

REMOVAL OF METHYLENE BLUE FROM INDUSTRIAL EFFLUENTS USING CORNCOB ACTIVATED CARBON

ABSTRACT

Water contamination by methylene blue (MB) is a threat to human health and aquatic biota due to its toxicity, persistence, and non-biodegradability. However, there is little data available on literature with methylene blue removal approach from industrial effluents by corncob activated carbon. The purpose of this study was to investigate the adsorption of methylene blue from aqueous solution and from industrial effluents by corncob activated carbon. The methylene blue adsorption capacities of corncob activated carbon were investigated by batch adsorption experiments both in synthetic solutions and industrial effluents. The optimum pH value was 10.3 with a removal percentage of 93.4 %. Methylene blue adsorption by activated carbon followed second-order kinetics and was well fitted by the Langmuir model. The maximum adsorption capacity ($Q_{\max}$) value was 11.36 mg/g. This study revealed that corncob activated carbon has successfully removed methylene blue from industrial effluents, with percentages ranging from 65.14 % and 76.28 %. The excellent methylene blue dye removal efficiency with corncob activated from industry effluents suggests its promising potential in remediating methylene blue contaminated wastewater.

Keywords : Methylene blue, adsorption, activated carbon, industrial effluents

1. INTRODUCTION

Water contamination by dyes is a global concern due to their negative effects on human health and the aquatic environment [1]. For example, the presence of dye in the aquatic environment reduces light penetration, which negatively affects photosynthesis [2, 3]. Therefore, it is important to remove dyes from wastewater.

Methylene blue is commonly used in many fields such as cosmetics, textile, food, pharmaceutical, and paper industries [4, 5]. Methylene blue ingestion by Humans even at low concentrations causes skin cancer, mental confusion, and high blood pressure [4]. However, methylene blue removal from wastewater is important. Thus, several methods such as filtration, electrocoagulation processes, oxidation, and adsorption have been developed to treat dyestuffs wastewater [6 - 10]. Among them, the adsorption technique is well used due to its simple operation conditions and chemical removal efficacy. The adsorption method has been carried out using several adsorbents such as metal oxides, chitosan, graphene, graphene oxides, and activated carbons [11 - 15]. To reduce the water treatment price, adsorbents from agricultural byproducts were used by many researchers [16 - 20]. These studies have shown that activated carbons developed from agricultural byproducts effectively

remove methylene blue from aqueous solutions. In addition, these investigations did not focus on industrial effluents. Recently, Kouassi et al. [21] showed that corncob activated carbon successfully removed Cu^{2+} and Pb^{2+} ions from industrial effluents. However, there are few studies on methylene blue removal from industrial effluents by corncob activated carbon. The objectives of this study were : (i) to investigate the influence of pH, contact time, adsorbent mass, and initial methylene blue concentration on methylene blue adsorption corncob activated carbon, and (ii) to explore the feasibility of removing methylene blue from industrial effluents by activated carbon.

2. MATERIALS AND METHODS

2.1. Materials, and reagents,

In this study, the reagents used include methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$), sodium hydroxide (NaOH), and hydrochloric acid (HCl). These reagents were purchased from Merck, Germany. The concentrations of methylene blue in the solutions before and after adsorption were determined using the spectrophotometer HACH DR 6000 at 664 nm. The pH values were measured using a pH meter HANNA HI.9828.

2.2. Preparation of activated carbon

The corncob activated carbon used in the present study was the best activated carbon prepared by Kouassi et al. [21]. The activated carbons were prepared taking into account the impregnation ratio which is defined as the ratio of the H_3PO_4 weight to the dried corn cob weight. The impregnation ratios were 0.25, 0.5, 1, 1.5, and 2. The mixture of H_3PO_4 and corncob was stirred for 24 h. After impregnation, corn cobs were dried in an oven at 80°C for 24 h and were carbonized at 500°C for 2 h in an electric furnace (Advantech KL-280).

2.3. Scanning Electron Microscopy (SEM)

The textural morphology of the best-activated carbon was determined using scanning electron microscopy (SEM) [21].

2.4. pH at the point of zero charge (pH_{pzc})

The pH_{pzc} of activated carbon was determined in the previous study of Kouassi et al. [21]. Various solutions of 0.01 M NaCl of pH ranging between 2 and 12 were prepared. The pH was adjusted with 0.1 M NaOH or 0.1 M HCl solution. Then, 0.1 g of activated carbon was suspended in 50 mL of 0.01 M NaCl solution and agitated for 48 h. After agitation and filtration of the as-prepared solution, the final pH of the filtrate was measured. The curve of $(\text{pH}_{\text{final}} - \text{pH}_{\text{initial}})$ vs. $\text{pH}_{\text{initial}}$ was used to determine the value of pH_{pzc} , which is the intercept point of the curve $(\text{pH}_{\text{final}} - \text{pH}_{\text{initial}})$ vs. $\text{pH}_{\text{initial}}$ with the $\text{pH}_{\text{initial}}$ line.

2.5. Adsorption experiments

The adsorption tests were carried out at room temperature. After shaking at 250 rpm, the solutions were filtered using Millex Millipore of 47 mm pore size before analyses.

2.5.1. Batch adsorption in aqueous solution

In the aqueous solution, the effect of contact time, pH, activated carbon dose, and initial methylene blue concentration were carried out. To study the effect of contact time, 1g of corncob activated carbon was added into 200 mL of 10 mg/L of methylene blue solution. The suspension was stirred at 25°C. At various time intervals (5 min, 10 min, 15 min, 30 min, 45 min, 60 min, 90 min, 120 min, 150 min et 180 min) 5 mL was collected. The isotherm experiments were investigated by varying initial concentration of methylene blue from 10 to 100 mg/L. The activated carbon mass of 0.2 g was added in methylene blue solutions. The suspensions were continuously stirred for the equilibrium time (45 min). To investigate the effect of activated carbon mass, the initial concentration of methylene blue (10 mg/L) and agitation time (45 min) were set at their optimum values. The experiment was done using 20 mL solutions of 10 mg/L of methylene blue for the various adsorbent masses 0.1, 0.3, 0.4, 0.5, 0.6 g, 0.7 g and 0.8g. The effect of pH was carried out by setting the concentrations of methylene blue and activated carbon mass at their optimum values of 10 mg/L and 0.4 g, respectively, and varying the pH from 2 to 11. The adsorption percent was calculated as follows :

$$\% \text{ Ads} = \frac{(C_0 - C_e) \times 100}{C_0} \quad (1)$$

Where C_0 (mg/L), and C_e (mg/L) are the initial, and the equilibrium concentrations of methylene blue, respectively.

The methylene blue amount adsorbed by the activated carbon at time t was determined using the following relationship :

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

In this equation, C_t (mg/L) represents the dye concentration in the solution after a contact time t (min), C_0 (mg/L) the initial concentration, V (L) the volume of the solution, and m (g) the mass of the activated carbon.

At the equilibrium, the amount of dye adsorbed was calculated as follows :

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (3)$$

Where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium dye concentrations, respectively ; V (L) is the volume of solution and m (g) is the activated carbon mass

2.5.2. Adsorption experiment with industrial dye effluents

The industrial effluent samples were collected around a paint manufacturing industry (sample 1) and a textile industry (sample 2) in Abidjan City which is the biggest town in Côte d'Ivoire.

0.4 g of activated carbon was added to 20 mL of sample 1 or sample 2. The suspensions were continuously agitated for 2 hours at room temperature.

2.6. Kinetic and isotherms models

2.6.1. Kinetic models

In this study, various models such as pseudo-first-order [22] and pseudo-second-order [23], were used to understand the kinetic adsorption of methylene blue.

Equation (4) gives the expression of the nonlinear form of the pseudo-first-order model :

$$q_t = q_e[1 - \exp(-k_1 t)] \quad (4)$$

Where k_1 (min^{-1}) represents the rate constant of the pseudo-first-order, q_t (mg/g) and q_e (mg/g) are the amounts of methylene blue adsorbed at time t (min) and equilibrium time, respectively.

For the pseudo-second-order model, the following equation gives the expression of nonlinear form.

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (5)$$

In these equations, k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) represents the rate constant of pseudo-second-order model

2.6.2. Adsorption isotherm models

In this study, the experimental data of adsorption isotherms were described by Langmuir [24] and Freundlich [25] adsorption models.

Equations (6), and (7) give the expressions of the nonlinear forms of Langmuir and Freundlich adsorption models, respectively :

$$Q_e = \frac{Q_{\max} \times K_L \times C_e}{1 + (K_L \times C_e)} \quad (6)$$

$$Q_e = K_F \times C_e^{1/n} \quad (7)$$

Where C_e (mg/L) is the equilibrium methylene blue concentration ; Q_e (mg/g) is the amount of methylene blue adsorbed at equilibrium, K_L (L/mg) is the Langmuir constant, K_F is the Freundlich constant, $Q_{\max}$ (mg/g) is the maximum adsorption capacity, and, n is the Freundlich model exponent,

The favorability of adsorption is indicated by the Langmuir parameter (R_L) which is calculated as follows :

$$R_L = \frac{1}{1 + b \times C_0} \quad (8)$$

Where C_0 is the highest initial solute concentration. $R_L < 1$ indicates unfavorable adsorption, the adsorption is favorable when $0 < R_L < 1$, and the adsorption is irreversible when $R_L = 0$

2.6.3. Error analysis

To find the best nonlinear model, an error analysis was performed. The Sum of Squares Errors (SSE), and the Chi-square (χ^2) were achieved by the following equations :

$$SSE = \sum_{i=1}^n (q_{e \text{ exp}} - q_{e \text{ cal}})^2 \quad (9)$$

$$\chi^2 = \sum_{i=1}^n \frac{(q_{e \text{ exp}} - q_{e \text{ cal}})^2}{q_{e \text{ cal}}} \quad (10)$$

Where $q_{e \text{ exp}}$ and $q_{e \text{ cal}}$ are experimental and predicted adsorption capacities, respectively.

3. RESULTS AND DISCUSSION

3.1. Properties of Activated Carbon

The properties of corncob activated carbon such as specific surface area (Table 1), surface morphology (Figure 1), and pH at the point zero charge (pH_{PZC}) of corncob activated carbon have been previously reported by Kouassi et al. [21]. The maximum value of the specific surface area of 810 m^2/g was obtained for an impregnation ratio of 1. The results also showed a porous structure of activated carbon at impregnation ratio 1 (figure 1). The value of the pH at the zero point charge (pH_{PZC}) of the activated carbon at impregnation ratio 1 was 3.8.

Table 1 Effect of different impregnation ratios on surface area of activated carbon

Impregnation ratio	Specific surface area S (m^2/g)
0	184
0.25	717
0.5	779
1	810
1.5	502
2	306

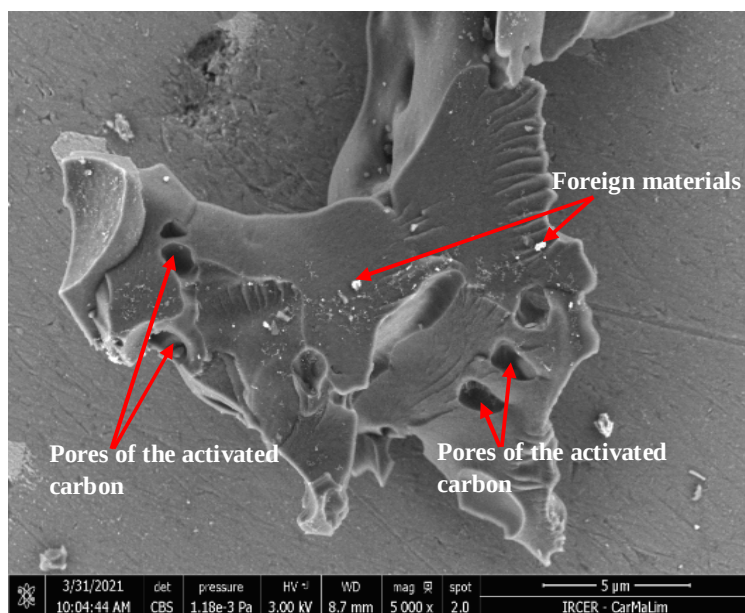


Fig. 1 SEM image of activated carbon at impregnation ratio 1

3.2. Effect of contact time on adsorption efficiency and kinetic study in aqueous solution

The influence of contact time on methylene blue adsorption is shown in figure 2. The results showed that the adsorption of methylene blue was very rapid during the first 5 min and slow near the equilibrium. This behavior is due to the large number of sites available at the beginning of the process, which are occupied throughout the process, making diffusion of methylene blue difficult [26]. The adsorption equilibrium was reached at 45 min with a maximum adsorption capacity of 1.98 mg/g. The pseudo-first-order, pseudo-second-order, models were applied to understand the methylene adsorption mechanism. The results are shown in figure 3 and table 2. Comparing the Chi-Square (χ^2), the sum of error squares (SSE), and the coefficient of determination (R^2) values, the pseudo second order was found to control methylene blue adsorption. Indeed, (χ^2), and SSE values obtained with pseudo second order were lower than those of pseudo first order. In addition, the R^2 value with pseudo second order was higher than that of pseudo first order. Moreover, the results of the pseudo-second model (Table 2) revealed that the maximum adsorption capacity obtained theoretically ($Q_{e2} \text{ theo} = 1.98 \text{ mg/g}$) are close to those obtained experimentally ($Q_{e \text{ exp}} = 2.08 \text{ mg/g}$).

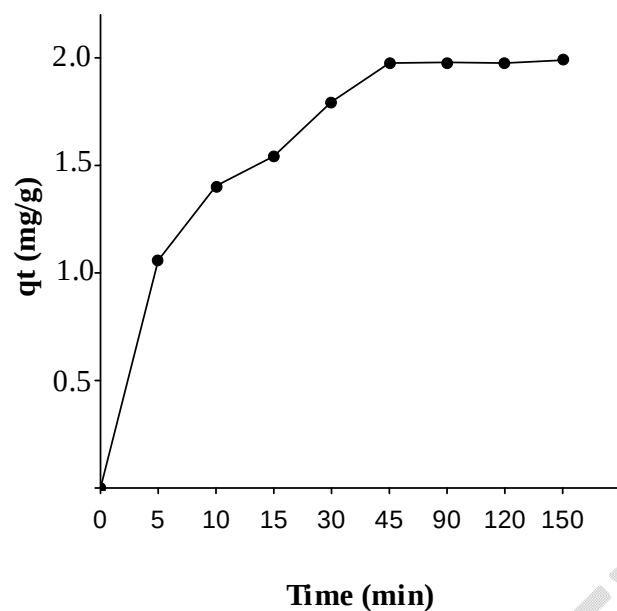


Fig. 2. Effect of contact time on adsorption capacities of methylene blue

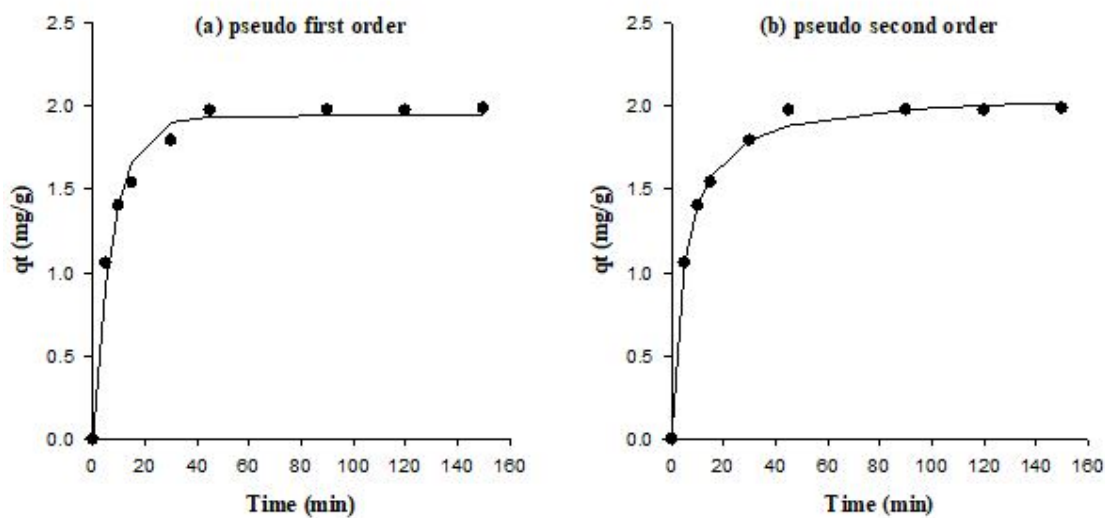


Fig. 3. Adsorption kinetics: (a) nonlinear pseudo-first order model and (b) nonlinear Pseudo-second-order model for removal of methylene blue

Table 2. Parameters of pseudo-first-order, pseudo-second-order, **Langmuir**, and Freundlich models using nonlinear analysis

Qe exp (mg/g) : 1.98			
Kinetic	Pseudo first order	Qe ₁ (mg/g)	1.94
		k ₁	0.13
		χ^2	0.04
		SSE	0.05
		R ²	0.984
	Pseudo second order	Qe ₂ (mg/g)	2.08
		k ₂	0.09
		χ^2	0.006
		SSE	0.011
		R ²	0.996
Isotherm	Langmiur	Qmax(mg/g)	11.36
		K _L	0.27
		R _L	0.04
		χ^2	0.55
		SSE	2.13
	Freudlich	R ²	0.97
		K _F	2.77
		n	2.06
		χ^2	0.91
		SSE	3.52
	R ²	0.94	

3.3. Effect of adsorbent **mass** on methylene blue removal in aqueous solution

The percentage removal of methylene blue increased with the mass of adsorbents (figure 4). This **observation** can be explained by the increase in active sites of activated carbon. The maximum **adsorption** percentage of methylene blue was 98.8 %, with an activated carbon mass of 0.4 g. Therefore, an activated carbon mass of 0.4 was used for further experiments.

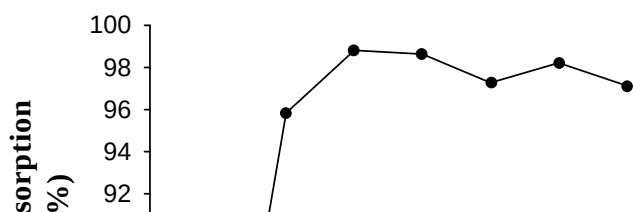


Fig. 4 Effect of activated carbon mass on methylene blue adsorption

3.4. Adsorption capacity of methylene blue in aqueous solution

The results of the influence of methylene blue initial concentration on methylene blue adsorption are shown in figure 5. The adsorption percentages of methylene blue decreased with increasing initial concentrations due to the reduction of the active sites of activated carbon [21, 27]. The maximum adsorption percentage (97.4 %) was obtained with an initial concentration value of 10 mg/L. The adsorption isotherms of methylene blue onto activated carbon are shown in figure 6. The adsorbed amounts of methylene blue increase with increasing equilibrium concentration, indicating that the activated carbon exhibited good adsorption capacity to methylene blue. The isotherm adsorption data were fitted by nonlinear forms of Langmuir and Freundlich models (Figure 6 and Table 2). The results indicated that R^2 value obtained with the Langmuir model (0.97) was higher than that of the Freundlich model (0.94). In addition, the Langmuir SSE and χ^2 values were the smallest. Therefore, methylene blue adsorption isotherm was well described by the Langmuir model, thereby indicating a monolayer adsorption process [27]. In addition, the value of $R_L = 0.04 < 1$ showed that methylene blue adsorption on corncob-activated carbon was favorable. The maximum adsorption capacity (Q_m) was 11.36 mg/g, indicating that corncob activated carbon could be a promising methylene blue adsorbent.

The maximum adsorption capacity ($Q_m = 11.36$ mg/g) of methylene blue obtained in the present study was compared to those of some authors (Table 3). It was found that Q_m 11.36 mg/g obtained in this study was higher than those obtained by Aboua et al. [28], Chandra et al. [29], and Sharma and Uma [30]. Whereas, data obtained by Gurer et al. [31], and by

Abdulhameed et al. [32], were higher than the one found in the current study. Therefore, corncob activated carbon has obvious advantages compared with some materials in Table 3.

Fig. 5. Effect of initial concentration

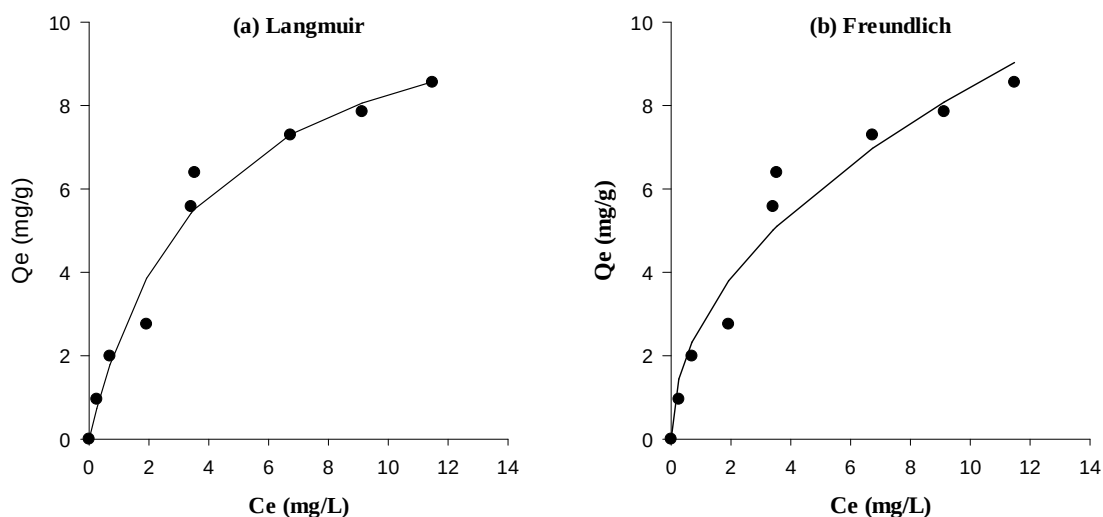


Fig. 6 Adsorption isotherms:(a) nonlinear Langmuir isotherm, and (b) nonlinear Freundlich isotherm for methylene blue adsorption

Table 3. Comparison of adsorption capacities of different adsorbents for methylene blue removal

Adsorbents	Adsorption capacity Q (mg/g)	References
Macore fruit shells	6.85	[28]
Leaginous microalga,S	7.80	[29]
Rice husk	9.83	[30]
Orange peels	98.9	[31]
Bamboo chip	305.3	[32]
Corn cob	11.36	Present study

3.5. Effect of pH on methylene blue adsorption in aqueous solution

Figure 7 showed the results of the influence of pH on the adsorption of methylene blue. The results indicated that the adsorption rates increased up to the optimum pH 10.3. Above this value, the adsorption rates decrease. Therefore, the adsorption of methylene blue on the activated carbons depends on the aqueous solution pH. The pH optimum value (10.3) was higher than pH_{pzc} value (3.8). At this pH (10.3) the corncob-activated carbon surface becomes negative. Hence, there was an electrostatic attraction between the negatively charged of the activated carbon and methylene blue which is a cationic dye ($(C_{16}H_{18}N_3Cl)S^+$). That can explain the higher percentage removal of methylene blue.

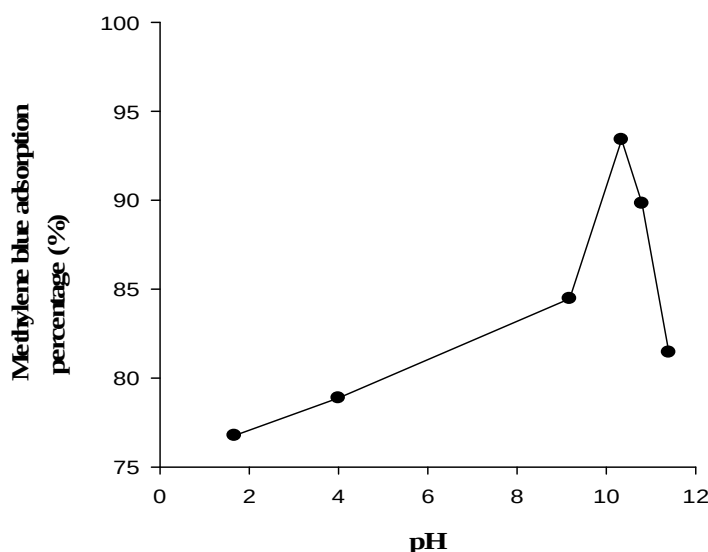


Fig. 7. Effect pH on adsorption capacities of methylene blue

3.6. Methylene blue adsorption mechanism onto activated carbon

Figure 8 shows the adsorption mechanism for methylene blue. Dye adsorption relies on several influential factors such as solution pH, pH of the point zero charge (pH_{pzc}), surface functional groups, and surface characteristics of the adsorbent [33, 34]. Methylene blue is a cationic dye, hence it adsorbs onto activated carbon via electrostatic interaction, hydrogen bonding, π - π interaction, and pore diffusion mechanism [33]. The negative charge of activated carbon favors methylene blue attraction by electrostatic interaction. The pH at the zero point charge (pH_{pzc}) of activated carbon was 3.8. At $pH > pH_{pzc}$ (3.8), the surface of activated carbon was covered with negatively charged hydroxyl (OH^-) and carbonyl ($-COO^-$) groups which electrostatically interact with positively charged (S^+ and N^+ atoms) groups of methylene blue. Several authors such as Kataria et al. [33], Thomas et al. [34], Benjelloun et al. [35], Ramutshatsha-Makhwedzha et al. [36] and Xia et al. [37] reported similar observations for methylene blue at higher pH. The corncob-activated carbon is a carbonaceous material having organic aromatic structure with C=C bond π -system. The π

electrons present in the aromatic ring of activated carbon interact with π electrons in the benzenic ring of methylene blue by π - π interaction. Hydrogen bonding also involved in methylene blue adsorption onto corncob-activated carbon. At $\text{pH} < \text{pH}_{\text{pzc}}$ (3.8), the water molecules and carboxyl ($-\text{COO}^-$) groups onto the activated carbon surface may be offered H^+ atoms to induce hydrogen bonding with polar S or N atoms of methylene blue. At basic pH, hydrogen bonding contribution is relatively less as compared to electrostatic interaction. Indeed, methylene blue adsorption percentage (93.4 %) onto corncob-activated carbon was high at basic pH (10.3). The SEM images indicated the porous structure of carbonaceous activated carbon material, thereby indicating the possibility of methylene blue adsorbed via pore diffusion or filling as its physical process also [33].

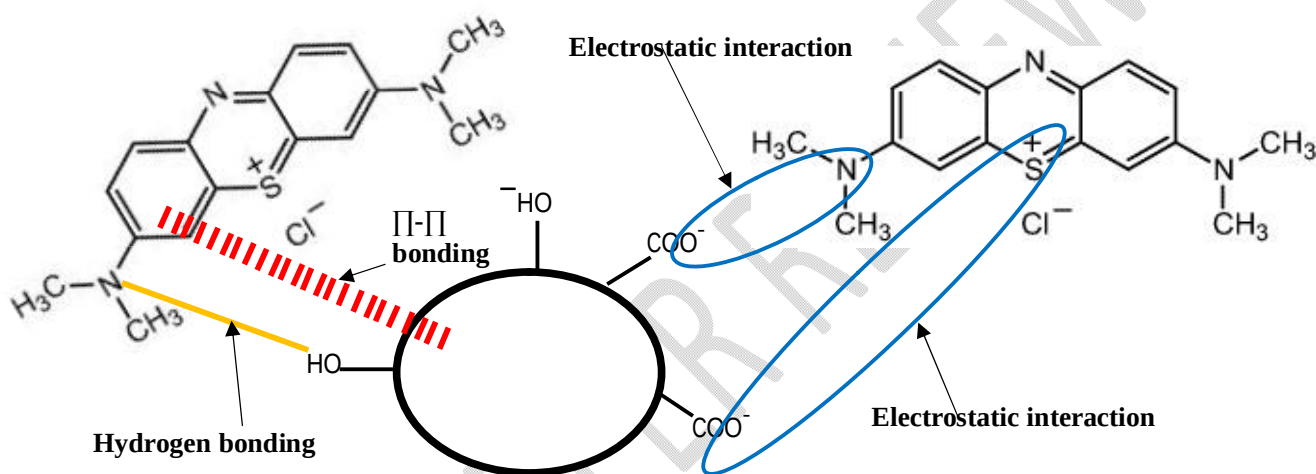


Fig. 8. Possible interaction and mechanism of methylene blue dye adsorption

3.7. Adsorption of methylene blue in industrial wastewaters

Table 4 gives the removal percentages of methylene blue from industrial effluents, and from synthetic aqueous solution. The removal percentages of methylene blue by corncob activated carbon were 76.28 % and 65.14 % for sample 1 and sample 2, respectively. These results showed that methylene blue adsorption percentages decreased in real effluents as compared to methylene blue synthetic solution (98.81 %). The decrease in methylene blue removal from real effluents can be explained by the competition effects between methylene blue and other pollutants present in industrial effluents [38]. Thus, corncob activated carbon may be proposed to purify real effluents contaminated by methylene blue.

Table 4. Industrial effluents treatment

Sample	Before adsorption (mg/L)	After adsorption (mg/L)	Removal percentage (%)
Methylene blue synthetic solution	10	0.12	98.81
Sample 1	2.53	0.6	76.28
Sample 2	4.02	1.40	65.14

4. CONCLUSION

In the present study, methylene blue removal from aqueous solution and industrial effluents was performed using corncob activated carbon. In synthetic aqueous solution, the adsorption tests indicated that pH, adsorbent mass, and methylene blue concentration affected methylene blue removal. The optimum pH value was 10.3 with a removal percentage of 93.4 %. The kinetic study showed that the methylene blue adsorption process was better described by the pseudo-second-order model, indicating that the chemisorption limits the adsorption process. The results also showed that the Langmuir model was the best model to fit methylene blue adsorption data, indicating a monolayer adsorption process. The maximum adsorption percentage in aqueous solution was 98.81 %. The investigations with industrial effluents indicated that the adsorption percentages of methylene blue by activated carbon varied between 65.14 % and 76.28 %. Therefore, corncob activated carbon may be proposed to purify real effluents contaminated by methylene blue.

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