bio-adsorbents for this dye. High removal efficiencies were achieved, for instance with laterite soils (99.61 %) or bentonite combined with Opuntia ficus-indica (98.25 %) in coagulation, and with cashew nut shells (99.97 %) or bamboo (99.67 %) in adsorption. Additionally, it can be noted that optimal MB removal via adsorption generally occurs at more acidic pH conditions, whereas alkaline conditions favor removal by coagulation-flocculation. This highlights the different mechanisms involved in these two processes.

Most of the studies did not use an experimental design in their work. However, the adoption of an experimental design allows for optimizing the process parameters, avoiding experimental errors, and determining the optimal conditions, which allows for maximizing the efficiency and profitability of the process. By comparing this result with other studies, we can deduce that WHP is very effective and competitive with existing natural adsorbents and coagulants.

4. Reuse of WHP

The reuse of WHP coagulant is of crucial importance in coagulation-flocculation processes because of its major role in wastewater clarification (Garvasis et al. 2020). Efforts to evaluate and improve the reuse of this coagulant are of paramount importance from the point of view of environmental sustainability (El Messaoudi et al. 2022). Studies have shown that WHP, as a coagulant, has a certain capacity to be recovered and reused in subsequent applications, thereby minimizing waste and the associated costs. The reuse of WHP is mainly dependent on factors such as the residual coagulant concentration in the treated effluent, one of the methods used to recover WHP involves simple filtration of the sludge after the coagulation-flocculation process, followed by a drying phase at 105 °C to facilitate its reuse under optimum conditions. This approach guarantees the recovery of the WHP, promoting resource efficiency without the use of chemicals. A visual representation, as shown in Fig. 9, illustrates the assessment of the WHP's suitability for reuse after undergoing five cycles. In particular, the results show that WHP can achieve commendable performance, with removal efficiencies of 35 % for MB and 56 % for TUR. It is imperative to recognize that the observed reduction in performance can be attributed to a variety of factors and merits further investigation.

5. Conclusion

This study explored the valorization of WHP as a biocoagulant via a coagulation-flocculation process. Optimal conditions for removing MB and TUR were determined using a BBD-RSM. The results demonstrated the effective elimination of both pollutants. Optimization revealed that MB removal efficiency depends primarily on dose (X_1) and initial pH (X_2), while TUR removal depends on dose (X_1) and granulation (X_3). Predicted optimal conditions were 99.59 % MB removal with X_1 at 900 mg. L^{-1}, X_2 at 9, and X_3 at 112 μm, and 95.12 % TUR removal with X_1 at 1 g.L^{-1}, X_2 at 9, and X_3 at 63 μm. IR, SEM, and XRF analyses suggested removal via adsorption and charge neutralization mechanisms. This study demonstrated the strong innovative potential of WHP as a natural

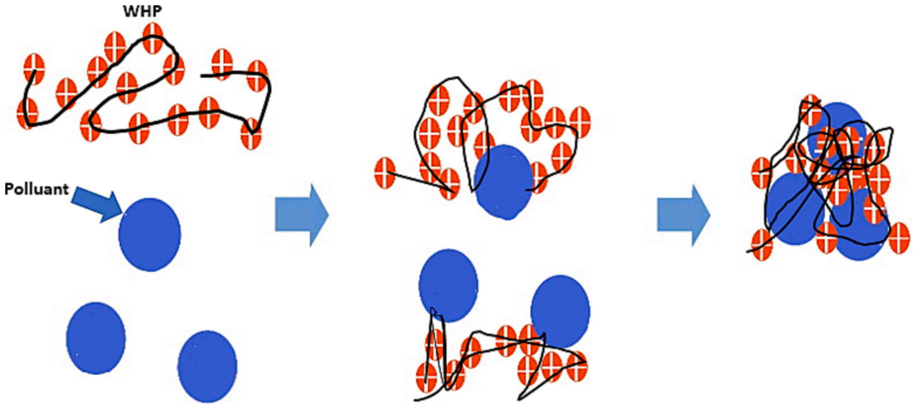

Fig. 8. Suggested mechanism during the coagulation-flocculation process.

Table 6
Optimum conditions and comparison of predicted and experimental data.

Response	Optimized condition			Removal (%)		Error
	Dose	Initial pH	Granulation	Predicted	Experiment	
MB	1000	9	112	99.59 %	98.47 %	1.12 %
TUR	1000	9	63	95.31 %	94.06 %	1.25 %

Table 7
Comparison of some biocoagulant and bioadsorbents for MB removal.

Coagulant / adsorbant	Process	experimental design	Dose (mg. L^{-1})	Initial pH	Efficiency (%)	Reference
Laterite Soil	Coagulation	————————	2500	2	99.61	(Lau et al., 2015)
Bentonite and Opuntia ficus indica	Coagulation	————————	400 + 900	6–7	98.25	(Ihaddaden et al., 2022)
Cashew NUT shell	Adsorption	Factorial central composite design / MSR	2184	10	99.97	(Subramaniam and Kumar, 2015)
Bamboo	Adsorption	—————————————	1000	3–5	99.67	(Guo et al., 2014)
Onion skins	Adsorption	—————————————	1000	10	95.54	(Saka and Sahin, 2011)
WHP	Coagulation	BBD-RSM	900	9	99.59	This work

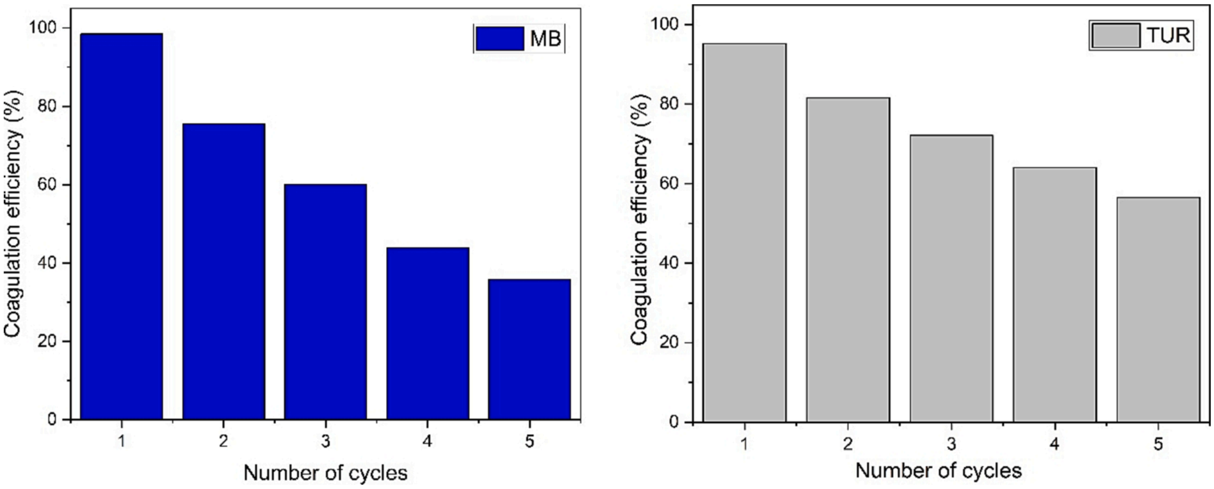

Fig. 9. Coagulation efficiency of MB and TUR with recycled WHP.

biocoagulant, achieving markedly higher decolorization and turbidity removal than conventional biosorbents. Systematic optimization identified optimal conditions to maximize treatment performance. These findings highlight the promising potential for sustainably upcycling this agricultural waste into eco-friendly water remediation applications.

CRediT authorship contribution statement

Ali Zourif: Writing – original draft. **Asmaa Benbiyi:** Writing – review & editing, Supervision, Validation. **Salma Kouniba:** Experimental data & Modeling. **Mohamed EL Guendouzi:** Writing – review & editing, Supervision, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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