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Investigating Competitive Adsorption in Milli-Q Water and Wastewater Treatment Plant Effluent using Activated Carbon

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Abstract: In the field of advanced wastewater treatment, activated carbon adsorption is used as an effective method for extracting organic compounds from wastewater. In this experiment, the efficacy of activated carbon adsorption in removing methylene blue from a solution was investigated. The objectives of the experiment were to determine adsorption isotherms for both Milli-Q water and effluent from wastewater treatment plant (WWTP), and to determine the parameters of the Freundlich and Langmuir approaches, as well as to compare the standard isotherm with the model isotherms. The results showed that the Langmuir isotherm had a higher r^2 value (0.9459) for Milli-Q water, while both Langmuir and Freundlich isotherms appeared to fit the standard isotherm for WWTP effluent. The q_{max} value for Milli-Q water was found to be higher than that of WWTP effluent, indicating that competitive adsorption was not as strong in Milli-Q water as in WWTP effluent. The study highlights the importance of considering different isotherm models for adsorption in various environmental conditions.

Keywords: Activated carbon, methylene blue, adsorption isotherms, Langmuir and Freundlich isotherms..

1. Introduction

Dyes play a significant role in the textile industry but have become a major contributor to global water pollution due to their toxic, cancer-causing, and genetic mutation properties [6]. Research has shown that biological treatment is not effective, electrochemical treatment requires a lot of energy, membrane filtration is not commonly used for trace analysis because it is expensive, and some other treatments are not economically feasible or appropriate for commercial applications [8]. In recent years, the removal of organic pollutants from wastewater has become a major concern for environmental protection and human health. Activated carbon adsorption has been recognized as a reliable and effective method for removing organic pollutants from wastewater due to its high capacity and specificity. The removal of contaminants by adsorption onto activated carbon is influenced by several factors, including the surface energy interaction between the adsorbent and the water. To understand this interaction, an adsorption isotherm can be used to demonstrate the relationship between the adsorbent and the contaminant.

The aim of this experiment was to investigate the efficacy of activated carbon adsorption in removing methylene blue from a solution. Methylene blue is a commonly used dye that is frequently used as a model pollutant to study the adsorption of contaminants onto activated carbon. The objectives of the experiment were to determine the adsorption isotherms for both Milli-Q water and WWTP effluent, to determine the parameters of the Freundlich and Langmuir approaches, and to compare the standard isotherm with the model isotherms.

The objectives of this research are:

a) Determination of adsorption isotherms for both Milli-Q water and WWTP effluent.
b) Determination of parameters of the Freundlich approach and Langmuir approach and compare the standard isotherm with model isotherms.

2. Literature Review

The presence of dyes in the wastewater from industries like textiles, leather, paper, printing, and cosmetics has prompted the search for cost-effective alternatives to expensive treatment methods. The ability of dye adsorption from wastewater has led to the exploration of low-cost adsorbent options [7]. Methylene Blue, discovered by Caro in 1878, is a widely used dark green powder that acts as a stain and has biological applications. Despite its usefulness, it also has harmful effects on humans, so removing it from wastewater is important [2]. Research conducted by Almeida et al., 2009 explored the use of montmorillonite clay to remove the methylene blue dye from an aqueous solution through the process of adsorption. The results of the study showed that the Langmuir isotherm equation best fits the data on the removal efficiency of the dye. The findings suggest that montmorillonite clay is an effective adsorbent for removing the cationic dye, methylene blue, from aqueous solutions and could be used as a cost-effective solution for treating wastewater contaminated with cationic dyes. The study conducted by [7] investigated the adsorption of methylene blue onto dehydrated wheat bran. The equilibrium isotherms were analyzed using three different equations: Freundlich, Langmuir and Redlich-Peterson, and were evaluated based on correlation coefficients. The results showed that the Langmuir model best described the adsorption data, although the Freundlich and Redlich-Peterson models were also able to fit the data. Hong et al., 2009 uses bentonite to adsorb methylene blue dye from aqueous solution and he also investigated to examine the influence of temperature on the equilibrium adsorption. The equilibrium adsorption data was evaluated using three common isotherms: Langmuir, Freundlich, and Redlich-Peterson. A non-linear approach was employed to determine the best fit of the isotherms. The results showed that the Redlich-Peterson isotherm provided the best fit. Han et al., 2006 uses cereal chaff to remove methylene blue (MB) from aqueous solutions. The study revealed that an increase in the amount of chaff resulted in a corresponding increase in the percentage of methylene blue sorption. The fallen phoenix tree's leaf has been tested as a new adsorbent for removing methylene blue from aqueous solutions and showed an increase in methylene blue sorption with an increase in the dose of leaf. The study used both the Langmuir and Freundlich isotherms to examine the equilibrium data. The results indicated that the Langmuir model provided a better fit to the data compared to the Freundlich model [4].

3. Methodology

Sample Milli-Q water and WWTP effluent were prepared with varying methylene blue concentrations and activated carbon was added according to the measurements. The samples were then spiked with different dosages of PAC (25, 50, 75, 100, 125, 150, 175, 200, 300 mg/L) to generate data points for the isotherm. After that, the samples were kept on a shaker for 24 hours, and the suspension of the carbon particles was allowed to settle. The absorbance of methylene blue was then measured at 660 nm wavelength and the calibration graph was drawn. The concentration of each sample was calculated, and the absorbance (q_e) values were determined. Finally, the parameters of the Freundlich and Langmuir models were calculated. A blank sample with no PAC was used as a check for the initial values, and non-spiked Milli-Q water was used as the zero reference for the spectrophotometer.

4. Data Analysis

4.1 Moisture Content of PAC

The moisture content of powdered activated carbon (PAC) is an important factor to consider in various industries such as water treatment, air pollution control, and food and beverage production. Moisture content affects the physical and chemical properties of PAC, such as its adsorption capacity, particle size distribution, and bulk density. It is important to properly store and handle PAC to maintain an optimal moisture content for optimal performance.

While measuring the PAC in each bottle, it absorbed moisture from the air, affecting its mass. So, it was necessary to remove the moisture content. Calculation of the moisture content is presented in table 4.1.

Table 4.1: Calculation of the moisture content

Item	Mass (mg)
Mass of Pan	1.3215
Mass of Pan +Moisture + Mass of PAC	6.3249
Mass of Pan +Dry mass of PAC	6.2288
Moisture Content (%)	2%

4.2 Methylene blue concentrations using the absorbance

4.2.1 Calibration Values

Calibration values are essential for maintaining the integrity of data and results in various fields and for ensuring accuracy and reliability in measurements.

Table 4.2: Absorbance at 660 nm for different methylene blue concentrations in Milli-Q water

	Absorbance at 660 nm (1/m) Milli-Q water		
Methylene blue Concentration(mg/L)	Measure1	Measure2	Avg. Absorbance
0.10	0.011	0.011	0.011
0.25	0.027	0.026	0.0265
0.50	0.081	0.081	0.081
1.00	0.178	0.179	0.1785
2.50	0.504	0.502	0.503
5.00	0.847	0.838	0.8425

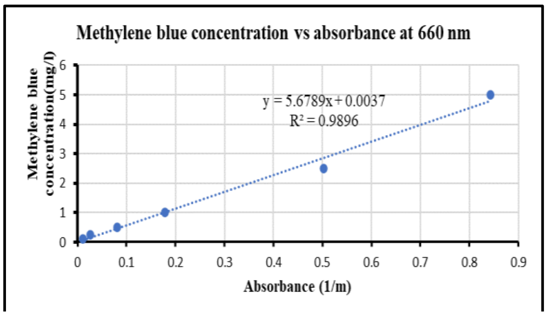

Figure 4.1: Methylene blue concentration as a function of absorbance at 660 nm for Milli-Q water.

The calibration curve in figure (4.1) is linear and fits well with a linear trend line and trend showing the maximum amount of dye that can be absorbed. Using the linear equation, the concentration (C_e) and absorbance (q_e) of methylene blue in the bulk fluid at equilibrium are calculated for each of the different batch reactor samples, for both Milli-Q water and WWTP effluent. Calculated values are shown in tables (4.3) and (4.4). These tables give an overview of the Milli-Q water and WWTP effluent batch reactor outcomes, respectively. We diluted the sample with lower PAC dosages, and therefore larger methylene blue concentrations. Some data were excluded from preparing linearization graph as there were dilution and PAC measurement errors.

4.2.2 Methylene blue concentrations of the samples

The methylene blue (MB) concentration in a sample is a crucial parameter in fields such as water treatment, pharmaceuticals, and biotechnology. MB is used as an indicator dye and its concentration can provide important information about treatment efficacy. MB concentration measurement is important for ensuring product quality and informed decision making.

Table 4.3: Calculation of methylene blue concentration of Milli-Q water using absorbance measurements.

Corrected PAC (mg)	Dilution	Absorption1	Absorption2	Mean Absorption	c_e (mg/L)	q_e (mg/mg)
56.6832	1	0.392	0.392	0.392	2.2298288	0.1861
39.2196	0.1	0.208	0.206	0.207	11.792323	0.2202
33.8002	0.1	0.316	0.324	0.32	18.20948	0.21757
30.6348	0.1	0.166	0.162	0.164	9.350396	0.2978
25.1076	0.1	0.237	0.237	0.237	13.495993	0.3304
20.3742	0.1	0.274	0.267	0.2705	15.3984245	0.3885
14.4452	0.1	0.504	0.502	0.503	28.601867	0.3652
10.8486	0.1	0.513	0.538	0.5255	29.8796195	0.4627
5.635	0.1	0.577	0.573	0.575	32.690675	0.7911
0	0.1	0.966	0.969	0.9675	54.9803575	-

Table 4.4: Calculation of methylene blue concentration of WWTP effluent using absorbance measurements.

Corrected PAC (mg)	Dilution	Absorption1	Absorption2	Mean Absorption	c_e (mg/L)	q_e (mg/mg)
59.78	1	0.567	0.567	0.0.567	2.9352	0.1117
40.18	0.1	0.162	0.164	0.163	8.7614	0.1372
33.32	0.1	0.15	0.152	0.151	8.149847	0.1691
29.4	0.1	0.255	0.256	0.255	13.47604	0.1555
24.598	0.1	0.365	0.365	0.365	19.0570	0.1404
19.992	0.1	0.447	0.447	0.447	23.24352	0.1310
14.798	0.1	0.494	0.492	0.493	25.58103	0.1453
10.192	0.1	0.491	0.491	0.491	25.4791	0.2130
4.998	0.1	0.509	0.506	0.507	26.3200	0.4007
0	0.1	0.704	0.704	0.704	36.3353	-

The standard isotherms were graphed (figure 4.2-a and 4.2-b) using the C_e and q_e values from tables (4.3) and (4.4). To identify probable outlines, the measured data were first analyzed. Four outliers have been identified for both experiments (Milli-Q water and WWTP effluent). They were labeled as outliers because their absorbance levels differed from the rest of the data. As a result, they were left out of the calculations and analysis.

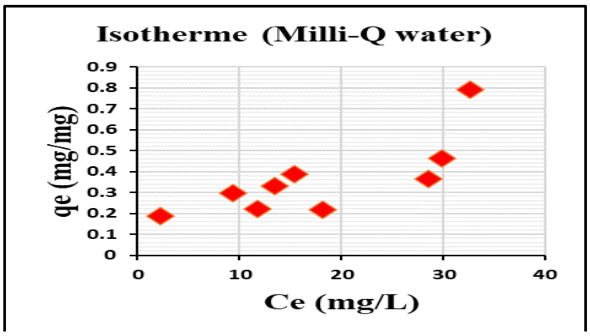

Figure4.2-a:Loading q_e as a function of C_e for milli-Q water.

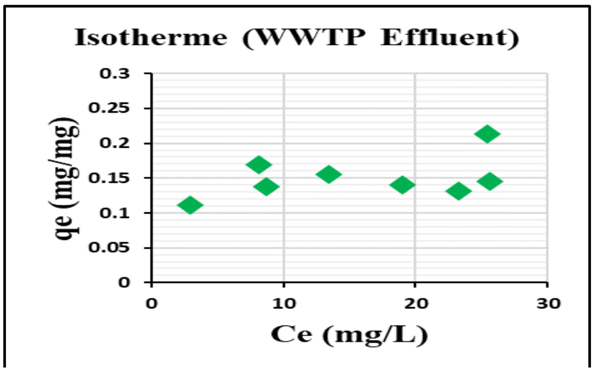

Figure4.2-b:Loading q_e as a function of C_e for WWTP effluent.

Figure (4.1) and (4.2-a and 4.2-b) illustrated that competitive adsorption for Milli-Q water is not as strong as it is for WWTP effluent. This is noteworthy, as Milli-Q water is pure water with very low levels of other chemicals. Because of the existence of additional chemicals such as natural organic matter (NOM), competitive adsorption is higher in WWTP effluent.

4.3 Linearization

The slope and intercept of Langmuir linearization (figure 4.3) and Freundlich linearization (figure 4.4) were used to calculate Langmuir parameters (q_{max}, K_L) and Freundlich Parameters (K_f, n). The parameters are shown in table (4.5) and (4.6) for both Milli-Q water and WWTP effluent.

a) Langmuir approach (Milli-Q water and WWTP effluent

The Langmuir approach is a commonly used isotherm model for the study of adsorption processes. In the case of Milli-Q water and wastewater treatment plant (WWTP) effluent, the Langmuir model is used to understand the relationship between the concentration of an adsorbate in solution and the amount of adsorbate adsorbed onto an adsorbent. The Langmuir approach assumes that the adsorbate molecules are homogeneously distributed on the surface of the adsorbent and that the adsorption process is mono layer in nature.

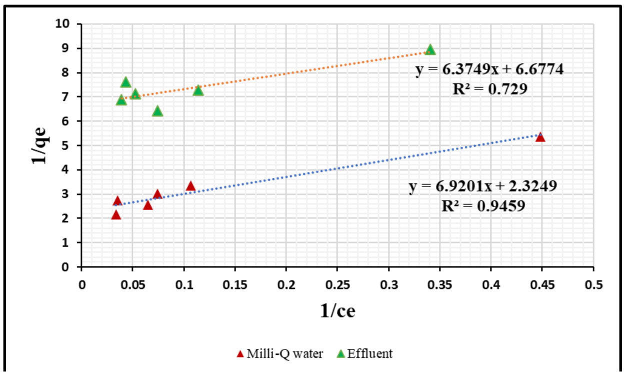

Figure 4.3: Linearization using Langmuir approach for Milli-Q water and WWTP effluent.

The calculated fractions $1/q_e$ and $1/C_e$, used for the Langmuir linearization for both Milli-Q water and WWTP effluent. Langmuir parameters are presented in table (4.5) for this case.

Table 4.5: Langmuir parameters for Milli-Q water and WWTP effluent

	Value	
Parameter	Milli-Q water	WWTP effluent
q_{max}	0.4301	0.1497
K_L (L/mg)	0.3359	1.0474
r^2	0.9459	0.729

b) Freundlich approach (Milli-Q water and WWTP effluent

The Freundlich approach is another commonly used isotherm model for the study of adsorption processes. Like the Langmuir model, the Freundlich approach can be used to understand the relationship between the concentration of an adsorbate in solution and the amount of adsorbate adsorbed onto an adsorbent. However, the Freundlich approach assumes that the adsorption process is multi-layer in nature, and that the adsorbate molecules occupy different sites on the surface of the adsorbent with different binding energies. By fitting the adsorption data to a Freundlich equation, it is possible to determine the adsorption capacity of the adsorbent and other important parameters related to the adsorption process.

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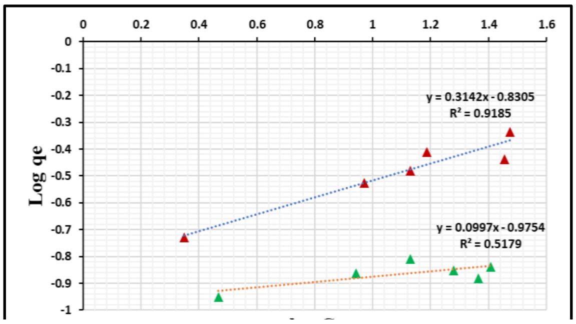

Figure 4.4: Linearization using Freundlich approach for Milli-Q water and WWTP effluent.

The logarithms log(q_e) and log(C_e) are used for the Freundlich linearization for both Milli-Q water and WWTP effluent. Freundlich parameters are shown in table (4.6) and figure (4.4).

Table 4.6: Freundlich parameters for Milli-Q water and WWTP effluent

	Value	
Parameter	Milli-Q water	WWTP effluent
K_f	0.1477	0.1058
n	0.3142	0.0997
r^2	0.9185	0.5179

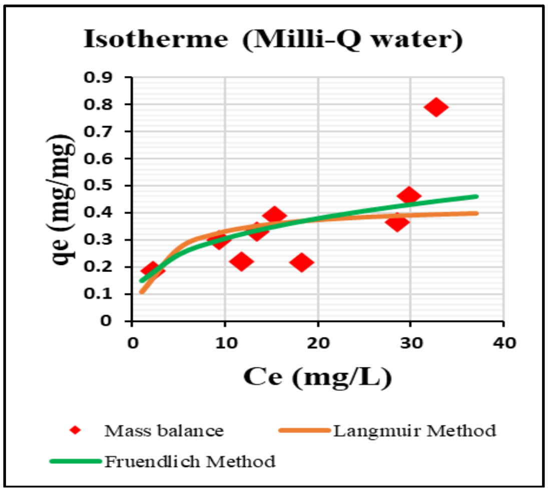

Figure 4.5-a: Comparison of standard Isotherm to model Isotherms for Milli-Q water

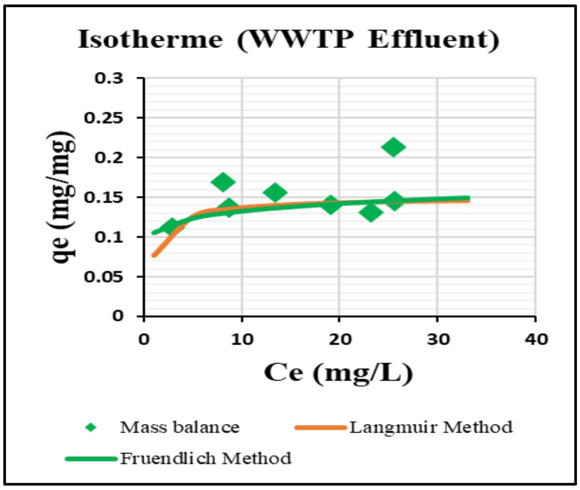

Figure 4.5-b: Comparison of standard Isotherm to model Isotherms for WWTP effluent.

By using the Langmuir and Freundlich parameters, model isotherms are shown in figures (4.5-a and 4.5-b) to compare with the standard isotherm from the experimental data.

5. Results and Discussions

When the two isotherms for Milli-Q water are compared, both appear to fit the data quite well, with the Langmuir isotherm having a higher r^2 value (0.9459). The Freundlich isotherm for Milli-Q water aligns more closely with the form of the standard isotherm, as seen in figures (4.5-a and 4.5-b). And can be considered to have the best fit. The decision for WWTP effluent, on the other hand, is not as obvious. Based on the graph (figure 4.5), it appears that both Langmuir and Freundlich fit the form of the standard isotherm. In this experiment q_{max} represents the amount of methylene blue concentration adsorbed at equilibrium. The q_{max} value of Milli-Q water (0.4301 mg/mg) was found to be greater than that of WWTP effluent (0.1497 mg/mg).This concluded that competitive adsorption in Milli-Q water is not as powerful as WWTP effluent. Competitive adsorption is greater in the WWTP effluent due to the presence of extra substances such as natural organic matter (NOM). NOM is challenging for activated carbon process. For the Freundlich method, a value of 0.3142 indicates a rapid rise in activated carbon input at the start of the experiment. The conducted experiment was limited by the fact that many absorbance values were outside of the range. This can be happened due to the dilution problem, errors in PAC measurement and unsteady temperature.

6. Conclusions

In conclusion, the study shows that activated carbon adsorption is an effective method for removing organic compounds from wastewater solutions. The Freundlich isotherm was found to have a better fit for Milli-Q water compared to the Langmuir isotherm. The results also indicate that the presence of additional chemicals in WWTP effluent makes competitive adsorption more challenging, as evidenced by the lower q_{max} value. Further studies may be required to evaluate the efficacy of adsorption onto activated carbon under different conditions and with different types of wastewater solutions.

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