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Review

Oil palm biomass-based activated carbons for the removal of cadmium—a review

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Abstract: Serious water pollution due to climate change as the consequences of non-ecological wastewater treatment and unsustainable agricultural activities had emerged water scarcity problem. The utilization of oil palm biomass into cadmium adsorbent could play a role in killing two birds with one stone, which is to solve the oil palm biomass disposal issue and cadmium pollution issue. The adsorbent modifications discussed in this review focused on furnace heating and microwave heating as well as the combined methods with chemical activating agents. Among the modification methods, the output of chemical activation followed by microwave-induced irradiation of palm kernel shells (PKS) produced activated carbon with high specific surface area (854.42 m^2/g) and high adsorption capacity, q_{max} (227.27 mg/g). This review is to provide a comprehensive understanding of cadmium adsorption mechanisms and up-to-date progress of modification technologies for different types of oil palm biomass.

Keywords: adsorption; activated carbon; oil palm biomass; cadmium

1. Introduction

Water quality worldwide is degrading gradually due to industrial wastewater and unsustainable agricultural activities which affected around one-tenth of all river stretches in Latin America, Africa, and Asia with severe and moderate salinity pollution (fertilizer runoffs, stormwater runoffs, and urban wastewater discharge). As in a report published by The United Nations Educational, Scientific and Cultural Organization (UNESCO) in 2020 entitled "Water and climate change", the quality of freshwater system is one of the consequences of climate change and this problem can be solved using some mitigation measures. These included pollutant discharge reduction through ecological wastewater treatment and source pollution reduction actions from the economic and domestic sectors which are the main wastewater generators [1]. Another organization that works towards climate policies since 1990 is European Union (EU) that had introduced the latest 2050 European Green Deal plan which not only focusing on 'water goal' itself but also reinforcing energy efficiency and renewable energy through the sustainable industry. According to the plan, EU has introduced some strategies to achieve their 2050 climate-neutrality target such as the 2030 Climate Target Plan as presented in 17 September 2020 as a prudent pathway to climate neutrality by 2050 which requires greenhouse gas emissions reduction target of at least 55% by 2030. As in Malaysia, the country continued its commitment to achieving the 2030 Agenda and the Sustainable Development Goals (SDG) implementation programs are monitored by the National SDG Council. Currently, Malaysia is in the execution process of the SDG Roadmap Phase 2 (2021–2025) for the 2030 Agenda achievement.

One of the pollutants that is still becoming a hot topic in the scientific review is cadmium; about 54735 scientific articles had been published and listed on the PubMed.gov website during 2021. Cadmium ranks seventh on the top of 20 toxic chemicals priority list and top 10 chemicals of major public health concern. For short-term effects, cadmium can cause nausea, vomiting, diarrhea, muscle cramp, sensory disturbances, liver injury, convulsions, shock, and renal failure. Meanwhile, cadmium can cause kidney, liver, bone, and blood damage for long-term effects [2]. Due to the regulatory restrictions on the amount of cadmium in effluents, effluent treatment must be addressed to reduce the cadmium concentration before discharging. "Ecological" wastewater treatment is desired as the conventional techniques for the heavy metal's removal such as electrocoagulation, ion-exchange, chemical precipitation, and photocatalysis are known to have disadvantages like high operation cost, high energy requirement, and generation of toxic sludge. Researchers have recently shown an increasing interest in adsorption technology because the system reduces energy consumption, improves yield, selectivity, and non-toxic sludge production. Adsorption is the physical adhesion or bonding of molecules (or ions) to another substance's surface, that is, to a two-dimensional surface [3].

A lot of agricultural waste is produced annually such as oil palm waste which is generated in millions of tons every year from Malaysia, Indonesia, Cameron, Africa, China, and Nigeria. Malaysia contributes 34% of palm oil world exports and produces approximately 168 Mt of biomass annually. Of this, over 80 Mt of solid biomass is generated by the palm oil industry whereby only 10% of oil palm biomass was utilized in 2015 for wood and bioenergy industries [4]. The rest of the biomass is left lying in the palm oil estate and vicinity of the mill, thus sacrificed its future economic value and usefulness. Therefore, there is a huge urgency to tackle this problem by finding alternate applications for biomass, such as utilization as adsorbent. Meanwhile, sustainable agriculture consumption and production are required as ways to reduce the source of water pollution.

Some main criteria need to be thoroughly studied before selecting waste as an adsorbent which are capacity, selectivity, regenerability, kinetics, compatibility, and cost. Adsorption capacity is the most critical characteristic of an adsorbent and it is defined as the amount of adsorbate taken up by the adsorbent, per unit mass or volume of the adsorbent. The capacity of adsorption is very importance to the cost of capital since it determines the amount of adsorbent required. The low adsorption capacity of raw agriculture waste can be significantly improved upon modifications.

In this literature review, the adsorption process by different types of palm oil biomass will be discussed with an evaluation of different types of adsorbent modification methods used.

2. Cadmium pollution in Malaysia

In Malaysia, the Langat River cadmium concentration of 1.22 ± 0.88 µg/L surpassed the limit of the continuous concentration criterion of 0.72 µg/L as set down in the United States Environmental Protection Agency (USEPA) and the annual average concentration of 0.2 µg/L as set down in the European Commission Standard. Electroplating, paint pigment, battery, smelting, mining, fertilizer, and alloy industries are among the industries that are responsible for the discharge of huge quantities of cadmium into the environment.

In Sarawak, a Malaysian state on Borneo, the majority of edible aquatic organisms such as mollusc and cockles have also surpassed both limits as shown in Table 1. This is quite alarming for the community to beware of the cadmium pollution that surrounds them as cadmium has detrimental impact on human health through build-up of Cd in human body through human food chain.

Table 1. Cadmium concentrations in the edible aquatic species from various rivers in Sarawak.

Location	Aquatic species	Cadmium (mg/kg)	Malaysia Food Act 1983/FAO/WHO (mg/kg)	Remark
Estuary area of Sarawak river [5]	Mollusc (*Polymesoda expansa, Meretrix meretrix, and Solen regularis)*	1.15–2.35	1.00/0.05	Exceeded the limit standard
Moyan [6]	Razor clam (*Solen regularis*)	0.7		Exceeded the FAO/WHO limit standard
Serpan [6]	Razor clam (*Solen regularis*)	0.6		Exceeded the FAO/WHO limit standard
Miri coast [7]	Shrimp *(Harpiosquilla harpax, Acetes indicus, Parapenaeopsis sculptilis, Litopenaeus vannamei, Penaeus merguiensis)*	0.12–2.10		Exceeded the limit standard
Village of Sambir, village of Tambirat, Beliong temple, and village of Tanjung Apong [8]	Cockles (*Anadara granosa*)	1.35–2.22		Exceeded the limit standard

3. Oil palm biomass

Six main types of oil palm biomass are generated as by-products of the palm oil industry which are oil palm mill effluent (POME), empty fruit bunches (EFB), oil palm fronds (OPF), palm kernel shells (PKS), oil palm trunks (OPT), and mesocarp fiber (MF). Other types of oil palm biomass including palm oil fuel ash (POFA), oil palm decanter cake (OPDC), and palm kernel cake (PKC). Currently, this biomass is used to produce wood products (plywood, flooring, and medium-density fiberboards (MDF)), bioenergy (co-firing at mills), fertilizer, animal feed, and palm pellet biomass as an ideal fuel to substitute other types of fossil fuel such as coal, firewood, and lignite. Other incoming technologies planning that is still in the development stage were set for biofuels, bioethanol, and bio-based chemicals. However, the real business was only utilized about 10% of total oil palm biomass in Malaysia, and a majority of the 90% balance is left unattended in the plantations and thus creates a disposal problem [4].

Oil palm biomass generated as shown in Table 2 is calculated based on the ratio of total wet basis of EFB, PKS, POME, and PKC to FFB extraction rate as in a study by Hamzah et al. [9]. These biomasses are produced daily and more consistent in term of supply compared to oil palm trunks which are mostly available during replanting while fronds can be obtained from the pruning activity. Therefore, the total amount of biomass generated worldwide is estimated at 379.5 Mt based on 317.57 Mt of FFB processed in 2017. Meanwhile, Malaysia and Sarawak generated about 120.7 and 29.37 Mt of oil palm biomass in 2019, respectively. POME contributes the largest number which is about 56% of total oil palm biomass in Malaysia. Malaysia is struggling to manage the biomass waste recycling and recovery biomass disposal issues due to this huge number of agricultural residues generated annually.

Table 2. Estimation of total oil palm biomass generated in worldwide, Malaysia, and Sarawak.

Aspect	Standard biomass to FFB extraction rate (wet basis)	Worldwide	Malaysia	Sarawak	References
Area (Mha)	-	21.09	5.9	1.59	[10]
Total palm oil mills	-	800	452	81	[11]
FFB yield (Mt/yr)	-	317.57	101	24.7	[10]
Crude palm oil (CPO) (Mt/yr)	1 t of CPO: 5 t of FFB	63.51	19.86	4.24	-
EFB production (Mt/yr)	22% of FFB	69.87	22.22	5.28	-
OPF production (Mt/yr)	36.7 t/(ha yr)	774	216.53	58.35	-
PKS production (Mt/yr)	5.5% of FFB	17.47	5.56	1.36	-
POME production (Mt/yr)	67% of FFB	212.77	67.67	16.55	-
OPT production (Mt/yr)	9.2 t/(ha yr)	194.03	54.28	14.63	-
MF production (Mt/yr)	13.5% of FFB	42.87	13.64	3.33	-
PKC production (Mt/yr)	1 t of PKC: 4 t of FFB	79.39	25.25	6.18	-
Estimates of total biomass generated (total wet basis of EFB, PKS, POME, and PKC) (Mt/yr)	-	379.5	120.7	29.37	-

Oil palm biomass residues are lignocellulosic materials that largely comprised of cellulose, hemicellulose, and lignin. Table 3 shows the lignocellulosic content of different types of oil palm biomass compared to the percentage content in cellulose standard.

Table 3. Chemical composition of different types of oil palm biomass and cellulose standard.

Type of biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
EFB	23.70–38.30	21.60–35.30	22.10–29.20	[12],[13],[14]
OPF	39.50–40.01	29.80–30.78	23.30–29.50	[12],[13]
PKS	20.50–27.70	21.60–22.70	44.00–51.50	[12],[13],[14]
OPT	30.60–34.44	23.94–33.20	28.50–35.89	[12],[13]
Cellulose standard	80.8	16.6	2.6	[15]

OPF contained the highest cellulose, 40.01% and higher percentage of these components provide higher number of chemical functional groups that could act as metal-binding sites. Cellulose is by far the most abundant resources of biopolymer that not only can be found in plant resources such as cotton and wood. These polymers of carbohydrate consist of tens to hundreds to several thousands of monosaccharide units (glucose). Depending on the source, age, growth stage, climatic conditions, and others, the composition of different lignocellulose materials varies significantly [15].

4. Raw oil palm biomass as cadmium adsorbent

The raw oil palm biomass adsorbents and the cadmium adsorption studies are summarized in Table 4. All studies were using single system, which means only one component adsorbate in an adsorption process, and this solution was prepared from metal ion stock solution. According to the Table 4, PKS showed the highest removal percentage of cadmium, 84.23% with q_{max} = 42.12 mg/g compared to other types of oil palm biomass listed. The high fixed carbon (18.09%) and very low ash contents of PKS (5.64%) signify that this biomass is suitable for the usage in the production of adsorbents. The optimum operating conditions of the study were at pH 6, adsorbent dosage of 1.5 g per 100 mL cadmium solution, initial concentration of 5 ppm, and contact time of 90 min [16]. The adsorption studies showed that the PKS was following the Freundlich model that assumes multilayer adsorption occurred on the surface of the adsorbent and also followed the pseudo-second-order model that assumes chemisorption is the main adsorption mechanism.

Table 4. The raw palm oil biomass adsorbents and the cadmium adsorption studies.

Biomass type	Specific surface area (m^2/g)	Adsorption studies			References
		Isotherm	Kinetics	Removal percentage (%)	
PKS	-	Freundlich	Pseudo-second-order	84.23	[16]
EFB	-	-	-	56.85	[17]
PKS	-	-	-	55.49	[17]
OPDC	2.74	-	-	43.95	[18]
POME	-	Freundlich	-	-	[19]
MF	248.42	-	Pseudo-second-order	-	[20]

There was a finding by Amaludin [17] that showed the cadmium removal percentage of raw EFB, raw PKS and commercial adsorbent (Amberlite XAD-16, Rohm and Haas Company) were 56.85%, 55.49%, 55.03%, respectively, and thus indicated that oil palm biomass is comparable to

Amberlite XAD's in terms of cadmium removal percentage. The cadmium removal percentage from the study conducted by Baby et al. [16] was higher (84.23%) than the finding from Amaludin [17] (55.49%) that is due to some different environmental factors that had not been optimized during the adsorption process. For example, for particle size, Baby et al. [16] used PKS powdered type whereas Amaludin [17] used 0.5–1.0 mm of particle size. As particle size decreases, specific surface area increases, resulting in the increment of the saturation adsorption per unit mass of the adsorbent and thus increase the removal percentage of cadmium.

Nevertheless, overall, the adsorption capacity of raw biomass is comparatively low and this natural material needs to undergo chemical as well as physical activation to develop a highly porous surface to increase the adsorption capacity so that it can compete with other conventional adsorbents in the market. Said et al. [21] had converted male oil palm flowers (MOPF) into hydrochar through physical activation (hydrothermal carbonization) and investigated its BET surface area. It was found that a higher surface area (5.30 m^2/g) was observed for the hydrochar than for the raw MOPF (1.28 m^2/g) because the carbonization process strongly affected the porosity of hydrochar-based porous carbon by removing some organic compounds and thus opened the material's pores, increasing the binding sites for appropriate interaction with adsorbate substances. In conclusion, the low adsorption capacity of raw palm oil biomass can be improved upon modifications. Section 5 below shows a review of the physical modification of palm oil biomass methods which were furnace heating and microwave heating as well as the combination of these methods with chemical modification methods in term of adsorption capacity.

5. Review on adsorption of cadmium through different types of oil palm adsorbent modification

The adsorbent modifications discussed in this section focused on furnace heating and microwave heating as well as the combined methods with chemical activating agents. Figure 1 schematizes the synthesis routes to activated carbons from oil palm biomass. Physical and chemical activation are the most common methods for producing activated carbon.

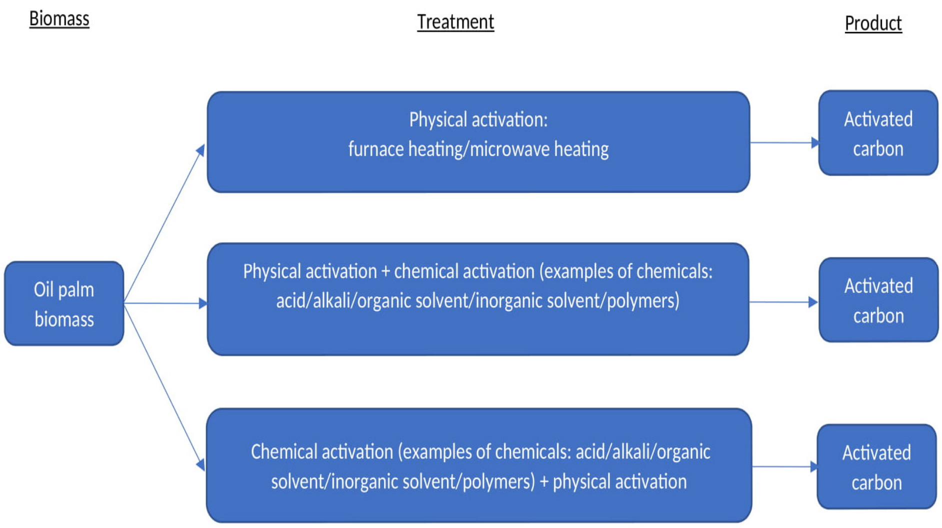

Figure 1. The synthesis routes to activated carbons from oil palm biomass.

5.1. Furnace heating

Furnace heating processing is a process in which the source of heat comes from outside and is transferred by convection, conduction, or radiation into the particles in the absence of oxygen. The sample is heated starting from the surface, then only the heat is transferred to the inner part [22]. The furnace heating modified biomass adsorbents and the adsorption studies are summarized in Table 5. In this method, the pyrolysis was done at fixed values of temperature, heating rate, and holding time. All of the adsorption studies listed in Table 5 used batch mode and synthetic cadmium solution as the single system except for Aziz et al. [23] who used both batch and continuous mode for adsorption studies. According to the table, POS shows the highest adsorption capacity, 38.61 mg/g with 98% of cadmium removal compared to other types of oil palm biomass listed. According to Goh et al. [24], it is acknowledged that the chemical properties of POS biochar prepared at a low temperature significantly affect cadmium adsorption. Surface functional groups were the dominating factor at low temperature while the surface area is the dominating factor at a higher temperature. Moreover, the product quality of charcoal resulting from pyrolysis by flowing nitrogen gas continuously is relatively higher than without flowing nitrogen gas into the reactor. This is what had been done by Goh et al. [24], purging the nitrogen gas continuously (500 mL/min) to minimize the amount of oxygen present and enters the reactor during pyrolysis.

Table 5. The furnace heating modified biomass adsorbents and the adsorption studies.

Biomass	Modification condition			BET	Adsorption studies			References
	Heating rate (ºC/min)	Temperature (ºC)	Time (h)	surface area (m^2/g)	Isotherm	Kinetics	q_{max} (mg/g)	
OPDC	10	500	1	27.27	Langmuir	Pseudo-second-order	24.30	[25]
EFB	-	300–350	-	46.32	Langmuir	-	15.1515	[26]
POFA	-	250	24	206.577	Langmuir	Pseudo-second-order	15.823	[27]
POFA	-	250	24	206.58	-	Bed depth service time (BDST)	34.9	[23]
POS	15	400	1.5	16.3	Langmuir	Pseudo-second-order	38.61	[24]

Given the fact that the adsorption processes for wastewater purification can be carried out either discontinuously, in batch reactors, or continuously, in fixed-bed columns, the performance of the adsorbent should be evaluated in both batch and column studies. Aziz et al. [23] had conducted cadmium removal by POFA using batch and column system and the findings showed that the adsorption capacity in continuous mode (34.9 mg/g) was higher than the batch mode (15.823 mg/g). This showed that column study is more preferred than batch study. A similar finding had also been found in the experiment of cadmium removal by activated charcoal from neem leaf powder [28]. However, checking the practicality of the adsorbent in continuous mode is important due to the lack of column study data that is usually attributed to the fact that adsorption in fixed-bed columns does not necessarily operate under equilibrium conditions since the contact time is not sufficiently long for the attainment of equilibrium.

Overall, the adsorption studies showed that most of the biomass was following the Langmuir model that assumes monolayer adsorption occurred on the surface of the adsorbent. The biomass also followed the pseudo-second-order model that assumes chemisorption is the main adsorption mechanism.

5.2. Combined furnace heating followed by chemical activation

Activated carbon can also be made through two steps, namely pyrolysis and activation or also known as impregnation. As the pyrolysis process is conducted in the absence of oxygen and other chemicals, impregnation is the treatment of physically activated carbon using chemical activators such as acids, bases, or salts and heated in an inert space. The impregnation treatment aims to enlarge the pore by breaking the hydrocarbon bond or oxidizing the surface molecule so that the activated carbon is changing in either its physics or chemistry as a larger surface area will increase the adsorption capacity [29].

The combined furnace heating followed by chemical activation modified biomass adsorbents and the adsorption studies are summarized in Table 6. In this method, the pyrolysis was done at fixed values of temperature, heating rate, and holding time and chemically activated afterwards using chemicals such as sodium hydroxide and hydrochloric acid. All of the adsorption studies listed in Table 6 used batch mode and synthetic cadmium solution as the single system except for Fuadi et al. [30] who used continuous mode and simulated wastewater containing heavy metals such as cadmium, zinc, nickel, chromium, vanadium, and lead for adsorption studies. According to the Table 6, PKS treated with NaOH showed higher adsorption capacity compared to PKS treated with liquid smoke at the same range of physical activation temperature. There are various content of organic acids in liquid smoke and acetic acid is the organic acid that has an important role in liquid smoke [31]. Indeed, alkali modified adsorbent has a larger surface area, a higher ratio of surface aromaticity (H/C), higher N/C ratio with a lower value of O/C as compared to acid-modified adsorbent. Both studies had a good agreement with Langmuir isotherm and Pseudo-first-order that assumes physisorption is the main adsorption. In contrast, adsorption studies from the adsorbent that was subjected to pyrolysis and chemically activated using hydrochloric acid (HCl) conducted by Ujile and Okwakwam [32] in the petrochemical plant effluent treatment showed that the second-order kinetic constants cadmium contaminant was 49.6 g/(min mg) and chemisorption is the main adsorption mechanism. This technique was also found to remove 90% cadmium.

Table 6. The combined furnace heating followed by chemical activation modified biomass adsorbents and the adsorption studies.

Biomass	Physical activation condition		Chemical activation condition		Surface area (m^2/g)	Adsorption studies			References
	Temp. (°C)	Time (h)	Agents	Immersion time (h)		Isotherm	Kinetics	q_{max} (mg/g)	
PKS	380	-	0.1 M NaOH	24	-	Langmuir	Pseudo-first-order	22.37	[33]
PKS	300–400	3	Liquid smoke (acetic acid)	24	-	Langmuir	Pseudo-first-order	14.81	[31]
PKS	500	5	Acetone and benzene	24	-	-	-	-	[30]
EFB	600–800	-	HCl	-	691.85	BET	Pseudo-second-order	-	[32]

Fuadi et al. [30] had conducted a comparison experiment between physically modified and combined physical and chemical modified palm shell activated carbon on cadmium removal in simulated wastewater using a continuous system. The results showed that the combined physical and chemical treatment using acetone and benzene exhibited a good adsorption capacity with a lower area under graph which represented a lower amount of cadmium left after adsorption compared to physical treatment only. Organic solvents are used over the years as surface modifiers in the adsorption process. Acetone and benzene are the examples of an organic solvent which are carbon-based solvents that have a C–H bond in their structure. The organic agents are capable to introduce several species that are needed for metal ions and dye molecules to be adsorbed. However, because of their high cost, safety, and lack of stability, the practical application of organic agents may get limited.

5.3. Combined chemical activation followed by furnace heating

Activated carbon from the palm kernel shells (PKS) was prepared by Rosmi et al. [34] and Kwasi Opoku et al. [35] using chemical activation followed by the furnace heating method as shown in Table 7. In this method, the biomass was chemically activated at first using chemicals such as phosphoric acid, potassium carbonate, and sodium bicarbonate and later, pyrolysis was done at fixed values of temperature and holding time. Rosmi et al. [34] used batch mode and synthetic cadmium solution as the single system whereas Kwasi Opoku et al. [35] used filter beds system and lubricating oil containing heavy metals such as Cu, Fe, Zn, Cd, Pb, Cr, and Mg for adsorption studies. It was found that both adsorbents had the BET surface area in the range of the most common values of chemical activated carbons (600 to 1000 m^2/g) [35]. The adsorption studies showed that both PKS adsorbents were following the Langmuir model that assumes monolayer adsorption occurred on the surface of the adsorbent. Kinetics study by Rosmi et al. [34] showed that the adsorption system followed the pseudo-second-order model that assumes chemisorption is the main adsorption mechanism and the adsorption study showed that only 30% of cadmium can be removed with a low adsorption capacity (0.1576 mg/g). The acid modification is mainly affected by the impregnation ratio, activation temperature, and time. The prolonged activation time might have damaged the pores developed earlier and therefore the cadmium adsorption capacity decreased. An optimum impregnation ratio is important to facilitate pore development, however, a higher impregnation ratio led to the rupture of the linkages between the lignin and cellulose followed by the formation of larger structural units and strong cross-linked solids [29].

Table 7. Combined chemical activation followed by furnace heating modified adsorbent and the adsorption studies.

Biomass	Chemical activation condition		Physical activation condition		BET surface area	Adsorption studies			References
	Activating agent	Time (h)	Temp. (ºC)	Time (min)	(m^2/g)	Isotherm	Kinetics	q_{max} (mg/g)	
PKS	Phosphoric acid (H_3PO_4)	-	500	120	900.81	Langmuir	Pseudo-second-order	0.1576	[34]
PKS	1 M K_2CO_3 and $NaHCO_3$	3	800	40	717.142	Langmuir	-	-	[35]

Alkali treatment using alkali activating agents such as K_2CO_3 and $NaHCO_3$ is a well-known method to improve the development of microporosity for porous materials. During the alkali treatment, the alkali dissolvable extractive and chemical constituents of the fiber are removed. According to Kwasi Opoku et al. [35], analysis of cadmium removal revealed that palm kernel shells activated carbons are very effective in the adsorption processes. The concentrations of cadmium metal in the 6 months old used lubricating oils before and after the filtration process with palm kernel activated carbons in the filter beds was 0.030 ± 0.008 ppm and 0.000 ± 0.000 ppm, respectively.

5.4. Combined chemical activation followed by microwave-induced irradiation

The method of microwave irradiation is to create a hot spot in the sample and generate heat from the inside, so the inner temperature is higher compared to the sample surface. In microwave processing, the electric energy is converted into heat energy through the interacting process of dielectric materials. The microwave irradiation method is effective as a source of thermal energy in terms of time-saving [22]. The microwave activation eliminated the volatile matter in the sample, resulting in the increment of fixed carbon content in the activated carbon [29]. The combined chemical activation followed by microwave-induced irradiation adsorbents and the adsorption studies are summarized in Table 8. In this method, the palm oil biomass was soaked with chemical activation agents such as phosphoric acid and polyacrylamide and later, the carbonization was done using microwave irradiation process at fixed values of microwave power level and microwave radiation time. All of the adsorption studies listed in Table 8 used batch mode and synthetic cadmium solution as the single system except for Ling et al. [36] who used continuous packed-bed column system for adsorption studies. According to the Table 8, oil palm shell PKS showed the highest removal percentage, 99% with an adsorption capacity of 227.27 mg/g compared to other types of oil palm biomass listed. The modification method that had been used by Tan et al. [29] was chemical activation using phosphoric acid followed by microwave-induced irradiation 700 W for 5 min. Adsorption studies showed that the adsorption process was following the Langmuir model that assumes monolayer adsorption occurred on the surface of the adsorbent. The adsorption system also followed the pseudo-second-order model that assumes chemisorption is the main adsorption mechanism.

Table 8. Combined chemical activation followed by microwave-induced irradiation modified adsorbent and the adsorption studies.

Biomass	Chemical activating agent	Physical activation condition		BET surface area (m^2/g)	Adsorption studies			References
		Power (W)	Time (min)		Isotherm	Kinetics	Removal percentage (%)	
PKS	Phosphoric acid (H_3PO_4)	700	5	-	-	Thomas	-	[36]
OPF	Polyacrylamide $(C_3H_5NO)_n$	100	2	-	-	-	56.84	[37]
PKS	Phosphoric acid (H_3PO_4)	700	5	854.42	Langmuir	Pseudo-second-order	99 (q_{max} = 227.27 mg/g)	[29]
PKS	Phosphoric acid (H_3PO_4)	700	8	-	-	-	97.38	[29]

From the Table 8, it shows that the cadmium removal percentage was lower at lower microwave power and this was due to low porosity. Surface area increases with an increase in microwave power until the optimum range is achieved. However, at a certain limit, even the highest surface area adsorbent produced the same pattern of adsorption, and thus chemical activating agents are needed to maximize adsorption. In a study conducted by Ukanwa et al. [38] which is using trona ore ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) also known as crude soda ash as an activating agent, the optimum microwave power range for PKS, MF, EFB, and combine palm waste was 600 W. There was no corresponding increase in porosity beyond this range and thus, wasting the energy and also increase the energy consumption cost. At 20 minutes of microwave heating time, the BET surface area of PKS, MF, EFB, and combine palm waste (CPW) (3:2:1 proportion by weight of EFB, MF and PKS) was 1030, 1220, 735, and 980 m^2/g, respectively. This showed that the type of feedstock did affected the carbonization process occured. A study by Tan et al. [29] revealed that the 5-minute microwave irradiation time showed marginally higher cadmium removal than the 8-minute heated sample, suggesting that prolonged exposure to the microwave may have damaged the earlier formed pores and thus decreased the capacity of cadmium adsorption.

Another study by Yacob [39] had discovered the effect of phosphoric acid (H_3PO_4) on the BET surface area of PKS activated carbon at constant immersion time (48 h), microwave power (350 W), and heating time (10 min). The increment of the H_3PO_4 concentration resulting in a more potential site that to be penetrated and occupied by the activating agent who causes the pore opening and widening while removing the heavier volatile organic compound (VOC) in the palm shells. For example, the BET surface area of 30% and 60% H_3PO_4 modified AC were 158 and 630 m^2/g, respectively. The effect of impregnation ratio on cadmium removal had been also conducted by Tan et al. [29] whereby H_3PO_4 impregnation ratio of 1:2 with microwave irradiation power of 700 W for 5 min showed the highest removal percentage for cadmium, that was 99%. Meanwhile, the removal percentage for the H_3PO_4 impregnation ratio of 1:1 and 1:3 adsorbents were 45% and 95.91%, respectively. An optimum impregnation ratio showed that the amount of acid was sufficient enough to react with the amount of precursor effectively to facilitate the pore development.

6. Comparison of the best adsorbent in section 5 with other adsorbents in terms of adsorption capacity

By comparing the maximum cadmium adsorption capacities from the findings in Section 5, the output of chemical activation followed by microwave-induced irradiation of palm kernel shells (PKS) produced activated carbon with highest adsorption capacity (227.27 mg/g). The comparison of adsorption capacity of the best adsorbent presented in Section 5 with other adsorbents was listed in Table 9. It was found that PKS treated with chemicals and microwave heating still outperformed as compared to other adsorbents.

Table 9. Comparison of adsorption capacity of different adsorbents for cadmium adsorption.

Adsorbents	Treatment Method	Maximum adsorption capacity, q_{max} (mg/g)	References
PKS (Best adsorbent in Section 5)	Phosphoric acid (H_3PO_4) activation followed by microwave-induced irradiation (700 W, 5 min)	227.27	[29]
Sunflower Head Carbon (SHC)	H_2SO4 activation followed by oven heating (150 ºC, 24 h)	15.95	[40]
Sunflower Stem Carbon (SSC)	H_2SO_4 activation followed by oven heating (150 ºC, 24 h)	17.61	[40]
Sunflower head waste activated carbon combined with iron oxide nanoparticles	H_2SO_4 activation + furnace heating (500 ºC, 1 h) + $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$	2.15	[41]
Sewage sludge and waste tires	Furnace heating (700 ºC, 2h)	50.25	[42]
Peanut shell	Furnace heating (565 ºC, 45 min)	1.038	[43]

The other modification methods produced very low adsorption capacities in the range of 1–50 mg/g. The similarity of the above-mentioned methods as they were all using furnace heating method which contributed to lower adsorption capacity as compared with microwave heating method. Microwave irradiation provided a greater BET surface area compared to conventional heating systems as proven by research conducted by Koo et al. [22]. The BET surface area of microwave processing and furnace heating processing of EFB were 807.54 and 255.77 m^2/g, respectively. The study also revealed that the microwave radiation method also performed a higher carbon yield and adsorption capacity due to micropore structure, the existence of carboxylic groups, and higher charge density on the surface of the absorbent. This is in line with a study by Ukanwa et al. [38] which concluded that a single-step activation with microwave has more unbroken pores while the two-step and conventional techniques produce activated carbons with broken and uneven pore linkages. Hence, this comparison helps the researchers to identify appropriate methods and conditions for application in cadmium adsorption as there is limited literature on single pollutant adsorption review using oil palm activated carbon with one recent review found for oil palm-derived activated carbon for CO_2 capture [44].

7. Conclusions and future directions

The utilization of oil palm biomass into cadmium adsorbent could play a role in killing two birds with one stone, which is to solve the oil palm biomass disposal issue and cadmium pollution issue. Worry less, the spent activated carbon can be recycled and sold as new by reactivation method. As the biggest biomass contributor in Malaysia, the oil palm biomass has been chosen to adsorb cadmium by more and more researchers in recent years. The modification of oil palm biomass has become the key point to improve the adsorption capacity. In fact, the modification process has been the emerging key challenge in the field of adsorption technology to industrial applications for a long time, and a wide variety of methods have been studied including physical modification such as heat pyrolysis and microwave irradiation, as well as dual modification of physical and chemical activation.

The output of chemical activation followed by microwave-induced irradiation of palm kernel shells (PKS) produced activated carbon with high BET surface area (854.42 m^2/g) and high adsorption capacity (227.27 m^2/g). Further studies are needed to look at the adsorption capacity of oil palm biomass adsorbent in terms of the selectivity adsorption of pollutants, cost comparison with other conventional adsorbents, and its performance at a larger scale (pilot-plant studies). Hence, sustainable palm oil industry and safe water quality are possible, if the authority and stakeholders in the supply chain are committed to implementing the recommended modified adsorbent through policy changes and management practices that will bring benefits to the supply chain in the long run. Indeed, oil palm biomass is a promising adsorbent candidate for the removal of cadmium from wastewater.

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Conflict of interest

All authors declare no conflicts of interest in this paper.

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