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Research Article

Effect of NaOH Treated Oil Palm Empty Fruit Bunch (OPEFB) on Adsorption of Cd (II) Under Acidic Condition

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Abstract

Adsorption is an effective way of extracting heavy metal ions from aqueous solutions. Alkali treatment is a chemical modification method that is influenced by concentration and time. The study aims to investigate the effect of NaOH treatment of OPEFB on Cd (II) adsorption under acidic condition. The alkali treatment was done by varying the concentration of NaOH (0.1 M, 0.5 M, and 1.0 M) and the immersion time (12 h and 24 h). SEM images confirmed the existence of pores on the treated OPEFB in comparison with the raw OPEFB. Characterization of treated adsorbent using FTIR resulted in a change of functional groups peak's position such as hydroxyl and carboxyl groups after the alkali treatment, which might involve Cd (II) adsorption. OPEFB treated with 1.0 M NaOH and 24 h immersion time showed the highest Cd (II) removal under acidic condition (pH 4). All the NaOH treated OPEFB showed an increment in adsorption efficiencies compared to raw OPEFB, suggesting that this treated biomass has a potential for application as an adsorbent for the removal of Cd (II) from wastewater

Keywords: Adsorbent, adsorption, cadmium, oil palm empty fruit bunch.

Introduction

As the industry is one of the largest consumers of water, it is necessary to treat wastewater to an appropriate standard before discharging it into waterways or reusing it for a variety of beneficial purposes, and hence, water conservation can also be achieved. In worldwide, over 80% of all wastewater returns to the environment without being treated [1]. An estimated 1.2 million people died as a result of unsafe water sources in 2017. This was 2.2% of global deaths [2]. More than 2 billion people live in countries experiencing high water stress due to the lack of freshwater resources to meet the standard water demand [1].

Cadmium is a non-biodegradable, toxic heavy metal that tends to accumulate in living organisms. The community needs to be aware of the cadmium pollution surrounds them as the cadmium has the chronic potential to cause kidney, liver, bone, and blood damage for long-term effects [3]. About 82% of cadmium consumption was contributed by batteries application, followed by 10% from pigments application, 6% from plating application, 1.5% from stabilizers in polymers application, and 0.5% from the other applications [4]. Due

to regulatory restrictions on the amount of cadmium in effluents, treatment of highly contaminated effluents must be addressed

to reduce cadmium concentration in discharged effluents. The maximum permissible limit of cadmium concentration in discharged industrial wastewater is 0.01 $mg \cdot L^{-1}$ [5].

Malaysia, the second world's largest exporter of palm oil contributes about 34 % of world exports [6]. However, the overall sustainability score of the palm oil industry in Malaysia was only 3.47 out of 5 and this was due to a lack of biomass waste recycling and recovery [7]. The goal of the assessment is to measure how sustainable crude palm oil production in Malaysia by using the Palm Oil Sustainability Assessment (POSA) framework. The sustainability score is calculated based on the rankings of Performance Measures (PMs) for social, economic, and environmental objectives of a common crude palm oil supply chain. In general, about 30-32% of oil palm biomass is from empty fruit bunch (EFB) which has low commercial value and constitutes a disposal problem due to its large quantity. About 69.87 $Mt \cdot yr^{-1}$ of EFB is produced worldwide, 21.61 $Mt \cdot yr^{-1}$ in Malaysia and 5.24 $Mt \cdot yr^{-1}$ in Sarawak, a Malaysian state on Borneo [8]. A typical 60 ton per hour mill will produce around 200 tons of EFB fiber (dry weight). Hence, the huge EFB waste generation in Malaysia is one of the factors that encourages research to utilize this biomass for a variety of additional high-value end-uses such as adsorbents for wastewater treatment.

Some of the main criteria that need to be thoroughly studied before selecting waste as adsorbent are efficiency, capacity, selectivity, regenerability, kinetics, compatibility, and cost. Adsorption efficiency or also known as removal percentage (%) is generally used to evaluate the adsorption performance of adsorbents and this percentage is calculated by subtracting the final metal concentration in solution at the contact time, t, from the initial metal concentration, dividing the difference by the initial metal concentration and then multiplying the result by 100. The low adsorption efficiency of raw agriculture waste can be significantly improved upon modifications.

NaOH treatment uses the alkalization method which is a process of eliminating the lignin, pectin, waxy substances, and natural oils coating the outside surface of the fiber cell wall and thus, increases the reactive functional hydroxyl groups. The process involved is a swelling process that allows more chemicals (NaOH) to penetrate the fiber structure and broke the hydrogen bonds between the cellulose molecular chains. The procedure exposes the fibrils, giving the fibers a rough surface topography, and contributes to the creation of crater holes where they can become interlocking points for compounding with a polymer matrix [9]. EFB contains high cellulose which is 40-43%, 22-25% hemicellulose, and approximately 19-21% lignin. These components provide chemical functional groups which could act as metal-binding sites [10].

In this paper, the effects of NaOH treatment of OPEFB on Cd (II) adsorption under acidic condition were investigated and the best adsorbent was determined based on the highest Cd (II) removal percentage obtained.

METHODOLOGY

Preparation of Raw Materials

The OPEFB fiber was obtained from Felcra Jaya Samarahan Palm Oil Mill Sdn. Bhd., located at Kota Samarahan, Sarawak state of Malaysia. The OPEFB was washed several times using tap water to remove dirt and mud and finally rinsed with distilled water. The sample was dried in an incubated oven (Binder Incubator

BF 56) at 90°C for 24 h. The dried sample was ground using a Glen Creston hammer mill and sieved using a sieve shaker. The $200 < Ø \leq 600$ μm size of OPEFB was then kept in an airtight container until further use.

Preparation of Modifying Agent (NaOH)

40.00 g of NaOH was dissolved up to 1 L of distilled water to produce a 1.0 M NaOH solution. It was then diluted accordingly to produce a NaOH solution of other concentrations (0.1 M and 0.5 M).

Preparation of Cadmium Solution

To prepare 1000 ppm of cadmium stock solution, 2.3049 g of 99% $3CdSO_4.8H_2O$ was dissolved in 1 L of distilled water. The initial solution of 5 $mg{\cdot}L^{-1}$ of Cd (II) was prepared by proper dilution from the stock solution. The initial pH of the solution was adjusted to pH 4 for all batch adsorption experiments.

Treatment of OPEFB Adsorbent

12.5 g of OPEFB fibers were immersed in a series of 0.1 M, 0.5 M, and 1.0 M NaOH solutions (500 mL) at room temperature. Each of the concentrations was categorized into two sets corresponding to immersion times of 12 and 24 h in a 1 L glass beaker. The fibers were then filtered from the NaOH solution and washed with deionized water until the filtrate wash solution reached pH 7. The fibers were dried in an oven at 80 ^oC for 48 h and stored in an airtight container until further use to avoid air contact.

Batch Adsorption Experiment

To evaluate the adsorption efficiency of the prepared adsorbents, 0.01 g of each adsorbent was equilibrated with 100 mL of 5 $mg{\cdot}L^{-1}$ Cd (II) ions solution in a 250 mL flask, respectively, for 120 min. The experiment was conducted in the physical settings of pH 4, the temperature of 25 ^oC, agitation rate of 150 rpm using a Thermo Scientific refrigerated incubating shaker. At the end of the contact time, the equilibrated mixture was filtered via Whatman 1 Ø 125 mm filter paper [11]. The final concentration was determined by atomic absorption spectrophotometer (Shimadzu AA-7000) using an acetylene-air flame, 228.8 nm wavelength, 0.7 nm slit width, < 0.01 ppm concentration limit of detection.

The removal percentage (%) was calculated using (1):

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C_0 ($mg{\cdot}L^{-1}$), and C_t ($mg{\cdot}L^{-1}$) are the initial and final metal concentrations at the contact time, t, respectively.

Scanning Electron Microscopy (SEM) Analysis

The surface morphology of the raw and treated OPEFB fibers was studied using a Jeol JSM–6390LV scanning electron microscope with an accelerating voltage of 15 kV at a magnification of 800x.

Fourier Transform Infrared (FTIR) Analysis

The FTIR analysis of the raw and treated OPEFB fibers was carried out using a Shimadzu IRAffinity-1 FTIR Spectrophotometer with a resolution of 4 cm^{-1} in the range of 400-4000 cm^{-1} and potassium bromide (KBr) as a standard. Before analysis, the samples were mixed with KBr and the mixture was pressed as a transparent pellet.

Results

The Effect of Different NaOH Treatment of OPEFB on Cd (II) Removal

In this experiment, three levels of NaOH concentration (0.1 M, 0.5 M, and 1.0 M) with different immersion times (12 h and 24 h) were used to treat OPEFB, and their effects in removing Cd (II) were compared in Fig. 1.

It was noticed that all treated OPEFB improved the adsorption efficiency of Cd (II) onto the adsorbents. The Cd (II) removal percentage was increased as NaOH concentration increase for both immersion times. For example, at 12 h immersion time, the adsorption efficiency of 0.1 M, 0.5 M, and 1.0 M adsorbents were by 58.58%, 59.96%, and 61.20%, respectively. As immersion time increases to 24 h, the adsorption efficiency of 0.1 M, 0.5 M, and 1.0 M adsorbents were also increased to 62.27%, 62.83%, and 64.54%, respectively.

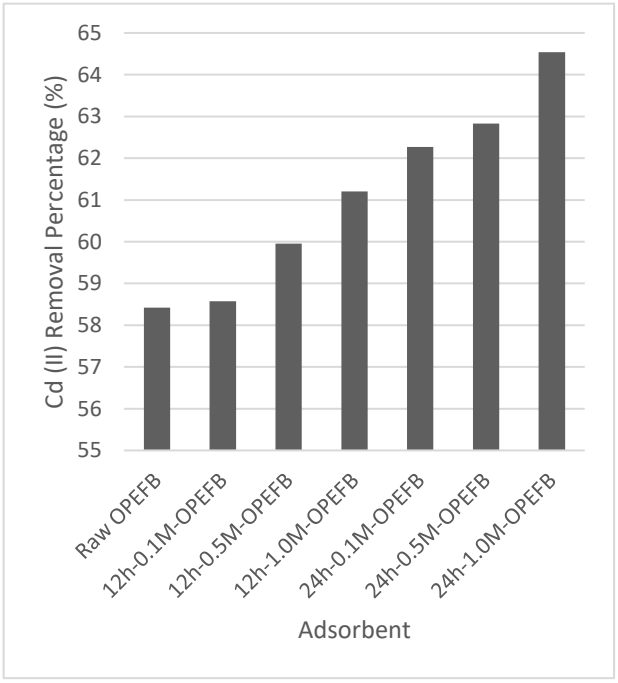

Fig. 1. Cd (II) ions removal percentage by different NaOH treatment condition adsorbents (conditions: adsorbent dose = 0.01 g per 100 ml solution, adsorbate concentration = 5 $mg \cdot L^{-1}$, pH = 4, contact time t = 2 h, temperature T = 25 ∘C, and stirring rate = 150 rpm)

According to a study by [12], when it comes to the -OH functionalization process, immersion time contributes marginally more than concentration. To allow for the optimal formation of -OH moieties, at least 24 hours had to pass. 24h-1.0M-OPEFB showed the highest removal percentage in Cd (II) adsorption, which was 6.1% higher than that of raw OPEFB. The results indicate a performance that is similar to the performance of NaOH treated wheat straw in a similar study conducted by [13]. According to the study, an increase from 1% to 4% NaOH concentration increased the heavy metal adsorption but the continual increment of NaOH concentration from 5% to 50% had caused a relatively large drop in heavy metal adsorption. This is because the massive concentration of NaOH resulted in violent hydrolysis of the wheat straw, and the important adsorption component of cellulose in wheat straw was decomposed.

Guo et al. [13] found out also that heavy metal removal percentage had improved as immersion time increased to 24 h. As the immersion time increased to 48 h, the heavy metal adsorption decreased. As a result, it can be assumed that NaOH immersion time should not exceed 24 hours, as after this time, caustic effects from the alkaline solution begin to occur, causing EFB fiber degradation and thus lowering the -OH presence [12]. Therefore, the result of optimal NaOH treatment in this study was 1.0 M of NaOH concentration and 24 h of immersion time.

At low pH, the hydrogen ions in the solution competing with the cadmium ions for sorption sites. As the adsorbed H^+ increased, the number of negative charges on the surface of the treated OPEFB decreased. This may increase the electrostatic repulsion between the adsorbent and positively charged adsorbate. At a higher pH value, the quantity of H^+ in the solution decreased, the adsorption competition reduced, and more negative charges on the surface of the treated OPEFB for better adsorption of Cd (II). However, when the pH is >7, Cd (II) will start to precipitate according to the solubility product constant K_{sp} (1.42×10^{-20}).

SEM Analysis

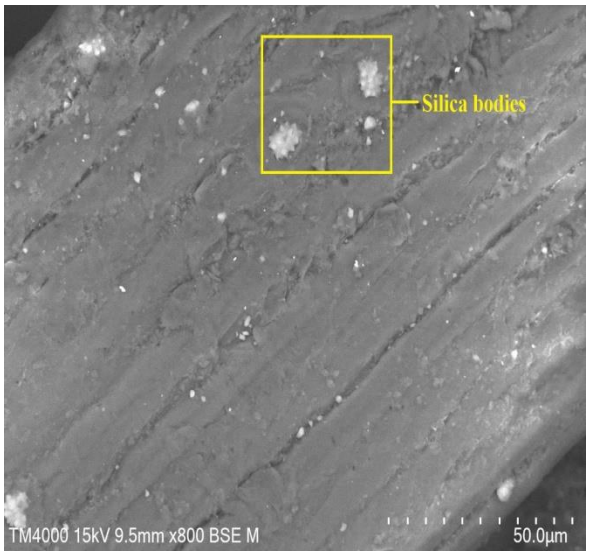

Fig. 2. SEM image of raw OPEFB

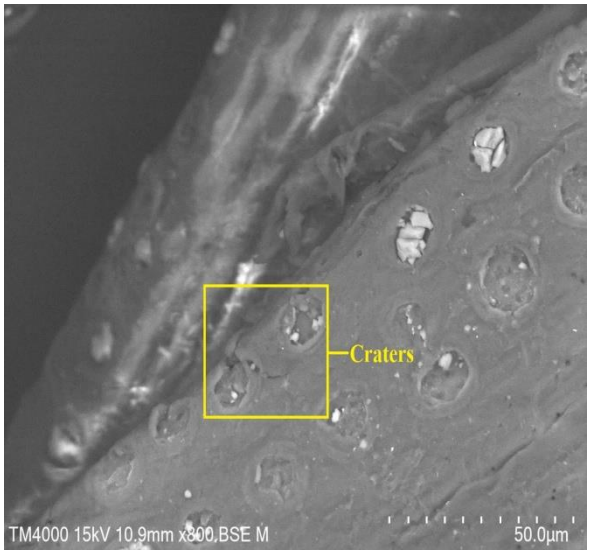

Fig. 3. SEM image of treated OPEFB

Fig. 2 and Fig. 3 show the SEM image of raw OPEFB and treated OPEFB fibers, respectively. Fig. 2 revealed that the surface morphology of the raw OPEFB fiber was smooth as it was covered by wax layers, deposited impurities, fatty substances, and silica bodies. Fig. 3 represented the surface morphology of the treated OPEFB fiber that was rough and the presence of uniform craters can be observed clearly as most of the impurities were removed. Some silica bodies in the crater hole as shown in Fig. 3 remained as spotted on the fiber surface but most of it had been removed. This formation of crater holes can increase the number of possible reaction sites and contact areas between OPEFB fibers and the adsorbate [12].

FTIR Analysis

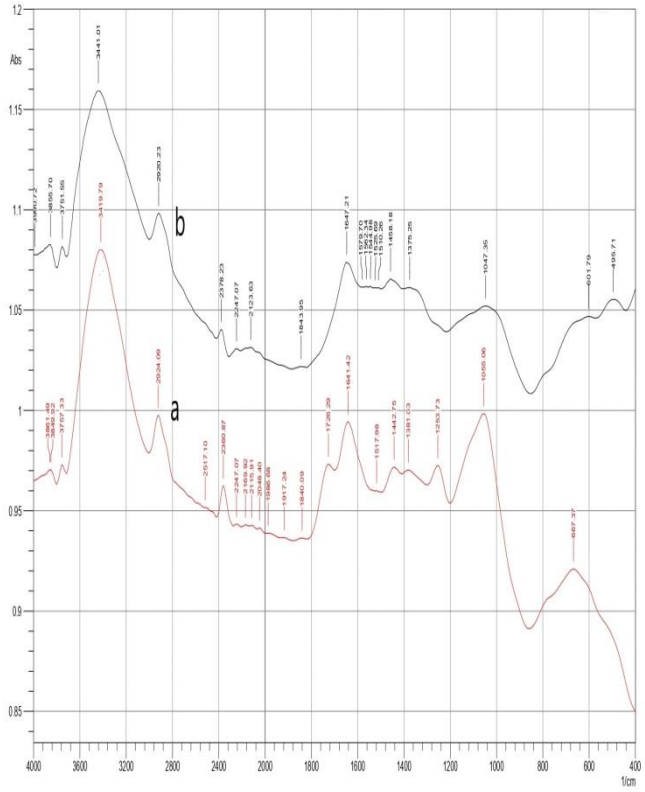

Fig. 4. FTIR spectra of raw OPEFB (a) and treated OPEFB (24h-1.0M-OPEFB) (b)

Table 1. The wavelength range of different groups

Wavelength range, cm^{-1}	Adsorbent		Groups
	Raw EFB	24h-0.1M-OPEFB	
3600 - 3200	3419.79	3441.01	O–H stretching vibration
2930 - 2850	2924.09	2920.23	C–H stretching
1738 - 1717	1726.29	-	C=O stretching
1648 - 1620	1641.42	1647.21	C=C C=O
1432 - 1319	1381.03	1375.25	C–H bending vibration
1264 - 1035	1055.06	1047.35	C–O stretching
897 - 665	667.37	-	C–H bending

The FTIR was used to analyze the functional groups on raw OPEFB and treated OPEFB (24h-1.0M-OPEFB). As shown in Fig. 4, it was found that the peak shape and intensity of raw OPEFB (a) and treated OPEFB (b) were very similar, but the positions of peaks were changed. According to the peak position of each adsorbent listed in Table 1, the peaks altered after treatment were hydroxyl and carboxylate probably resulted from NaOH treatment. This result is consistent with those found by [14] and [15]. The hydroxyl and carboxyl groups have been reported to be the main functional groups responsible for the adsorption of heavy metals. Peak observed at 1253.73 cm^{-1} for raw EFB suggesting C-O-C stretching vibration of aromatic ether linkages which indicated the presence of lignin. This peak was no longer present after alkali treatment.

The intensities of the broad -OH band can be used to describe the population of hydroxyl moieties of the cellulose structure itself. For example, -OH band intensities at 3335 cm^{-1} for the raw and treated OPEFB were 1.0646 a.u. and 1.1431 a.u., respectively. For the treated adsorbent, hydroxyl moieties within the cellulose structure have increased. This means that the treated OPEFB has a higher amount of hydroxyl moieties for Cd (II) adsorption compared to raw OPEFB. This may be due to the formation of more -OH groups as a result of the breaking of crosslinks between lignin and hemicellulose with cellulose after alkali treatment. Generally, the concentration of NaOH used for alkalization had a significant impact on the amount of -OH present after treatment. At low concentrations, the volume of sodium hydroxide hydrates ($NaOH.xH_2O$) produced is larger, which can induce fiber swelling by entering the amorphous phase of the fiber. As the concentration of NaOH rises, the hydrate volume decreases, resulting in less swelling but have the potential to reach the crystalline phase and then alter the crystal structure [12].

There was a relative change in the spectral intensities of the carboxyl group in the raw and treated OPEFB which can be seen at the wavelength range of 1648–1620 cm^{-1} (carboxylate) and 1738–1717 cm^{-1} (ester). A band at 1726.29 cm^{-1} of raw OPEFB attributed to C=O stretching in the ester linkages of carboxylic groups of the ferulic acid and ρ-coumaric acids of lignin. Hydroxyl ions from NaOH converted the ester in the OPEFB fiber to carboxylate, which can bind Cd (II) [14]. The peak was dominant in the raw OPEFB but became diminished after alkalization. Thus, because high concentrations of NaOH (1.0 M) were used for the alkali treatment, the amount of ester in the OPEFB fiber was reduced while the amount of carboxylate was increased. This can be proved by the increment of carboxylate moieties at 1620 cm^{-1} of the treated OPEFB which was 1.0680 a.u. as compared to raw OPEFB (0.9879 a.u.). Therefore, it can be concluded that the amount of oxygen-containing functional groups such as hydroxyl and carboxyl groups have a great impact on Cd (II) adsorption.

Conclusion

The chemical treatment OPEFB by NaOH surface modification has a significant effect in removing Cd (II) compared to raw OPEFB. OPEFB that was treated with 1.0 M NaOH for 24 h showed the highest Cd (II) removal with an efficiency of 64.54%. The higher Cd (II) adsorption was attributed to effective surface modification of negatively charged hydroxyl and carboxyl that can be proved by FTIR analysis and the formation of crater holes as in SEM analysis. This study proved that chemical modification through NaOH treatment generally improved the removal percentage of OPEFB due to a higher number of active binding sites after treatment that favored Cd (II) ion sorption. The determination of optimum conditions for Cd (II) adsorption using NaOH-treated OPEFB would be the task that needed further study by varying environmental conditions such as adsorbent dosage, contact time, initial concentration, and temperature

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