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The Influence of pH on Cd (II) Adsorption onto NaOH-Treated Oil Palm Empty Fruit Bunch (OPEFB)

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Abstract

This study aims to investigate how pH affects the removal of Cd (II) ions using both raw and NaOH-treated oil palm empty fruit bunch (OPEFB). As the NaOH concentration increases from 0.1 M to 1.0 M, the removal percentage increases from 58.58% to 61.20% after a 12-hour immersion duration and 62.27% to 64.54% as the immersion duration was raised to 24 hours. Stronger interactions with Cd (II) ions are made possible by the increased number of active sites on the OPEFB surface caused by higher NaOH concentrations. Extending treatment duration allows NaOH to penetrate OPEFB structure, enhancing its cadmium binding ability. The best NaOH treatment was 1.0 M of NaOH concentration with 24 hours of immersion time (64.54% Cd (II) removal with q_e= 32.3 mg/g). Energy-dispersive X-ray (EDX) analysis showed that the O/C ratio increased by 44.77% after alkaline treatment indicating the partial removal of the OPEFBs' lignin and hemicellulose primarily made up of C which enhances adsorption capabilities. The optimal starting solution pH for raw and treated OPEFB was pH 6, with maximal adsorption being 65.2% (q_e= 32.6 mg/g) and 70.8% (q_e= 35.4 mg/g), respectively. The results demonstrated that the NaOH-treated OPEFB can be used as an alternative for Cd (II) removal in wastewater treatment.

Keywords: - pH, adsorption, NaOH, cadmium, empty fruit bunch

1. Introduction

Cadmium is a significant public health issue with 69,293 scientific articles published up to 2024 on the PubMed.gov website. About 4162 articles were published regarding cadmium in 2024 which was almost double as compared to 2014 (PubMed, 2024). Cadmium is found at high levels in various countries, including China, Nigeria, and Romania (Gao et al., 2020). The Langat River in Malaysia has higher Cadmium levels than the European Commission and USEPA standards, and the amount of cadmium in cockles from Kuala Selangor is higher than the permitted levels (Ahmed et al., 2020; Yunus et al., 2014). Mining activities contribute to pollution, and Malaysia must make greener processes to reduce pollution. Cadmium is toxic and can cause diarrhea, nausea, and liver damage in humans. Remediation of heavily contaminated wastewater is crucial to reduce concentration before release due to regulatory constraints. Researchers are exploring potential solutions to lower Cadmium concentration in industrial effluents before they can be released into the environment (Herrera-Barros et al., 2020).

Agricultural waste, including oil palm biomass, is generated annually in countries like Malaysia, Africa, Indonesia, and China. Malaysia is the leading palm oil supplier, with 452 mills nationwide. Around 90 million tonnes of oil palm waste are globally generated annually (Baby et al., 2019). OPEFB, once used as compost, is no longer relevant due to labor-intensive processes, high transportation costs, fire hazards, and landfill disposal. Identifying new uses for OPEFB, such as an adsorbent, is crucial to address these issues. Raw OPEFB is an ideal adsorbent for heavy metals due to its hemicellulose content and lignin content. Microorganisms, eggs, and oyster shells are currently used as adsorbents for Cadmium (II) removal. However, contamination issues and costs remain (Ahmad et al., 2006; Tizo et al., 2018). OPEFB waste is targeted to address availability and contamination issues, while a simple chemical modification method addresses cost concerns.

Adsorption technology has gained interest due to its potential to reduce energy costs, improve selectivity, yield, and non-toxic sludge formation (Ujile & Okwakwam, 2018). Although physical modifications are straightforward and affordable, chemical modifications are preferred due to their simplicity and effectiveness. Alkali treatment is a popular method for pre-treating cellulose (Mopoung & Kengkhetkit, 2016). Table 1 shows a comparison of several types of modification methods used for Cd^{2+} removal using OPEFB. Meanwhile, Table 2 shows a comparison of maximum adsorption capacity, q_m (mg/g) for other modified NaOH adsorbents in Cd (II) removal. There is a research gap in understanding the effect of NaOH treatment conditions for OPEFB adsorbent on the Cd (II) adsorption process at different pH.

Table 1. Comparison of several types of modification methods used for Cd^{2+} removal using OPEFB

Adsorbate / Adsorbent	**Type of Adsorbent / Modification Method / Contacting System**	**Kinetics / Isotherm Model**	**Equilibrium Adsorption Capacity q_e (mg/g)**	**Maximum Adsorption Capacity q_m (mg/g)**	**Removal Percentage (%)**	**Reference**
Cd^{2+}/ OPEFB	Composite / Polymer grafting / Batch	Pseudo-first- and second-order	13.2 (best fitted: Pseudo-second-order)	113.6 (best fitted: Langmuir)	91.1	Issa & Abidin, 2020
Cd^{2+}/ OPEFB	Composite / Polymer grafting / Batch	Langmuir & Freundlich	-	204.082 (best fitted: Langmuir)	84	Rahmi et al., 2023
Cd^{2+} (waste water) / OPEFB	Activated carbon / Pyrolysis / Continuous	BET Theory & Pseudo-second-order	49.6g/(mg/min) (best fitted: Pseudo-second-order)	-	90	Ujile & Okwakwam, 2018
Cd^{2+}/ OPEFB	Fibre / Organic and inorganic solvent / Batch	Pseudo-second-order (Type 1, Type 2, Type 3 and Type 4)	7.855 (best fitted: Pseudo-second-order type 1)	-	-	Abia & Asuquo, 2008
Cd^{2+}/ OPEFB	Raw fibre / Batch	Pseudo-second-order (Type 1, Type 2, Type 3 and Type 4)	7.199 (best fitted: Pseudo-second-order type 1)	-	-	Abia & Asuquo, 2008

Table 1. Comparison of maximum adsorption capacity, q_m (mg/g) for other modified NaOH adsorbents in Cd (II) removal

Adsorbent	**Removal Percentage (%)**	**Maximum Adsorption Capacity q_m (mg/g)**	**Kinetics / Isotherm Model**	**Fitted Kinetics Model**	**Fitted Isotherm Model**	**Reference**
NaOH modified Auricularia Auricular matrix waste	-	47.62	Pseudo-first-order kinetic, Pseudo-second-order kinetic & Elovish / Langmuir & Freundlich	Elovish		Song et al., 2017
NaOH modified Juniper fibre	-	29.54	Pseudo-first-order, Pseudo-second-order / Langmuir & Freundlich			Min et al., 2004
NaOH modified rice husk	97	20.24	Pseudo-first-order, Pseudo-second-order / Langmuir & Freundlich	Pseudo-second-order		Kumar & Bandyopadhyay, 2006
NaOH modified cassava peel waste	-	19.5	Pseudo-first-order kinetic, Pseudo-second-order kinetic, Elovish & Fick's Law / Langmuir & Freundlich			Scwantes et al., 2016
NaOH modified corn cob	~93	19.862	Langmuir		Langmuir	Mahmood-ul-Hassan et al., 2015
NaOH modified sunflower	~58	14.281	Langmuir			Mahmood-ul-Hassan et al., 2015
NaOH modified oil shale ash	91	12.05	Langmuir	-		Zhu et al., 2014
NaOH modified banana stalks	~80	5.815				Mahmood-ul-Hassan et al., 2015
NaOH modified sawdust (Cedrus Deodar wood)	97	73.62	Pseudo-first-order & Morris-Weber / Lagmuir & D-R	Pseudo-first-order		Memon et al., 2008

2. Methodology

2.1 Material

The OPEFB fibre was supplied by Felcra Jaya Samarahan Palm Oil Mill Sdn. Bhd. in Sarawak, Malaysia; in this work, OPEFB was chosen due to its good qualities in adsorbing various pollutants. The OPEFB was washed multiple times with tap water before being rinsed with distilled water to remove debris and soil. The sample was dried in an oven at 90°C for 24 hours to reach a moisture content of 8% (wet basis). This technique was developed following a study conducted by Sajab et al. (2017). The dry fibre was ground with a Glen Creston hammer mill and sifted with a sieve shaker. As described by Kumar & Bandyopadhyay (2006) and Nasir et al. (2015), the OPEFB in the 200 < Ø (diameter) ≤ 600 µm size was stored in an airtight container. As a stock solution (Cd (II) adsorbate), Cadmium sulfate, 8/3-hydrate, $3CdSO_4.8H_2O$ (ThermoFisher Scientific, Fair Lawn, NJ) heavy metal salts with analytical grade content of 99% weight pellets were employed. As a chemical activating agent in alkali treatment and pH adjusters, analytical-grade sodium hydroxide, or NaOH (Merck, Darmstadt, Germany) pellets were utilized. Without doing any extra purification, all the chemical reagents were used.

2.2 Modification of OPEFB Adsorbent

Three 1-liter glass beakers containing 500 mL of 0.1 M, 0.5 M, and 1.0 M NaOH solutions were filled with 12.5 g of OPEFB fibers, respectively at room temperature. Two groups were created for each concentration, and these categories matched immersion durations of 12 and 24 hours, respectively. The fibers were then filtered out and cleaned with deionized water until the pH of the filtrate wash solution was 7. The fibers were labeled as follows being dried for 48 hours at 80 degrees Celsius: 12h-0.1M-OPEFB, 12h-0.5M-OPEFB, 12h-1.0M-OPEFB, 24h-0.1M-OPEFB, 24h-0.5M-OPEFB, 24h-1.0M-OPEFB. All the adsorbents were then stored in an airtight container to avoid air contact.

2.3 Initial Adsorption Performance (Best Adsorbent) Experiment

Finding the best OPEFB with the maximum Cd (II) removal percentage was the aim of the first adsorption performance experiment. This OPEFB would then be utilized in the subsequent phase of the study, which involved an adsorption study experiment at various pH levels. Using a Thermo Sci 491 Forma Orbital Shaker, 0.01 g of each adsorbent sample that had previously been treated at various NaOH concentrations and immersion times was tested with 100 ml of Cd^{2+} solution. The initial concentration of Cd^{2+} solution, contact time, agitation speed, and process temperature were set at 5 mg/L, 120 min, 150 rpm, and ±25 °C, respectively (Sonal et al., 2020). Every experiment was conducted twice.

2.4 Energy-Dispersive X-ray (EDX) Analysis

The elemental composition of the raw and modified OPEFB was determined using EDX spectrums obtained with a Hitachi TM9000Plus Scanning Electron Microscope (SEM). The number of energy of X-rays emitted from the samples determines their elemental composition.

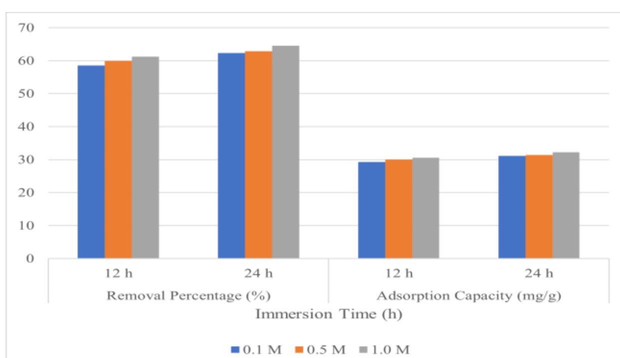
2.5 Effect of pH on Cd (II) Adsorption

To examine how the starting pH affected the treated adsorbent's Cd (II) removal percentage, 0.01 g of the adsorbent was submerged in 100 mL of a solution of Cd (II) ions (5 mg/L) in a 250 mL flask. The duration of this experiment was 120 minutes. The experiment was carried out in a Thermo Sci 491 Forma Orbital Shaker at pH 2, 25°C, and 150 rpm agitation rate. A Whatman 1Ø125 mm filter was used to filter the sample following the experiment. A Shimadzu AA-7000 atomic absorption spectrophotometer with a wavelength of 228.8 nm, an acetylene-air flame, a slit width of 0.7 nm, and a concentration limit of detection of 0.01 ppm was used to determine the final concentration (Martins et al., 2014). The following pH was subjected to the same adsorption experiment protocols as previously described: 4, 6, 8. The pH solutions were changed using 0.01 M NaOH/0.01 M HCl. The pH at which Cd (II) metal ions adsorb best was found. Each trial was conducted in pairs.

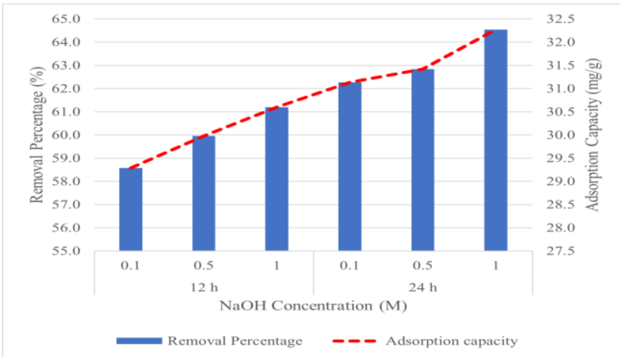
3. Result and Discussion

3.1 Initial Adsorption Performance (Best Adsorbent) Experiment

Adsorption efficiency increases with NaOH concentration, with removal percentages increasing from 58.58% to 61.20% after 12 hours and 62.27% to 64.54% after 24 hours. According to a study by, the -OH moieties in NaOH-treated OPEFB fibre decreased as NaOH concentration increased from 4 w/v% (1.0 M) to 12 w/v% (3.0 M). Higher -OH moieties indicate more active sites for Cd (II) adsorption. Immersion time adds more to the -OH functionalization process than concentration, with at least 24 hours needed for optimal development. Time is crucial for NaOH solution to enter the amorphous phase of OPEFB fibre.



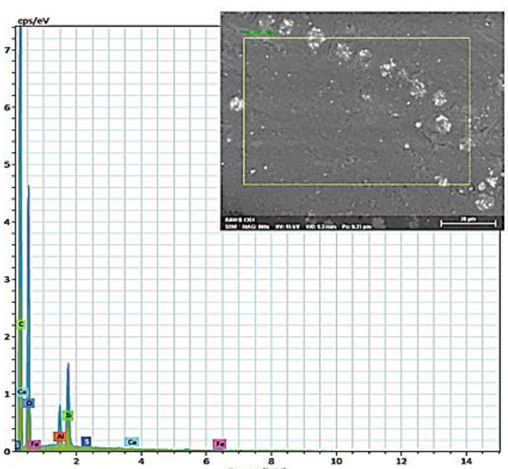
(a)



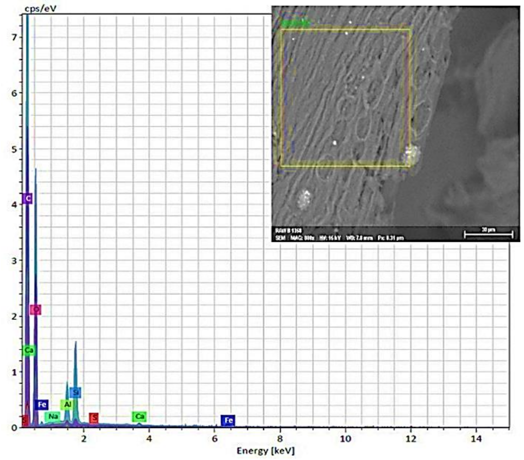
(b)

Fig. 1. Graph of (a) removal percentage/adsorption capacity vs immersion time (b) removal percentage/adsorption capacity vs NaOH concentration

The EDX analysis (Fig. 2 (a)-(d)) revealed that raw biomass primarily contained carbon and oxygen elements. Alkaline treatment increased the O/C ratio by 44.77%, reducing the carbon content of treated OPEFB (Table 2). This resulted in a crosslinked reaction between fiber surface and modifying agents, leading to a higher O/C ratio and more polar oxygen-containing surface functional groups. The EDX spectrum showed Cd (II) presence in both raw and treated OPEFB after Cd (II) adsorption (Ma et al., 2014). In this study, the elemental weight of Cd (II) increased from 0.1010% to 0.1722% which is about a 70% increment after NaOH treatment. NaOH treatment enhances Cd adsorption capacity in lignocellulosic biomass, similar to palm frond carbon and biochars studies, demonstrating increased metal adsorption efficiency (Hammad et al., 2025; Sugawara et al., 2022).



(a)



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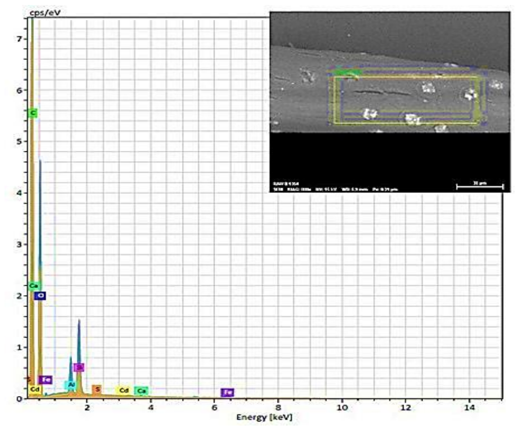

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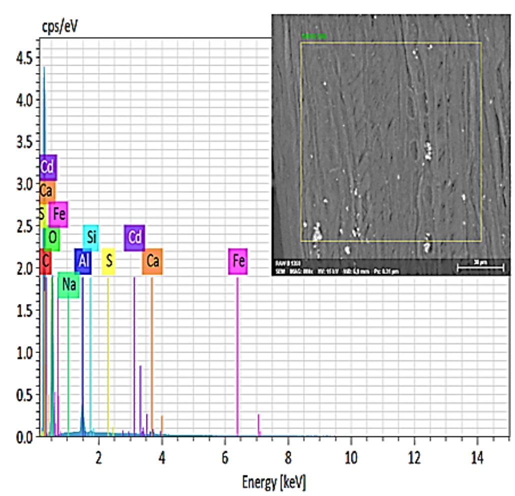

(d)

Fig. 2. (a) EDX spectrum of raw OPEFB before Cd (II) adsorption (b) EDX spectrum of 24h-1.0M-OPEFB before Cd (II) adsorption (c) EDX spectrum of raw OPEFB after Cd (II) adsorption (d) EDX spectrum of 24h-1.0M-OPEFB after Cd (II) adsorption

Table 2. Elemental composition results of EDX analysis

Adsorbent	Element wt.%			
	C	O	Cd	O/C ratio
Raw OPEFB	61.5384	34.1434	0	0.5548
24h-1.0M-OPEFB	54.7969	44.0124	0	0.8032
Raw OPEFB after Cd (II) adsorption	60.9078	37.3484	0.1010	0.6132
24h-1.0M-OPEFB after Cd (II) adsorption	57.0233	40.3995	0.1722	0.7085

3.2 Effect of pH on Cd (II) Adsorption

Fig. 3 shows the optimal starting solution pH for untreated and treated OPEFB is pH 6, with maximal adsorption of 65.2% and 70.8%, respectively. The removal percentage and adsorption capacity of Cd (II) rose with pH, reaching a plateau between pH 6 and pH 7, and then declining slightly at pH 8. The adsorption rate is slower at pH 2 than at pH 6, and the anion becomes the preferable adsorbate for adsorption if the solution pH is less than pH_{pzc}. According to Pineda-Ayala & Durán-Herrera (2019) report from 2019, raw OPEFB has a pH_{pzc} of 6.1. The ideal pH for adsorption is pH 6, where the removal percentage is highest. The adsorption of Cd (II) by rice husk treated with NaOH (Kumar & Bandyopadhyay, 2006) and pineapple waste treated with NaOH (Mopoung & Kengkhetkit, 2016) both revealed a similar observation. Moreover, another study found that the same charges between the adsorbate (Cd^{2+}) and the film adsorbent cause a repulsive electrostatic force, which accounts for the small adsorption capacity at low pH levels (2–5) (Iqhrammullah et al., 2021). A separate study demonstrated that the NaOH treatment improves the adsorption capacity of heavy metals, including cadmium, in biochars derived from plant biomass under optimal pH conditions (Sugawara et al., 2022).

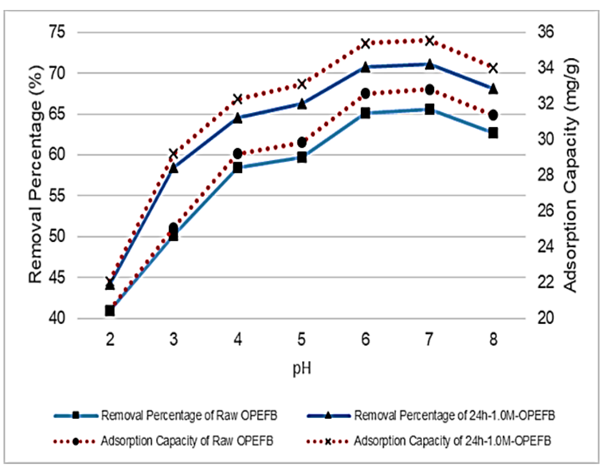

Fig. 3. Effect of pH solution on Cd (II) Adsorption

$$Cd\ (II) + H_2O \leftrightarrow Cd(OH)^+ + H^+ \quad pK_1 = 7.9 \quad (1)$$

$$Cd(OH)^+ + H_2O \leftrightarrow Cd(OH)_2 + H^+ \quad pK_1 = 10.6 \quad (2)$$

$$Cd(OH)_2 + H_2O \leftrightarrow Cd(OH)_3^- + H^+ \quad pK_1 = 14.3 \quad (3)$$

The chemical form of heavy metals in the solution at a certain pH, such as their pure ionic or hydroxyl-metal forms, was linked to the impact of pH on the biosorption capability. Depending on the pH of the solution, cadmium species can be found in aqueous solutions as $Cd(OH)_{2(S)}$, Cd^{2+}, $Cd(OH)_4^{2-}$, $Cd(OH)^+$, and $Cd(OH)_3^-$ (Garg et al., 2008). As shown in Fig. 4, the concentration of the hydrolyzed Cadmium species is related to both the concentration of Cadmium and the pH of the solution (Oyetade et al., 2018). At pH values below 7.9, the metal ions are free metal ions that can be adsorbed; at higher pH values, they exist as hydrolyzed or protonated species. Some recent studies emphasize the crucial role of pH in adsorption efficiency, with optimal performance typically occurring at neutral to slightly alkaline pH levels (Feng & Wang, 2025; Kim et al., 2025; Tayyab et al., 2024).

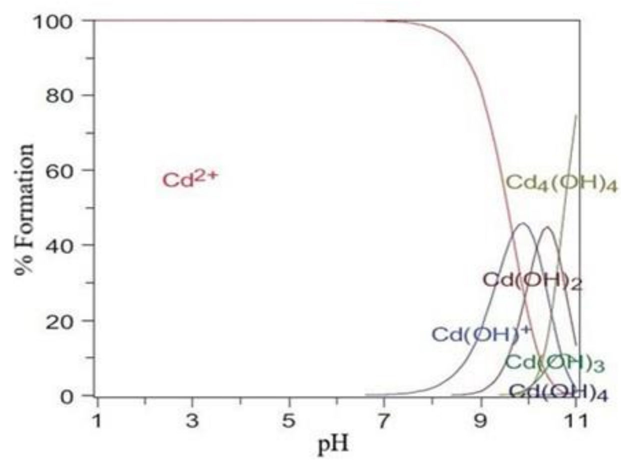

Fig. 4. Distribution of Cd (II) in Solution System as a function of pH

4. Conclusion

The study found that the pH of a solution significantly impacts the adsorption efficiency of cadmium ions onto sodium hydroxide-treated oil palm empty fruit bunch (OPEFB). The optimal pH for maximum adsorption was pH 6, with NaOH-treated OPEFB achieving a removal efficiency of 70.8% with an adsorption capacity of 35.4 mg/g. The energy-dispersive X-ray (EDX) analysis shows a significant increase in the O/C ratio after NaOH treatment, attributed to the removal of lignin and hemicellulose, enhancing adsorption capacity and demonstrating the effectiveness of chemical modification. Increasing the NaOH concentration from 0.1 M to 1.0 M and extending the immersion time from 12 to 24 hours significantly enhanced the removal efficiency of Cd (II) ions. This research suggests that NaOH-treated OPEFB could be a sustainable adsorbent for wastewater treatment. To fully understand the application of the NaOH-modified OPEFB, additional studies are recommended to explore various environmental conditions that could optimize Cd (II) adsorption further.

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Author Contributions: The research study was carried out successfully with contributions from all authors.

Conflicts of Interest: The authors declare no conflict of interest.

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