

Oil Palm Biomass as an Adsorbent for Heavy Metals

Mohammadtaghi Vakili, Mohd Rafatullah, Mahamad Hakimi Ibrahim, Ahmad Zuhairi Abdullah, Babak Salamatina, and Zahra Gholami

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M. Vakili • M. Rafatullah (✉) • M.H. Ibrahim
School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia
e-mail: mohd_rafatullah@yahoo.co.in; mrafatullah@usm.my

A.Z. Abdullah • Z. Gholami
School of Chemical Engineering, Universiti Sains Malaysia,
14300 Nibong Tebal, Penang, Malaysia

B. Salamatina
School of Engineering, Monash University Sunway Campus,
Jalan Lagoon Selatan, 46150 Bandar Sunway, Selangor, Malaysia

1 Introduction

In recent decades, increases in the world's population, unplanned urbanization, industrialization, agricultural activities, and expanded use of chemicals, has contributed to environmental contamination via emission of wastes and pollutants. Wastes (both inorganic and organic) that are produced by human activities have resulted in high volumes of contaminated water, contact with or consumption of which poses health threats to living organisms, including humans (Ahmad et al. 2010, 2012).

Among inorganic pollutants, heavy metals are hazardous pollutants of wastewaters that have become a serious public health concern (Demirbas et al. 2006). Heavy metals harm flora and fauna because they are both toxic and stable; moreover, some of these metals can accumulate in living organisms (Das et al. 2008). The most significant toxic metal ions that pose risks to humans and the environment include Cr, Cu, Pb, Hg, Mn, Cd, Ni, Zn, and Fe (Chatterjee et al. 2010). Duruibe et al. (2007) reported that heavy metals cause adverse health effects, such as gastrointestinal disorders, diarrhea, stomatitis, tremors, hemoglobinuria, ataxia, paralysis, vomiting, and convulsions, although each of these heavy metals exhibits its specific toxicity profile. Wastewater generated from various industrial activities such as battery manufacturing (Ahmaruzzaman 2011), ceramics production (Khraisheh et al. 2004), metal refineries (Chandra Sekhar et al. 2004), pulp and paper production (Sthiannopkao and Sreesai 2009), rubber and plastics manufacture (Srivastava and Majumder 2008), electroplating (Sekomo et al. 2012), smelting (Fu et al. 2012), mining (Ying and Fang 2006), mineral processing and extractive metallurgy (Ahluwalia and Goyal 2007) and metal surface treatment (Karvelas et al. 2003) are contaminated with one or more of these toxic ions. The quantity of these heavy metals that exists in effluents released into the natural environment is often higher than the acceptable level. Hence, heavy metals should be removed or their quantities reduced from effluents by suitable treatment methods before they are discharged into the environment. The industrial sources and health risks of commonly utilized heavy metals are listed in Table 1.

Different treatment methods have been applied to remove heavy metals from wastewaters. Among the common methods are the following: ion exchange (Xing et al. 2007), coagulation/flocculation (Chafi et al. 2011), chemical precipitation (Kurniawan et al. 2006), electrochemical reaction (García-Gabaldón et al. 2006), electro-dialysis (Mohammadi et al. 2004), physisorption (Chen et al. 2012), biosorption (Tsekova et al. 2010), and membrane filtration (Barakat and Schmidt 2010). Each of these methods has been applied to decrease the concentrations of detrimental metal ions in wastewaters. Moreover, each of the methods exhibit limitations, such as high capital or operating costs, low efficiency, and disposal of excess sludge, whereas some of these methods are inappropriate for use by small-scale industries (Kobya et al. 2005).

Ideriah et al. (2012), Ahmed Basha et al. (2008) and Al Aji et al. (2012) studied the advantages and disadvantages of some of these methods, and discovered that precipitation methods are cost effective, but produce high amounts of precipitate

Table 1 Sources of environmental contamination by several heavy metals and their toxic effects

Heavy metals	Sources	Health risks
Lead	Lead batteries, paint, oil, metal, phosphate fertilizer, electronics, wood production, some petrol types, explosive manufacturing, mining activity, automobile emissions, sewage wastewater, sea spray, insecticides, plastic industries, food, beverages, ointments and medicinal concoctions (Khalid et al. 2007)	Dysfunction of kidneys, reproductive system, liver, brain and central nervous system. Reduction in hemoglobin formation, mental retardation, infertility and abnormalities in pregnant women. Anemia, headache, chills, diarrhea, poisoning (Karvelas et al. 2003)
Cadmium	Cadmium–nickel batteries, phosphate fertilizers, pigments, stabilizers, alloys, and electroplating industries (Mortaheb et al. 2009)	Renal disturbances, lung insufficiency, bone lesions, cancer, hypertension (Sankararamakrishnan et al. 2007)
Copper	Mining operations, tanneries, electronics, electroplating, petrochemical industries, and textile mill products (Kazemipour et al. 2008)	Abdominal pain, nausea, vomiting, headache, lethargy, diarrhea, tachycardia, respiratory difficulties, hemolytic anemia, gastrointestinal bleeding, liver and kidney failure and death (Akar et al. 2009)
Mercury	Refineries, coal-fired power plants, mining, chloralkali plants utilizing the Hg-cell process, municipal wastewaters (Urgun-Demirtas et al. 2012)	Neurological and renal disturbances, mental dysfunction, impairment of the nervous system and pulmonary systems and kidney function, and cause chest pain and dyspnea (Zahir et al. 2005)
Manganese	Steel industries, dry battery cells and electrical coils, mining and smelting, pigments and paints, and ceramics (Li et al. 2010)	Damage to brain, liver, kidneys and nervous system (Silva et al. 2010)
Nickel	Stainless steel, super alloys, metal alloys, coins, batteries (Vieira et al. 2010)	Gastrointestinal distress like nausea, vomiting, diarrhoea, damage to lungs and kidney, and cause pulmonary fibrosis, renal edema, and skin dermatitis (Akhtar et al. 2004)
Zinc	Mining, tanneries, painting, car radiator manufacturing, agricultural sources, electroplating, galvanizing plants (Abdelwahab et al. 2013)	Cause abdominal pain, nausea, vomiting, and diarrhea (Pereira et al. 2010)

sludge that requires further treatment. Ion exchange and reverse osmosis efficiently remove heavy metal ions (by approximately 90–95%), but the materials and operational procedures are expensive, and operational problems are often encountered. Electrolysis is an expensive method and requires high energy levels. Commercial activated carbon (CAC) can be applied to remove heavy metals via adsorption, but these adsorbents are very expensive.

More cost-effective and efficient methods and substances are needed to remove heavy metals. Among treatment strategies, adsorption is regarded to be an effective and preferable method for removing heavy metal ions from wastewater, because this method is cost effective and produces high-quality effluent (Oluyemi et al. 2012; Rafatullah et al. 2010; Salleh et al. 2011). Adsorption is a separation process, in which the amount of chemical components being collected (adsorbate) are increased at the surface of a solid (adsorbent) (Yadla et al. 2012). This adsorption process incorporates both physical and chemical actions that involve van der Waals forces, or other actions between an adsorbate and an adsorbent (Wang et al. 2009). Adsorption can function in solid or liquid matrices, and certainly can be used to remove heavy metal ions from polluted aqueous solutions. Adsorption is preferred over other methods because it is rapid, conveniently designed and operated, impenetrable to toxic contaminants, and does not produce hazardous by-products (Qiu et al. 2009). Adsorption is often applied to clean effluents by using low-cost materials.

In this review, we describe the different methods that are used to eliminate heavy metals from wastewaters by using oil palm biomass as a form of low-cost adsorbent.

2 Commercial Adsorbents

The nature and type of adsorbent are important parameters that influence adsorption efficiency. Some of the prominent substances that are commonly used as commercial adsorbents are activated carbon (Mohan and Pittman 2006), activated alumina (Mahmoud et al. 2010), silica gel (Najafi et al. 2011), and zeolite (Egashira et al. 2012). Below, we describe the characteristics of these important adsorbents.

2.1 Activated Carbon

Activated carbon is efficient, adsorbs many chemicals, and is an adsorbent that is particularly important for wastewater treatment (Yin et al. 2008a, b). Activated carbon is produced by dehydration and carbonization in the presence of heat and in the absence of oxygen. Activated carbon contains tiny pores with a large surface area (300–4,000 m²/g). Although activated carbon is put to many uses, it does possess some limiting features: utilizing it entails high cost, requires regeneration after adsorption, and it loses adsorption capability after regeneration (Igwe and Abia 2006; O’Connell et al. 2008; Rafatullah et al. 2013).

2.2 Activated Alumina

Activated alumina is produced by thermally treating hydrous alumina granules. Hydroxyl groups are forced to leave, producing a porous solid structure of activated alumina that has a large surface area (200–300 m²/g). Activated alumina possesses

a surface area that makes it appropriate for removing heavy metals from aqueous solutions, and absorbing organic liquids (e.g., kerosene, gasoline, and oil) from water (Ku and Chiou 2002; Singh and Pant 2004).

2.3 Zeolite

Zeolites are hydrated porous aluminosilicate minerals. These minerals are naturally created from the changes occurring in glass-rich volcanic rocks (tuff) in the sea or in playa lake waters. Zeolites are appropriate adsorbents for removing heavy metal ions from wastewaters, because such adsorbents exhibit favorable properties that include the following: high ion exchange capability, molecular sieving, catalysis, and sorption properties (Ji et al. 2012; Wang and Peng 2010).

2.4 Silica Gel

Silica gel, invented in the 1920s, is a concentration of $\text{Si}(\text{OH})_4$ in siloxane chains. It is produced in three forms: regular-, intermediate-, and low-density gels with surface areas of 750 m^2/g , 300–350 m^2/g , and 100–200 m^2/g , respectively. Such gels are considered to be suitable adsorbents because they remain stable under acidic conditions, exhibit a rapid adsorption capacity, contain a porous structure that has high surface area, and are non-toxic, non-flammable, and not chemically reactive (Fan et al. 2011; Gübbük et al. 2009).

In general, the use of conventional adsorbents increases costs, particularly when high purity adsorbents are used. Therefore, the use of such adsorbents is not commercially economical, and cost is an important when selecting adsorbents. Generally, an adsorbent is regarded to be inexpensive when it is readily available, is environmentally friendly and is cost-effective. Hence, rather than using high-cost adsorbents, researchers are encouraged to produce and use inexpensive adsorbents that are based on natural by-products, such as agricultural wastes, when possible (Bailey et al. 1999; Khan et al. 2008).

In this review, we have searched and summarized the literature that addresses the use of palm oil biomass as a low-cost adsorbent for removing heavy metal contaminants from wastewaters.

3 Agricultural-Waste Adsorbents

Ho (2003) investigated agro-based waste materials as resources to both produce new adsorbents and to modify currently used ones. Previous studies (Basso et al. 2002; Hashem 2007) have demonstrated that agricultural wastes absorb heavy metal

ions and can be used as low-cost adsorbents in wastewater treatment. Such wastes have been used for adsorption tasks because they offer several advantages: they are readily available and exist in abundance, they are cost effectiveness, renewable, require less processing time, offer suitable adsorption capability, are selective for heavy metals, and can easily be regenerated (Elizalde-González et al. 2008). Examples of agricultural or related biomass products that can be used in adsorption applications are: peanut skins (Asubiojo and Ajelabi 2009), hazelnut shells (Bulut and Tez 2007a), peanut hulls (Hashem et al. 2005), corn cobs (Sun and Webley 2010), flamboyant pods (Vargas et al. 2010), coconut husks (Tan et al. 2008), Gular fruits (Rao and Rehman 2010), olive stones (Aziz et al. 2009), sawdust (Bulut and Tez 2007b), and chestnut shells (Vázquez et al. 2009).

Saeed et al. (2005) evaluated the efficiency of papaya wood as an adsorbent to remove heavy metals. The percentages of heavy metals removed within 60 min from a solution containing 10 mg/L of Cu (II), Cd (II), and Zn (II) at pH 5 were 97.8%, 94.9%, and 66.8%, respectively. Babarinde et al. (2006) reported the potential of maize leaves for removing Pb ions from wastewater. Agarwal et al. (2006) investigated the efficiency of *Tamarindus indica* seeds, crushed coconut shells, almond shells, groundnut shells, and walnut shells as inexpensive adsorbents for removing Cr (VI). Among these materials, the Cr (VI) sorption capacity of *T. indica* seed was higher than that of the others; crushed coconut shell exhibited the lowest sorption capacity. Abu Al-Rub (2006) studied the effectiveness of palm tree leaves for removing Zn ions from wastewater and found that sorption by Zn was rapid; 90% of Zn was adsorbed in approximately 10 min. Amarasinghe and Williams (2007) investigated the adsorption of Pb and Cu ions from aqueous solutions by using tea waste. They observed that the rate of Pb adsorption was higher than for Cu over a period from 15 to 20 min. Table 2 presents examples of low-cost adsorbents made from various agricultural wastes that are used to remove heavy metals from wastewater.

In general, agricultural wastes are composed of basic components (e.g., cellulose, hemicellulose, and lignin) that contain various functional groups (Amarasinghe and Williams 2007). Lignocellulosic materials are composed of β -D-glucopyranose units, which is one of the most important components of plant cell walls. Each β -D-glucopyranose units contain one primary hydroxyl group and two secondary hydroxyl groups that are commonly involved in chemical reactions. Functional groups present in lignocellulosic materials bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution (Demirbas 2008). However, the adsorption capacity and physical stability of unmodified lignocellulosic materials are not suited to adsorbing heavy metals. To improve the adsorption capacity for metals, and to enhance metal ion binding, researchers chemically modify these lignocellulosic materials by integrating them with other sources of functional groups in ways that alter their surface characteristics (Mahmoud et al. 2010).

Table 2 Performance parameters of agricultural waste adsorbents that are used for removing heavy metals

S. No.	Agricultural waste	Adsorbate			Adsorption conditions			References		
		Particle size	Dosage	Metals	Concentration (mg/L)	Contact time (min)	Agitation speed (rpm)		Temp. (°C)	Adsorption capacity (mg/g)
1.	Coconut shell Neem leaves Hyacinth roots Rice straw	250–350 µm	10 g/L	Cu(II)	25	6	300	–	19,8886 17,4886 21,7959 18,3519	Singha and Das (2013)
2.	Mushroom biomass	0.1 mm	10 g/L	Cu(II)	30–100	5	30	150	0.664	Ertugay and Bayhan (2010)
3.	Potato peel	0.2 mm	1.0 g/100 mL	Cu	150	6	120	150	0.3877	Aman et al. (2008)
4.	Waste tea fungal biomass	1–2 mm	0.5 g/L	Cu(II)	254	4	360	200	4.64	Razmovski and Šćiban (2008)
5.	Sugar beet pulp	250 µm	0.1 g/100 mL	Cu (II)	250	4	600	150	28.5	Aksu and Işoğlu (2005)
6.	Lemon peel	0.10–0.07 mm	10.0 g/L	Cr(VI)	0–1,000	6	600	200	22	Bhatnagar et al. (2010)
7.	Parthenium hysterophorus weed	68.5 µm	0.1 g/100 mL	Cr(VI)	10–50	1	420	200	24.5	Venugopal and Mohanty (2011)
8.	Pomegranate husk	≤0.063 mm	0.3 g/100 mL	Cr(VI)	75–150	1	180	200	35.2	Nemr (2009)
9.	Maize bran	<178 µm	–	Cr(VI)	200	2	180	125	312.52	Hasan et al. (2008)
10.	Tea factory waste	0.15–0.25 mm	10 g/L	Cr(VI)	400	2	60	360	54.65	Malkoc and Nuhoglu (2007)
11.	Grapefruit peel	355 µm	4 g/L	Ni	10–200	5	60	180	46.13	Torab-Mostaedi et al. (2013)
12.	Sugarcane bagasse	<1 mm	1 g/100 mL	Ni (II)	10–200	5	120	300	2	Alomá et al. (2012)
13.	Moringa oleifera bark	–	0.2 g/50 mL	Ni	20–200	6	120	300	30.38	Reddy et al. (2011)
14.	<i>Acacia leucocephala</i> bark	–	0.1 g/100 mL	Ni	50–200	5	240	150	294.1	Subbaiah et al. (2009)
15.	<i>Alternanthera philoxeroides</i> biomass	<125 µm	0.25 g/50 mL	Ni (II)	100	6	300	200	9.73	Wang and Qin (2006)
16.	coconut (<i>Cocos nucifera</i> L.) coir dust	50 µm	5 g/100 mL	Zn	5–200	7.5	60	–	17,857	Israel and Eduok (2012)
17.	Sulfured orange peel	0.45 mm	50 mg/10 mL	Zn	50	5–6	120	120	80	Liang et al. (2011)
18.	<i>Coffee husks</i>	–	1 g/50 mL	Zn	50–100	4	–	100	5.6	Oliveira et al. (2008)
19.	<i>Alternanthera philoxeroides</i> biomass	<125 µm	0.25 g/50 mL	Zn (II)	100	6	300	200	18.57	Wang and Qin (2006)
20.	Rice husk ash Neem bark	0.297–0.400	10 g/L	Zn	25	5	240	–	14.30 13.29	Bhattacharya et al. (2006)

(continued)

Table 2 (continued)

S. No.	Adsorbent	Adsorbate			Adsorption conditions			Adsorption capacity (mg/g)	References		
		Particle size	Dosage	Metals	Concentration (mg/L)	pH	Contact time (min)			Agitation speed (rpm)	Temp. (°C)
21.	Sulfured orange peel	0.45 mm	50 mg/10 mL	Pb	100	-	120	120	30	164	Liang et al. (2011)
22.	Olive tree pruning waste	<1,000 mm	10 g/L	Pb	10	5	120	-	25	26.24	Blázquez et al. (2011)
23.	<i>Moringa oleifera</i> tree leaves	0.6–0.85 mm	0.40 g/100 mL	Pb	50	5	120	200	40	209.54	Reddy et al. (2010)
24.	Orange peel	-	0.050 g/25 mL	Pb	50	5.5	180	120	-	476.1	Feng et al. (2011)
25.	Pine bark	150–355 µm	50 mg/10 mL	Pb	50–1,000	4	240	400	-	76.8	Gundogdu et al. (2009)
26.	Grapefruit peel	355 µm	4 g/L	Cd (II)	10–200	5	60	180	-	42.09	Torab-Mostaedi et al. (2013)
27.	Areca catechu	200 µm	0.5 g/100 mL	Cd (II)	20	6	30	120	29	10.66	Chakravarty et al. (2010)
28.	Banana peel	0.250 mm	30 g/L	Cd (II)	50	3	20	100	25	5.71	Anwar et al. (2010)
29.	Mungbean husk	1.0–2.0 mm	0.5 to 100 mL	Cd (II)	50	5	60	150	25	35.41	Saeed et al. (2009)
30.	Parthenium	0.104–0.152 mm	0.5 g/50 mL	Cd (II)	10–100	4	60	100	20	27	Ajmal et al. (2006)
31.	Hazelnut hull	-	0.5 g/100 mL	Fe(III)	20–60	3	60	-	30	13.59	Sheibani et al. (2012)
32.	Orange peel	0.841 mm	0.1 g/100 mL	Fe(III)	30	3	360	-	Room temp.	18.19	Lugo-Lugo et al. (2012)
33.	Green tomato husk	0.075–0.150 mm	100 mg/10 mL	Fe(III)	10	6	-	-	20	19.83	García-Mendieta et al. (2012)
34.	Tamarind bark	-	2 g/50 mL	Fe(III)	20–120	2.5	180	200	25	11.75	Prasad and Abdullah (2009)
	Potato peel									7.87	
35.	Bengal gram husk	-	1 g/100 mL	Fe(III)	20–500	2.5	200	100	-	72.16	Ahalya et al. (2006)
36.	Sugarcane bagasse	-	5 g/L	Hg	76	4	180	700	30	35.71	Khoramzadeh et al. (2012)
37.	Gum karaya (<i>Sterculia urens</i>)	180–300 µm	1 g/L	Hg	10	6	60	200	25	62.5	Vinod et al. (2011)
38.	Garlic (<i>Allium sativum</i> L.) powder	0.02 mm	12.5 g/L	Hg	200×10 ⁻³		360	-	Room temp.	0.6497	Eom et al. (2011)
39.	Peat moss	1.0 m	0.125 g/25 mL	Hg	40–523	6	-	-	25	98.94	Bulgariu et al. (2009)
40.	Leaves of castor tree	125–150 µm	0.25 g/100 mL	Hg	5–100	5.5	120	-	Room temp.	37.2	Al Rmalli et al. (2008)
41.	Green tomato husk	0.075–0.150 mm	100 mg/10 mL	Mn	10	6	-	-	20	15.22	García-Mendieta et al. (2012)
42.	Maize stalks	150 µm	0.1 g/25 mL	Mn	40–1,000	5	90	100	35	16.61	El-Sayed et al. (2011)
43.	Pecan nutshell	250 µm	5.0 g/L	Mn	10–1,000	5.5	360	-	25	85.9	Vagheti et al. (2009)
44.	Black carrot residues	0.250 mm	-	Mn	1,000	5.5	360	-	20	3.871	Güzel et al. (2008)

4 Oil Palm Biomass: Potential Heavy-Metal Adsorbents

Oil palm (*Elaeis guineensis*) biomass is an important and low-cost agricultural waste that exhibits adsorption potential adequate to eliminate heavy metal ions from wastewater (Ibrahim et al. 2010; Ahmad et al. 2011). Oil palm is a tropical tree that originated from Africa. This species has geographically been spread to regions of 42 tropical countries in Africa, the Americas, and Asia. Oil Palm is worldwide covers approximately 27 million acres. Oil palm has been traditionally regarded as an important industrial crop, because it was also utilized for food, in medicine, in woven materials, and in wine over the past 5,000 years. At present, oil extracted from oil palm is used in cooking, cosmetics, pharmaceuticals, and as a bio-fuel (Mohammad et al. 2012). Furthermore, palm oil is one of the largest vegetable oil sources in the world and is a significant economic crop in tropical areas of Africa, America, and Asia, particularly in Southeast Asian countries, such as Indonesia and Malaysia (Kalinci et al. 2011).

Malaysia and Indonesia are among the largest producers of palm oil in the world, and produce approximately 85% of the world's total palm oil (Malaysia 41% and Indonesia 44%). The palm oil industry in Malaysia has expanded rapidly during the past 25 years. This expansion increased the total planted area of oil palm trees from 3.87 million ha in 2004 to 4.17 million ha in 2006 (Sulaiman et al. 2009). In addition, the amount of palm oil produced has increased from 2.5 million tons in 1980 to 17.8 million tons in 2009. Despite growth in area planted, and the oil high production, environmental concerns are increasing about the accumulation of huge quantities of produced biomass wastes (Rupani et al. 2010). Annually, approximately 184 million tons of palm oil residue worldwide, and 53 million tons of oil palm tree residue in Malaysia are generated; these amounts are increasing by ~5% annually (Mohammed et al. 2011).

Large amounts of several components of oil palm biomass are generated and utilized for various purposes. These components include oil and lignocellulosic materials, such as palm pressed fibers (PPF), kernel shells, empty fruit bunch (EFB), oil palm frond (OPF), oil palm trunks, oil palm bark (OPB), palm kernel cake, and palm oil mill effluent (POME) from palm oil production (Uemura et al. 2011). Lignocellulosic oil palm biomass is rich in carbohydrates and contains organic compounds such as cellulose, hemicelluloses and lignin that have numerous natural polymeric materials containing different functional groups that absorb heavy metal ions (Mahmoud et al. 2010). In Table 3, we depict the chemical composition of palm oil biomass.

Table 3 Chemical composition of oil palm biomass

Component	Chemical composition				
	EFB	Frond	Fiber	Trunk	Shell
Cellulose (%)	49.6	25.08	47.6	37.14	27.7
Hemicellulose (%)	18	24.06	25.7	31.8	21.6
Lignin (%)	21.2	18.46	14.1	22.3	44
Ash (%)	2	11.66	1.5	4.3	2.1

Oil palm biomasses can be converted to high-value by-products that can be used as energy sources, erosion control products, soil conditioner, animal feed, fertilizers, as well as in the furniture- and paper-making industries (Radzi bin Abas et al. 2004). Moreover, as we have explained above, palm oil biomass can serve to adsorb heavy metal ions from wastewater.

4.1 *Unmodified Oil Palm Biomass*

Ho and Ofomaja (2005) studied the kinetics and thermodynamics of Pb ion sorption from aqueous solutions of palm kernel fiber, and discovered that the kinetics followed a pseudo-second-order mechanism. Palm kernel fiber adsorbs Pb ions from aqueous solutions via a spontaneous and endothermic process. The activation energy and equilibrium sorption capacity of Pb ions on palm kernel fiber were determined as 13.5 kJ/mol and 49.9 mg/g at 65 °C, respectively. Salamatinia et al. (2007) assessed the sorption capacity of unmodified OPB, OPF, and EFB for Zn and Cu removal from wastewater. In this study, experiments were conducted in a batch system with 250 mL Cu and Zn solutions at 100 mg/L, using between 0.5 and 1.0 g of adsorbent. OPB, OPF, and EFB adsorbed Cu ions more efficiently than did Zn ions. The sorption capacities of the Zn ions by OPF and EFB were 51.5% and 46.0%, respectively. The Cu sorption capacities of OPF and EFB were 54% and 56.5%, respectively. OPB exhibited the lowest rate of Cu ion removal. Hossain et al. (2012) investigated the removal of Cu from water and wastewater by using untreated palm oil fruit shells as the adsorbent. The raw materials were washed, dried, and ground into powder (<75 mm). Results were that the equilibrium sorption capacity of Cu ranged between 28 and 60 mg/g at room temperature at pH 6.5. Palm oil fruit shells effectively acted as bio adsorbents and eliminated Cu ions from the tested wastewater. Chong et al. (2012) studied the application of oil palm shell as a constructed wetland medium and adsorbent to remove Cu (II) and Pb (II). Results indicate that oil palm shell can be used as filter bed media and can be applied in constructed wetlands to eliminate heavy metals, even without agitation. The sorption capacities determined for this adsorbent were respectively 1.756 and 3.390 mg/g for Cu (II) and Pb (II) ions.

Although unmodified biomass have advantages as adsorbents, they also cause certain problems. Such problems include low adsorption capacity, increased chemical oxygen demand (COD) and biological chemical demand (BOD), and increased total organic carbon (TOC) from release of soluble organics within the biomass. These effects of unmodified biomass adsorbents decrease the oxygen content of water and endanger aquatic life (Peng and Sun 2010). To overcome these disadvantages, and to improve adsorption properties, researchers have sought ways to modify these biomass wastes before using them as adsorbents. Modification is generally designed to improve sorption capacity by creating a charged surface and by increasing the heavy-metal-ion binding capacity (Tijani 2011). In Table 4, we summarize what effects of several unmodified oil palm biomass types have on heavy metal adsorption parameters.

Table 4 Performance parameters of unmodified oil palm biomass-based adsorbents for removing heavy metals

S. no.	Adsorbent	Adsorbate			Adsorption conditions			Adsorption capacity (mg/g)	References		
		Particle size	Dosage	Metals	Concentration (mg/L)	pH	Contact time (min)			Agitation speed (rpm)	Temp. (°C)
1.	Natural oil palm pressed fibers	250–500 mm	0.1 g/25 mL	Cu	5–25	6	120	250	Room temp.	2.41	Low et al. (1996)
2.	Palm pressed fibers	0.30–0.85 mm	–	Cu, Ni	50–100 × 10 ⁻³	6	–	–	–	–	Tan et al. (1996)
3.	Oil palm bark	–	0.5 g/250 mL	Cu	100	–	180	150	25	8.3	Salamatinia et al. (2007)
				Zn						6.3	
				Cu						8.6	
				Zn						6.4	
	Oil palm frond		0.5 g/250 mL	Cu						13.8	
				Zn						13	
			1 g/250 mL	Cu						13.5	
				Zn						12.9	
	Empty fruit bunch		0.5 g/250 mL	Cu						13.0	
				Zn						13.2	
			1 g/250 mL	Cu						14.1	
				Zn						12.3	
4.	Oil palm leaves	250–500 μ	0.5 g/50 mL	Cu	1–100	6	240	125	30	11.22	Sulaiman et al. (2010)
5.	Palm oil fruit shells	<75 μm	0.5 g/100 mL	Cu	10	6.5	600	120	Room temp.	59.502	Hossain et al. (2012)
6.	Bornean oil palm shell	6.5–8 mm	1 g/100 mL	Cu	10	4.1	480	150	–	1.756	Chong et al. (2013)
				Pb						3.390	
7.	Palm kernel fiber	50–60 μm	1 g/400 mL	Pb	120	5	–	200	65	49.9	Ho and Ofomaja (2005)

4.2 Modified Oil Palm Biomass

4.2.1 Chemical Modification

Results have shown that chemically modifying biomass improves heavy metal removal and sorption capacity. Biomass can be modified by treating it with different chemical agents (e.g., alkalis, acids, organic compounds, etc.). Such chemical modification increases the level of metal uptake by releasing certain soluble organic compounds within the biomass (Abdullah et al. 2009).

Tan et al. (1993) removed Cr (VI) from wastewater in batch and column systems by treating PPF and coconut husk (CHF). The substrates, after boiling in distilled water, were treated stepwise with 1.5 M NaOH, distilled water, 2 M HNO₃ and distilled water. In the batch system, Cr (VI) was efficiently removed at pH ranges of 1.5 to 3 and 1.5 to 5 by PPF and CHF, respectively. The sorption capacities of PPF and CHF are 14 and 29 Cr/g substrate at pH 2.0, respectively. In the column system, PPF and CHF removed Cr (VI) ions from wastewater at various flow rates and bed depths. These substrates were also used as barriers in landfills to prevent Cr (VI) from leaching. Low et al. (1996) showed that the amount of Cu removed from wastewater by dye-treated oil PPF was higher than that by an untreated PPF. The results obtained from batch and column tests indicated that the use of PPF to remove Cu (II) ions was efficient. The sorption capacities of natural and dye-coated PPFs were 2.41 and 7.71 mg/g, respectively; the sorption capacity of these adsorbents was dependent on pH and Cu ion concentration in the solution. Further, Abia and Asuquo (2008) compared the sorption capacities of modified and unmodified oil palm fruit fibers as adsorbents to remove Pb and Cd ions from wastewater. Chemically modified adsorbents (treated with 0.3 HNO₃) increased the sorption capacities of Pb and Cd to 5.579 and 7.980 mg/g, respectively.

Salamatinia et al. (2006) modified OPF by applying a chemical pre-treatment and then using it to remove Zn and Cu ions from wastewater. Different pre-treatments (e.g., acid, base, steam, and reactive dye) were used to improve the sorption capacity of OPF. OPF treated with a base (1.0 M NaOH) for 45 min at 25 °C showed the highest improvement in heavy metal removal capacity (64%). The effect of base concentration was greater than the effect of treatment time. Abia and Asuquo (2007) compared the effects of unmodified and mercaptoacetic acid-modified oil palm fruit fiber to sorb Cd (II) and Cr (III) from wastewater. The sorption equilibrium of both metals was reached after 1 h. The modified adsorbent exhibited better removal efficiency, because the thiolation reaction influenced adsorbent behavior. In addition, the rate of Cr (III) ion removal by both adsorbents was higher than that of Cd (II) ion removal. The intraparticle diffusion rate constants of Cd (II) ion were 62.04, 67.01, and 71.43 min⁻¹; for Cr (III) these values were 63.41, 65.79, and 66.25 min⁻¹. Akaninwor et al. (2007) analyzed the efficacy of thioglycolic-modified oil palm fiber to remove Fe, Zn, and Mg ions from wastewater. In Southern Point tests, the highest sorption capacities for Fe (II), Zn (II), and Mg (II) were respectively 83.6%, 75.6%, and 50.8%; in Northern Point tests, the highest sorption capacities for Fe

(II), Zn (II), and Mg (II) were 79.1%, 78.3%, and 77.5%, respectively at pH 6. Therefore, the removal efficiency of these ions was influenced by pH and ionic size. The volume of adsorbed Fe (II) was the highest, followed by Zn (II) and Mg (II).

Abdullah et al. (2009) improved heavy metal sorption by treating OPF with 0.1 and 1.1 M NaOH for a maximum of 5 h. The maximum sorption capacities of Zn and Cu removal were 61.5% and 64.0%, respectively, under the following optimum conditions: 1.0 g of OPF treated with 1.0 M NaOH in 250 mL of 100 mg/L Zn and Cu solutions for 45 min. NaOH treatment improved the sorption capacity by increasing the rate of metal binding. Haron et al. (2009) used hydroxamic acid-modified EFB for Cu (II) sorption. The raw material was grafted by treatment with polymethylacrylate and then was treated with hydroxylammonium chloride, thereby decreasing the intensity of the adsorption band from $1,734\text{ cm}^{-1}$ to $1,640\text{ cm}^{-1}$. An absorption band was also obtained at $1,568\text{ cm}^{-1}$, which corresponds to the N–H amide group. Therefore, a new maximum sorption capacity of 74.1 mg/g was obtained at 25 °C and at pH 4 to 6 by a spontaneous and exothermic process. As a result, hydroxamic acid grafted oil palm empty fruit bunch (PHA-OPEFB) can be used as an adsorbent to remove Cu (II) from wastewater. In Table 5, we summarize how different heavy metal ions are adsorbed by chemically modified forms of oil palm biomass.

4.2.2 Thermal Modification (Activated Carbon)

Activated carbon is widely used as an adsorbent to eliminate heavy metals from wastewater, because this substance exhibits good adsorption properties as a result of having numerous tiny pores and a large surface area. When choosing adsorbents cost is important, and using activated carbons commercially generally increases adsorption costs. Therefore, utilizing other more cost-effective adsorbents that are environmentally friendly, such as agricultural wastes, have been investigated. As previously mentioned, researchers have investigated oil palm biomasses an alternative adsorbent, because these materials are great sources of high-quality and low-cost activated carbon.

Wan Nik et al. (2006) utilized shell waste from palm oil trees to produce activated carbon as a heavy metal adsorbent. The activated carbon produced by phosphoric acid-treated raw material was used to adsorb Cu, Pb, Cr, and Cd. This treatment decreased the concentration of inorganic elements and increased the surface area of the activated carbon. The optimum Brunet Elmer Teller (BET) surface area ($1,058\text{ m}^2/\text{g}$) and pore diameter (20.64 nm) were obtained under the following controlled conditions: 30% phosphoric acid concentration and an activation temperature of 500 °C, with a holding time of 2 h. The adsorption capacities of Cr, Pb, Cd, and Cu were 100%, 99.8%, 99.5%, and 25%, respectively. Issabayeva et al. (2006) analyzed the sorption capacity of Pb from wastewater by using a commercially available palm shell activated carbon. This form of activated carbon can be efficiently used as an adsorbent to remove heavy metals, particularly Pb ions, from wastewater with a high adsorption capacity of 95.2 mg/g at pH 5. The effect of adding malonic acid and boric acid on the sorption capacity of Pb ions was also examined. Boric acid

Table 5 Performance parameters of chemically modified oil palm biomass-based adsorbents for removing heavy metals

S. no.	Adsorbent	Adsorbate					Adsorption conditions				References
		Particle size	Dosage	Metals	Concentration (mg/L)	pH	Contact time (min)	Agitation speed (rpm)	Temp. (°C)	Adsorption capacity (mg/g)	
1.	Dye-treated oil palm pressed fibers	250–500 µm	0.1 g/25 mL	Cu	5–25	6	120	250	Room temp.	7.71	Low et al. (1996)
2.	Palm kernel fiber	50–60 µm	1 g/100 mL	Cu	50–250	5.01	60	200	26	–	Ho and Ofomaja (2006a)
3.	Treated oil palm frond	–	1 g/250 mL	Cu, Zn	100	–	30	150	25	–	Abdullah et al. (2009)
4.	Hydroxamic acid modified oil palm empty fruit bunch	100–200 µm	0.1 g/20 mL	Cu	100	4	120	–	25	74.1	Haron et al. (2009)
5.	Palm kernel fiber	50–60 µm	1 g /100 mL	Cu	90.24	5.1	1.5	200	24	20.12	Ofomaja (2010)
6.	Palm pressed fibers	0.30–0.85 mm	0.40 g/L	Cr (VI)	20	2	120	–	–	14	Tan et al. (1993)
7.	Treated oil palm fuel ash	0.5–1.0 × 10 ⁻³ mm	–	Cr	–	6	–	300	25	16.11	Chu and Hashim (2003)
8.	Acetic acid modified oil palm fruit fiber	106 µm	0.5 g/L	Cr (III), Cd	50	–	120	–	28	–	Abia and Asuquo (2007)
9.	Oil palm fruit fiber	106 µm	0.5 g/100 mL	Ni, Pb	50	6.2	120	–	28	–	Abia and Asuquo (2006)
10.	Modified oil-palm fibre	106 µm	1 g/50 mL	Zn, Mn, Fe(III)	–	6	60	–	–	–	Akaninwor et al. (2007)
11.	Modified oil palm fruit fiber	106 µm	0.5 g/100 mL	Pb	50	6.2	60	–	28	5.579	Abia and Asuquo (2008)
12.	Palm kernel fiber	50–60 µm	0.6 g/400 mL	Pb	120	5	20	200	36	7.980	Ho and Ofomaja (2006b)

enhanced the total amount of Pb removed, particularly at pH 5. By contrast, malonic acid decreased adsorption because an aqueous Pb-malonate complex was formed. Iyagba and Opete (2009) used palm kernel shell- and husk-activated carbon as adsorbents in a batch test to remove Cr and Pb from wastewater. The removal rate of Cr and Pb depends on pH, contact time, and adsorbent concentration; the highest removal rates were obtained at an optimum pH of 3 and 5 for Cr and Pb, respectively. Equilibrium times were 90 and 120 min for the activated palm kernel shell and activated palm kernel husk, respectively. The maximum sorption rates for Cr and Pb were 90% and 88%, respectively, and these rates were achieved at an adsorbent loading of 4 g.

Considering adsorbent and method costs as well as adsorption efficiency of heavy metals in industrial wastewater, Nomanbhay and Palanisamy (2005) utilized chitosan-coated acid-treated oil palm shell charcoal to remove Cr ions from polluted industrial wastewater. The adsorption capacity (154 mg Cr/g at 25 °C) of this adsorbent was estimated by using a Langmuir isotherm model under equilibrium conditions. After adsorption was completed, the adsorbent was regenerated with 0.1 M of sodium hydroxide. This adsorbent was technically feasible, environmentally friendly, and highly efficient. Sugawara et al. (2007) used a carbonaceous adsorbent from palm shell to remove Pb^{2+} and Zn^{2+} from wastewater. This adsorbent was prepared by pyrolysis and sulfur impregnation. The pyrolyzed samples with KOH were sulfurized with impregnated H_2S to produce a sulfur-impregnated char exhibiting heavy metal sorption capability. Sulfur impregnation increased sulfur content and enhanced adsorption capacity. Alam et al. (2008) used activated carbon made from empty fruit bunches of oil palm to remove Zn ion from polluted wastewater. The samples were thermally activated at 500, 750, and 1,000 °C for 15, 30, and 45 min. The activated carbon obtained at 1,000 °C for 30 min showed the maximum sorption capacity of 1.63 mg/g, at which 98% of Zn concentration was removed from the wastewater. Wahi et al. (2009) assessed the ability of activated carbon from palm oil EFB to remove Hg, Pb, and Cu from wastewater. The adsorption efficiencies of activated carbon made from EFB for Pb (II), Hg (II), and Cu (II) were 100%, 100% and 25%, respectively. The sorption of these ions by activated carbon of EFB was dependent on the amount of adsorbent and the initial concentration of the metals. Therefore, EFB in the form of activated carbon can be used as an effective adsorbent to remove heavy metals and solve environmental problems caused by high amounts of agricultural wastes.

Granular activated carbon made from palm kernel shell can also be used as an adsorbent to remove Cu, Ni, and Pb ions from industrial wastewater (Onundi et al. 2010). The sorption capacities for Pb, Cu, and Ni were 1.337, 1.581, and 0.130 mg/g, respectively. These values were obtained under the following optimum conditions: pH 5 and 1 g/L of adsorbent. The following equilibrium time was obtained: for Pb, 30 min; for Cu and Ni, 75 min. The proportions of metal ion removal achieved at equilibrium were 100%, 97%, and 55% for Pb, Cu, and Ni: $Pb(II) > Cu(II) > Ni(II)$. Kabbashi et al. (2011) analyzed the adsorption efficiency of an empty-fruit-bunch activated carbon to remove Hg (II) from wastewater. Hg binding was influenced by pH, mixing speed, sorbent concentration and contact time. The sorption capacity of

99.53% was obtained under the following conditions: pH 6.5; mixing speed, 100 rpm; contact time, 70 min; and sorbent concentration, 20 mg. Isa et al. (2008) conducted batch tests with sulfuric acid and heat-treated oil palm fiber to remove Cr(VI) from wastewater. The results showed that the removal efficiency for Cr(VI) was dependent on pH, contact time, initial Cr concentration, and amount of adsorbent used. Oil palm fiber can be used as an inexpensive adsorbent to remove Cr(VI) from wastewater.

Chemical modifications produce increased sorption capacity. Nwabanne et al. (2011) and Nwabanne and Igbokwe (2012) used oil palm empty-fruit-bunch activated carbon and oil-palm-fiber activated carbon in a packed bed column to remove Pb(II) from wastewater. Adsorption efficiency was dependent on initial ion concentration, bed height, and flow rate. Sorption capacity was improved as initial ion concentration and bed height increased, because metals can access more sorption sites under these conditions. By contrast, sorption capacity decreased as flow rate increased, because of decrease time for saturation. Gulnaziya et al. (2012) used commercial untreated palm shell activated carbon (PSAC) and modified PSAC by *Aspergillus niger* and *Bacillus subtilis* to remove Pb ion from wastewater. The experiments were conducted in a batch system at pH 3 to 6 with 20 mg/L to 300 mg/L of Pb. At pH 6, the highest values of Pb uptake were recorded for PSAC-*B. subtilis*, PSAC-*A. niger*, and the original PSAC uptake values were 74, 72, and 65 mg Pb/g, respectively. At pH 3, the lowest uptake values were obtained: 34, 37, and 40 mg Pb/g, respectively. Therefore, biomodification of a PSAC matrix can enhance sorption capacity of Pb ions (90%).

Rahman et al. (2012) assessed the adsorption capacity of chemically-modified activated carbon of palm shell to eliminate Cr, Pb, Cd, and Cu ions from polluted aqueous solutions by using a water filtration column. Palm shells were converted to activated carbon that had a large pore surface area ($1,058 \text{ m}^2/\text{g}^{-1}$) and a large pore size (20.64 nm diameter) under the following optimum conditions: treatment with 20% H_2SO_4 in solution at 24 h in 30% H_3PO_4 solution, and maintained at 500°C for 2 h. The adsorption capacities of this adsorbent were 100%, 99.8%, 99.5%, and 25% for Cr, Pb, Cd, and Cu, respectively. In Table 6 we summarize how different heavy metal ions are adsorbed by oil palm biomass carbonaceous adsorbents.

5 Conclusions

The significant increase in production and use of heavy metals in industry has contributed to environmental pollution as a result of the release of high amounts of contaminated water. This increasing heavy metal pollution of waters threatens human health and the environment. Different methods have been used to remove heavy metals from wastewater for the purpose of improving the quality of water that is ultimately discharged to the environment. Although no single method is completely successful in eliminating heavy metals from water, some adsorption solutions produce high quality effluents at relatively low cost. The nature and type of

Table 6 Performance parameters of thermally modified oil palm biomass-based adsorbents for removing heavy metals

S. no.	Adsorbent	Adsorbate				Adsorption conditions				References	
		Particle size	Dosage	Metals	Concentration (mg/L)	pH	Contact time (min)	Agitation speed (rpm)	Temp. (°C)		Adsorption capacity (mg/g)
1.	Oil palm ash	-	2.5 g/L	Ni (II)	40	5	120	200	25	9.9	Chu and Hashim (2003)
2.	Palm shell activated carbon	0.8–1.0 mm	-	Pb	10–700	5	-	150	27	95.2	Issabayeva et al. (2006)
						3				82.0	
3.	Palm oil empty fruit bunch activated carbon	0.5–1.0 mm	1 g/100 mL	Cu	10–20	4.5	-	150	29–31	0.84	Wahli et al. (2009)
				Hg						52.67	
				Pb						48.96	
4.	Activated carbon from palm kernel shell	1.68–2.38 mm	1 g/L	Cu	2.0	5	120	100	27	1.581	Onundi et al. (2010)
				Ni						0.130	
				Pb						1.337	
5.	Modified activated carbon from waste palm shell	2.0 mm	-	Cu	100		-	-	-	75.404 × 10 ⁻³	Rahman et al. (2012)
				Cr						-	
				Pb						0.204 × 10 ⁻³	
				Cd						0.455 × 10 ⁻³	
6.	Acid-treated oil palm shell charcoal coated with chitosan	100–150 µm	40 g/L	Cr	20	4	180	200	25	154	Saifuddin and Kumaran (2005)
7.	Empty fruit bunch activated carbon	250 µm	10–30 mg/50 mL	Hg	0.1	6.5	70	100	-	-	Kabbashi et al. (2011)
8.	Sulphuric acid and heat-treated oil palm fiber	-	0.5 g/100 mL	Cr (VI)	20	1.5	360	350	28	-	Isa et al. (2008)
9.	Palm kernel shell	-	2 g/50 mL	Cr, Pb	-	3	90	-	-	-	Iyagba and Opete (2009)
	Palm kernel husk									120	

(continued)

adsorbent used is critical in influencing the ultimate adsorption efficiency achieved. In general, an adsorbent is considered to be good when it is cost effective, available, environmentally friendly, and does not require a lot of processing. The use of palm oil biomasses as adsorbents to remove heavy metals from contaminated water has been studied by numerous researchers. These adsorbents have specific characteristics that offer several advantages that include: low cost, high absorption capability, environmentally friendly, and biodegradable. If processed appropriately, palm oil biomasses are efficient adsorbents that have extraordinary absorption capability for eliminating heavy metals from waste streams.

In this paper, we have reviewed and compared the adsorption efficiency of several different palm oil biomasses for heavy metals. Increasingly, bio adsorbents like palm oil biomasses are being considered as alternatives to replace conventional adsorbents for removing heavy metals from waste streams. In addition, scientists are working to chemically or structurally modify palm oil biomasses to improve their performance characteristics. Results indicate that such modification can improve sorption capacity by creating a charged surface and by increasing the heavy metal ion binding capacity. Although palm oil biomasses (modified and unmodified) represent good alternatives for replacing commercial adsorbents, additional information on their performance is needed if they are going to be useful for applications at the industrial scale. Developing a multipurpose adsorbent that can remove multiple pollutants from industrial effluents is a reasonable future goal, if the proper research work is undertaken and is successful. From our review, we have concluded that more information is specifically needed in the following areas:

- More complex adsorbents capable of treating industrial wastewater must be investigated.
- Detailed regeneration studies must be performed to enhance the understanding of the economic feasibility of using bio adsorbents such as palm oil biomass. To date, few regeneration studies have been reported. Regeneration studies will determine the reusability of adsorbents made from palm oil biomasses and will contribute to their effectiveness.
- In work performed to date, cost information on oil palm biomasses as adsorbents is seldom addressed or reported in publications. Such cost information is urgently needed. Although modified biomasses can enhance the adsorption of heavy metal ions, the expense of chemicals used and methods of modification also have to be taken into consideration if low-cost adsorbents are to be developed.
- The potential of oil palm biomasses as adsorbents for multi-component pollutants must be assessed. Moreover, these materials must be tested under real industrial effluent conditions. Having such data would significantly assist in moving toward the potential commercial use of biomasses to treat and clean industrial pollution.
- Most researchers have studied oil palm biomass adsorption only in small scale batch processes. Research must now be extended to the pilot-plant scale to better assess oil palm biomass as adsorbents feasible for use at the commercial and industrial scale.

6 Summary

Many industries discharge untreated wastewater into the environment. Heavy metals from many industrial processes end up as hazardous pollutants of wastewaters. Heavy metal pollution has increased in recent decades and there is a growing concern for the public health risk they may pose. To remove heavy metal ions from polluted waste streams, adsorption processes are among the most common and effective treatment methods. The adsorbents that are used to remove heavy metal ions from aqueous media have both advantages and disadvantages. Cost and effectiveness are two of the most prominent criteria for choosing adsorbents. Because cost is so important, great effort has been extended to study and find effective lower cost adsorbents. One class of adsorbents that is gaining considerable attention is agricultural wastes. Among many alternatives, palm oil biomasses have shown promise as effective adsorbents for removing heavy metals from wastewater. The palm oil industry has rapidly expanded in recent years, and a large amount of palm oil biomass is available. This biomass is a low-cost agricultural waste that exhibits, either in its raw form or after being processed, the potential for eliminating heavy metal ions from wastewater. In this article, we provide background information on oil palm biomass and describe studies that indicate its potential as an alternative adsorbent for removing heavy metal ions from wastewater. From having reviewed the cogent literature on this topic we are encouraged that low-cost oil-palm-related adsorbents have already demonstrated outstanding removal capabilities for various pollutants.

Because cost is so important to those who choose to clean waste streams by using adsorbents, the use of cheap sources of unconventional adsorbents is increasingly being investigated. An adsorbent is considered to be inexpensive when it is readily available, is environmentally friendly, is cost-effective and be effectively used in economical processes. The advantages that oil palm biomass has includes the following: available and exists in abundance, appears to be effective technically, and can be integrated into existing processes. Despite these advantages, oil palm biomasses have disadvantages such as low adsorption capacity, increased COD, BOD and TOC. These disadvantages can be overcome by modifying the biomass either chemically or thermally. Such modification creates a charged surface and increases the heavy metal ion binding capacity of the adsorbent.

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