



Coupling of Physical and Biological Techniques for the Treatment of Wastewater - Kinetic Study

Adel M.A. Elhdad¹, El-Shahat H.A. Nashy², Hussein M. Ahmed³, M.A. El-Khateeb^{4*}

¹Madinah Higher Institute of Engineering and Technology, Giza, Egypt

²Chemical industries institute, National Research Center, Dokki, Giza 12622, Egypt

³Housing and Building Research Center (HBRC), Sanitary and Environmental Institute. Dokki, Egypt, Giza, 12613, Egypt

⁴Water Pollution Research Department, National Research Centre, Dokki, Cairo, Egypt



Abstract

Palm fibers (PF) were estimated for the wastewater treatment. An investigation into the effects of varying dosages, starting concentrations, pH, and contact time was conducted in a lab setting to assess palm fiber's potential as a bioadsorbent in the treatment of wastewater. The palm fibres were characterized using different experimental approaches. The adsorption procedures were obtained to be contact time (90 min), pH-dependent (6.0), dose (25 g), and the height removal efficiency appeared at a starting concentration of 100 mg/L. Under these circumstances, the COD removal effectiveness of (PF) was almost 76%. Room temperature equilibrium adsorption studies were conducted and compared to the Freundlich and Langmuir models. The outcomes for the removal of COD by palm fibre (PF) are noteworthy, and this technique may prove to be an affordable wastewater treatment option.

Keyword: Palm fibers; wastewater treatment bioadsorbent; kinetic, isotherm;

1. Introduction

Water contamination from a variety of hazardous contaminants, including viruses, bacteria, heavy metals, organic compounds, and colors, has increased as a result of industrialization. These pollutants pose a serious threat to both humans and aquatic life. In addition to causing numerous harms to the ecosystem and the lives of living things, toxic and non-degradable organic chemicals in wastewater can build up in human bodies and result in major illnesses such as kidney failure, liver damage, ulcers, inflammation, and skin cancer [1-4]. Even at low concentrations, these organic pollutants are thought to be extremely harmful [5] and are also frequently present in wastewater from various industries [6], including the

extraction of gas and oil [5]. Millions of individuals are affected by serious and cancerous illnesses as a result of untreated contaminated water being released into bodies of water. Therefore, in order to shield people and the environment from these pollutants' harmful effects, organic compounds in particular need to be removed [7]. To remove harmful organic materials and lower wastewater's chemical oxygen demand (COD), a number of treatment techniques have been used [7-9]. These technologies do, however, have several disadvantages, including high energy consumption, high costs, intricate designs, and the creation of hazardous byproducts. Consequently, these methods' application has grown complicated and unfeasible. For the purpose of eliminating organic matter from wastewater, simple,

*Corresponding author e-mail elkhateebcairo@yahoo.com;(M.A. El-Khateeb)

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easy to use, high-performing, inexpensive, and efficient treatment techniques are required. Adsorption has been shown in numerous studies to be a successful method for eliminating the majority of contaminants from industrial wastewater. One of the most popular and widely utilized adsorbents is the activated carbon, despite its continued high cost [10-12]. The surface of the adsorbents is distinguished by containing many functional groups that help in the occurrence of a physico-chemical interaction with the sorbent materials present in the reaction liquid medium [13]. As a result, the sorbents catch impurities as water flows through them and, upon saturation, become activated for further usage [14]. There are many factors on which adsorption depend, the most important of which are the amount of absorbent material, particle size, specific surface area, ion concentration, pH, contact time and stirring speed [15]. In recent years, many researchers have presented several researches aimed at using low-cost agricultural waste to treat waste water from many pollutants, especially heavy metals and organic pollutants, the most famous of these agricultural wastes are sawdust [10, 16], rice husk [17], sugar cane [18], coconut husk [19], oil palm shell [20], neem bark [21], and fruit peels, neem leaves, date palm waste [22]. The study compared the organic matter produced from palm bark and maize cobs and found that the organic matter released from the palm bark is more stable and had a better bioavailability. Furthermore, the releasing capacity of palm bark significantly increased when bio- and alkaline-treatment techniques were used. Research on the effectiveness of nitrogen removal in partially saturated and vertically created wetlands also showed that nitrogen removal efficiency and replacement cycle of palm bark are higher than those of corncob. This suggests that using palm bark as an additional carbon source can be a cost-effective and efficient option [23].

The level of treatment needed and the adsorbent material's local availability determine its cost. It is an inexpensive substance if it is found in large quantities in nature or is a waste product or by-product of another industry. A high adsorption capacity could make up for the higher processing costs [24]. Therefore, it is necessary to explore many cheap adsorbents, which can be used to remove various types of pollutants from wastewater, and this is the goal of our current study about using of palm bark in reduce of organic pollution of industrial waste water. Palm fibre is a firm fibre derived from the leaves of the dwarf palm (*Chamaerops humilis*), a member of the palm family (*Palmae*), and is a byproduct of date palm production. Another name for it is vegetal horsehair. The current study examined the ability of

palm fibres to adsorb contaminants from wastewater. The cellulose fibres found in palms often contain polysaccharides. These refer to a wide range of polymers, mainly referred to as carbohydrates, which are the main ones according to their abundance in nature: cellulose, hemicellulose, and lignin. Due to its small charge compared to activated carbon and high hydroxyl functional group content, as well as its high surface area and carbon content, palm fibres have drawn particular attention as an effective biosorbent for the removal of contaminants from wastewater [25]. The current study's goal is to determine whether palm fibres can be used to remove COD from synthetic solutions and then apply the best possible conditions for wastewater treatment. The examined adsorption operating conditions were the adsorbent dosage, pH, contact time (CT), and beginning concentration. The parameters of kinetic models and adsorption isotherm models were also examined.

2. Materials and methods

2.1 The adsorbent's preparation

To obtain palm fibre (PF), palm fronds were gathered from Egyptian palm plantations. The (PF) was thoroughly cleaned many times using deionized water, dried for six hours at 105 °C, and sieved. The adsorption tests were carried out at room temperature, 25°C (± 2). The PF were crushed at the ends where they split into their hard portions. The tough portion of the PF was submerged in water to rot. After cleaning the rotted materials, the fibre was separated and allowed to dry in the sun. Following that, the fibre was held at 100°C for a whole day in order to partially remove moisture. For a full day, tiny palm fibres were dried at 50°C in a dryer.

2.2 Preparation of adsorbate

Potassium phthalate (Merck) stock solution was mixed with distilled water to achieve the necessary concentration of COD, which ranged from 100 to 700 mg/L. The COD solutions were generated in the laboratory based on the COD content in the industrial effluent. Before the adsorbent was added, the pH of each test solution was adjusted to the appropriate value using both concentrated and diluted HCl and NaOH. The COD levels were measured by spectrophotometric analysis after adsorption at 600 nm.

2.3 Adsorbent characterizations

The PF's chemical makeup was determined, and the gravimetric measurements of lignin, hemicellulose, and cellulose content were made. By subtracting the hemicellulose from the cellulose content, the hemicellulose content was determined. The functional groups were determined using Fourier-

transformed infrared spectroscopy (FT-IR; 4200-FTIR JASCO, Japan). The samples were used to create the study's specimens. Using an Edwards model S 140A sputter coater, gold ions were applied to a circular specimen measuring 10 mm in diameter to produce a conducting medium. The samples that had been sputter-coated were examined using a JEOL Model JSM-T20 SEM.

2.4 Adsorption Studies

Using an orbital shaker set to 100 rpm, batch adsorption experiments were conducted at room temperature by agitating various dosages (5-30 g) of palm fibres (PF) in 1000 ml of COD solutions with specified concentrations and pH levels. By employing 1.0 N HCl or 1.0 N NaOH solution to adjust the pH of the solutions, the impact of pH was taken into consideration. A pH metre was used to measure the pH. By combining 25 g of the adsorbent with 1000 ml solutions of the required concentrations (100-700 mg/L), the impact of initial COD concentrations was investigated. Prior to the addition of the adsorbent, the samples were finally brought to the ideal pH. In order to avoid discrepancies in the investigative calculations, every test was repeated, and COD solution regulators were kept intact throughout the experiment to maintain superiority control. Equations 1 and 2 were used to get the percentage removed (R%) and the amount of COD eliminated at equilibrium (q_e).

$$R\% = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$$q_e = \frac{(C_i - C_e)V}{W} \quad (2)$$

where V (L) is the volume of the reaction medium, W (g) is the mass of the PF utilised, C_i and C_e (mg/L) are the COD concentrations at beginning and equilibrium conditions, respectively, and q_e (mg/g) is the quantity of COD adsorbed at equilibrium.

2.5. Isotherm study

2.5.1 Langmuir isotherm

Adsorption isotherms, which are usually the ratio between the amount adsorbed and that was left in solution at equilibrium at a specific temperature, describe equilibrium studies that offer the capacity of the adsorbent and adsorbate. The adsorption energy is constant, there is no adsorbate molecule migration in the surface plane, and maximal adsorption happens when a saturated monolayer of solute molecules is present on the adsorbent surface [26]. These are the underlying presumptions of the Langmuir model. The Langmuir isotherm model states that physical processes are responsible for monolayer sorption. The Langmuir isotherm equation is as follows:

$$q_e = \frac{CKq_{max}}{1 + KL} \quad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot KL} + \frac{C_e}{q_{max}} \quad (4)$$

$$RL = \frac{1}{1 + C_0KL} \quad (5)$$

where C_e is the solution's equilibrium concentration (mg/L), q_{max} is the greatest dose of COD concentration required to form a monolayer (mg/g), and q_e is the amount of COD adsorbed on a specific dose of adsorbent (mg/g). The symbols K and q_{max} stand for the Langmuir constants. The values of q_m and K can be computed using the linear plot of C_e/q_e vs. C_e .

2.5.2 Freundlich pattern

The empirical connection that depicts the adsorption of solutes from a liquid surface to a solid surface contains many sites with various adsorption energies, according to the Freundlich pattern of isotherm. The parameters of the system are denoted by K_f and n , which stand for the adsorption intensity and capacity, respectively. We looked at how well the Freundlich model suited the experimental data. The intercept value of K_f and the slope of n were found for this case using the plot of $\log C_e$ vs. $\log q_e$. The Freundlich isotherms appear when the surface is heterogeneous, the absorption is multilayered, and it is bonded to certain locations on the surface.

$$\text{Log}q_e = \text{Log}KF + \frac{1}{n}\text{Log}C_e \quad (6)$$

where $1/n$ = Intensity parameter and K is the Freundlich equilibrium constant (mg/g). C_e is the adsorbate's equilibrium concentration, and q_e represents the amount of material adsorbed. Equation 6 depicts the Freundlich pattern, which is linearly expressed as $\log q_e$ vs. $\log C_e$. The Freundlich formulation yields the constants K_f and $1/n$ in a linear form. The Freundlich pattern in a multilayer covering assumes non-ideal adsorption on heterogeneous surfaces. It suggests that stronger binding sites occupy their position before weaker binding sites. Stated differently, binding strength decreases as site occupation increases [26].

2.6 Kinetic Study

The kinetics of every adsorbent could be represented with pseudo-first and pseudo-second-order kinetic patterns. Equation 7 represents the Lagergren model, which is followed by the pseudo-first-order kinetics:

$$\text{Log}(q_e - q_t) = \text{Log}q_e - K_1 \frac{t}{2.303} \quad (7)$$

where q_t is the adsorbed dosage of metallic ions (mg/g) in t time (min) and k_1 is the pseudo-first-order constant (min^{-1}). Using the linear and angular constants of the log graphic ($q_{eq} - q_t$) in the function of time, q_{eq} and k_1 can be independently calculated. Comparing the experimentally obtained values of q_{eq} , which were derived from Equation 8:

$$\frac{t}{qt} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \quad (8)$$

where k_2 is the pseudo-second-order constant (g/mg.min), which is obtained by computing a linear coefficient, and q_{eq} is calculated using an angular coefficient.

Results and Discussion

Palm fibrous waste is a hard fibre derived from the leaves of the dwarf palm (*Chamaerops humilis*), a member of the palm family (Palmae), and a byproduct of date palm production. Another name for it is vegetal horsehair.



Figure 1: Date Palm Fiber

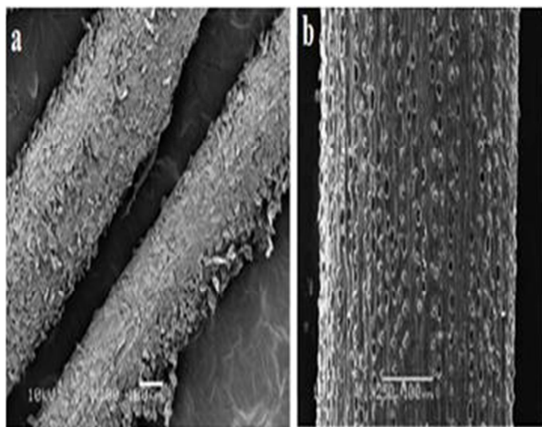


Figure 2: Scanning Electron Microscope for (a) Untreated Date Palm Fiber, (b) Treated Date Palm Fiber with 1.5% NaOH

One significant and primary chemical treatment for natural fibres is alkaline treatment. This treatment's primary alteration is the breaking down of hydrogen bonds within the network structure, which is accompanied in this case by a rougher surface. Here, the lignins, wax, and oils are extracted from the cell walls using aqueous NaOH. As a result, the degree of polymerization, the cellulosic fibril, and therefore the

extraction of lignin and other non-cellulosic components were frequently directly impacted by alkaline treatment.

Adsorption behavior at different operating conditions

Effect of doses

The bulk of the adsorbent has a significant impact on the adsorption process. Changeable adsorbent doses ranging from 5.0 g/L to 30.0 g/L were used to investigate the effect of biosorbent dose on the percentage removal of COD. At 25.0 g/L, the proportion of COD removed was equal to 56.16 %. It was shown that as the adsorbent dose increases, so did the percentage removal of COD (Figure 3). With a constant initial concentration of 600 mg/L and a dose of 30 g/L of biosorbent, the maximum percentage removal of COD was 59.83 %. The percentage removal of COD increases as the adsorbent dose increases. This may be explained by the fact that the rate of adsorption increases as more surface becomes available for organic contaminants to adsorb.

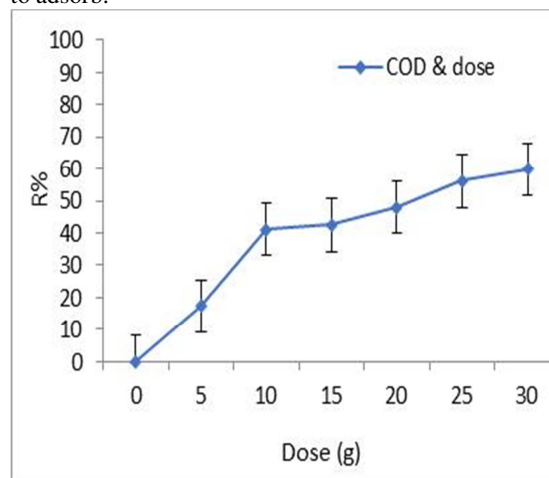


Figure 3: Adsorbent dose effects on COD biosorption by PF at a starting concentration of 600 mg/L for 90 minutes

Effect of contact time (CT)

The level of COD adsorption rate was affected by the CT with the adsorbent as seen in Figure 4. It was shown that when the contact time increased from 60 to 105 minutes, the adsorption performance increased from 56.16% to 75.83%. In 90 minutes, the highest COD elimination was reached. It might be supported by the fact that there were initially a lot of vacant sets for adsorption, but they eventually decreased because of the wear and tear on the remaining surface sets and the repulsive interaction between the solute molecule and the bulkiness phase. It is quite clear that the unoccupied surface spots are unavailable later [10].

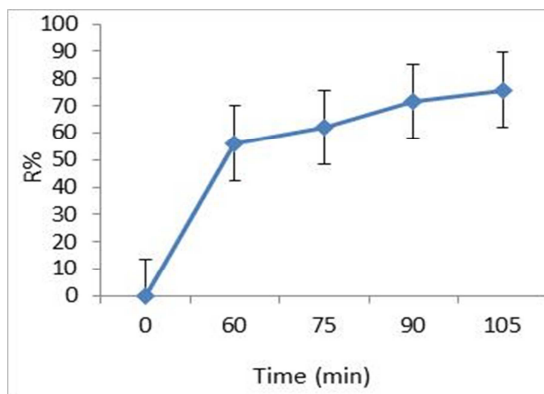


Figure 4: The contact time affects COD biosorption by PF at a 600 mg/L starting concentration.

3.3.3 Effect of starting concentrations

The adsorption capacity rose when the COD concentration rose from 100 to 700 mg/L (Figure 5).

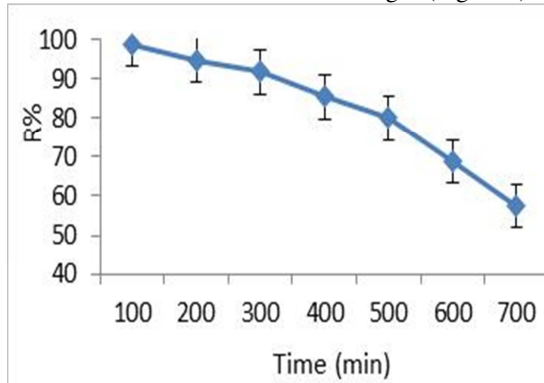


Figure 5: Starting ion concentration impact on the COD biosorption by PF after 90 minutes

3.3.4 Effect of variance pH

There is a strong correlation between pH and the percentage of COD elimination. To ascertain how pH affected the adsorbent's capacity to remove COD, batch adsorption analyses at various pH values were conducted within the 1.0–12.0 range. According to the data (Figure 6), at pH 6.0, the maximum R% of COD was 76%. The pH of the solution has a major impact on the organic pollutants' absorption. The chemistry of degradation in the solution, as well as the binding sets of organic pollutants and adsorbent surfaces, is all influenced by the pH of the solution. Organic contaminants compete with adsorbent surfaces for forcing sets at low pH levels, which reduces COD uptake. Furthermore, a reduced binding between the organic contaminants and the adsorbent surface was seen at higher pH values.

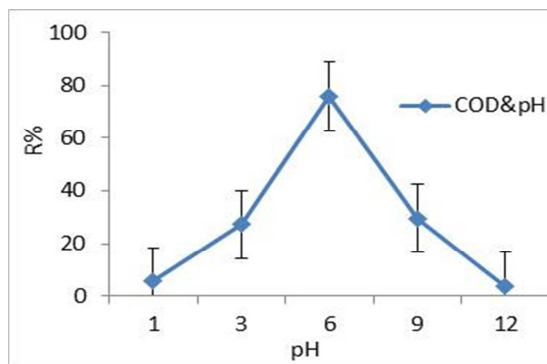


Figure 6: At the starting concentration of 600 mg/L and 90 minutes, the impact of pH value on the bio-sorption of COD by PF

3.4 Isotherm study

The bio-sorption isotherms, which also characterize the interaction between the adsorbate and the bio-sorbent, establish the equilibrium between the adsorbed organic pollutants on the PF bio-sorbent and the residual COD pollutants in the solution during the surface bio-sorption. To find the biosorbent's COD concentration capability, equilibrium isotherms are computed (Figure 7). Two parameter isotherms, the Freundlich and Langmuir isotherm models, were used to analyze the equilibrium records.

Regarding the isotherm's models, the correlation coefficient (R^2) values are regarded as an indicator of how well the experimental data performed. The two isotherm models' applicability to the current data roughly goes as follows: Kindly ~ Langmuir.

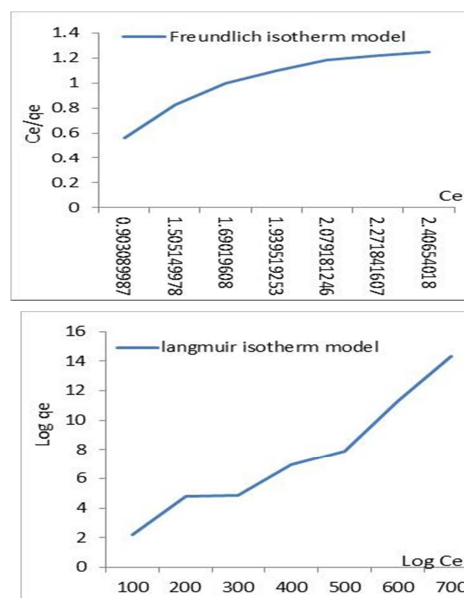


Figure 7: The isotherms models (Langmuir and Freundlich) of COD onto adsorbent

3.5 Kinetic study

Figures 8 showed the kinetics trends for COD pollutant adsorption by adsorbent. The relation between $\log (q_{eq} - q_t)$ and t was examined. The slope and intercept yield the K_1 and q_e , respectively. The pseudo-First order kinetic model has lower correlation coefficients (R^2) than the second-order kinetic pattern. The findings indicated that physical adsorption regulates the total rates at which COD is added by the adsorbent [26].

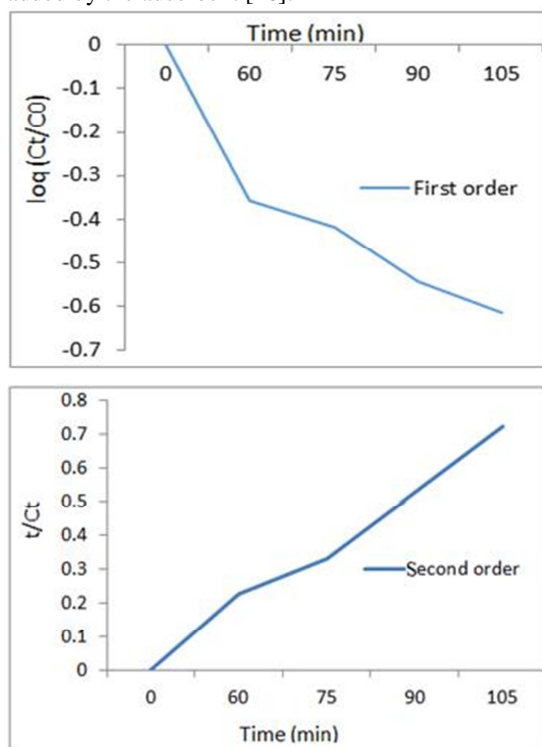


Figure 8: The pseudo-first-order and pseudo-second-order of COD

4. Conclusion

It is imperative to stop the unchecked release of pollutants that lead to water pollution. Nowadays, research is concentrated on creating a technology that can either prevent pollution or reduce it to a minimal amount. The only way to stop contaminants from entering water bodies directly is to lessen their direct discharge into the stream. The conventional techniques of treating wastewater that are now in use have a number of drawbacks, including high startup and operating costs, unsuitability for small-scale companies, and insufficient efficiency. One method that shows promise for eliminating contaminants from wastewater is the adsorption treatment technique. The palm fibre materials are employed as an adsorbent of pollutants. As a result, low-cost

adsorbents are increasingly used instead of palm fibre materials.

Given the chance to utilise waste biomass to eliminate COD contamination, palm fibre (PF) biomass was applied successfully as bio-sorption investigation. A pH 6.0 was found to be optimal for adsorption. System compliance with both Langmuir models was demonstrated by equilibrium adsorption. This study's outcome will help in recommending bio-sorbents that are used in the industry to remove contaminants from wastewater.

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