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Locally Derived Activated Carbon From Domestic, Agricultural and Industrial Wastes for the Treatment of Palm Oil Mill Effluent

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2.1 Introduction

Activated carbon is the most effective adsorbent known for the treatment of domestic, municipal, agricultural and industrial wastewater. The use of activated carbon as adsorbent material is widely applicable due to readily available large surface for the attachment of solutes from wastewater. Others types of adsorbent materials are silica gel which is usually hard and granular made by precipitating solution of sodium silicate with acid. Activated alumina is made by activating aluminum oxide at very high temperature. The activated alumina is applicable for moisture adsorption. Aluminum silicates are the product of synthetic zeolite. They are mostly used in the separation process. Activated carbon is widely applied for adsorption because of its small particle sizes and good adsorption capacity (Pérez-González et al., 2012). It has been applied to adsorb heavy metals ions (Gabaldon et al., 2000), it was applied for the removal of phenol (Carrott et al., 2005; Mourao et al., 2006). It has been widely applied for the removal of dyes (Azad et al., 2016) for the removal of pesticides from water (Salman, 2014) and also used for the removal of poly chlorinated biphenyls PCBs (Antonetti et al., 2016). Activated carbon is

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available in two forms, either as powdered activated carbon (PAC) or granular activated carbon (GAC). Powdered activated carbon (PAC) comprises of organic materials having high content of carbon such as wood, lignite, and coal. PAC is widely applicable for wastewater treatment for the removal of taste, odor, and organic pollutants from water. PAC is added in the treatment process and removed subsequently by sedimentation or by backwashing using filter beds. The dosage of PAC is in the range of 1−100 mg/L depending on the concentration of the pollutants. Dosage of 1 to 20 mg/L are usually applied for taste and odor control (O' Donnel et al., 2016). According to the International Union of Pure and Applied Chemistry (IUPAC), the pore size distribution determines the total volume of active sites available for the adsorption and desorption of solutes from the adsorbate. The pore of adsorbent can be classified as micropore if $d < 2$ nm, mesoporous adsorbent surface is in the range of 2−50 nm while macropore is when $d > 50$ nm (Hesas et al., 2013). Granular activated carbon (GAC) is made from organic materials having high content of carbon. GAC is different from PAC because of the particle size diameter between 1.2 and 1.6 mm. The uniformity coefficient of GAC is usually large due to reduce desorption and the ability to aid stratification after backwashing (O' Donnel et al., 2016).

The contact volume of GAC is affected by the breakthrough time, empty bed contact time (EBCT) and design flow rate. The break through time is the time taken for the concentration of the contaminant in the effluent of the GAC unit to exceed the treatment requirement. As a rule of thumb, if the concentration of the effluent is more than the performance benchmark for three consecutive days, the GAC should be replaced or regenerated. The EBCT is usually calculated as ratio of the bed volume and the flow rate through the carbon. The EBCT can be achieved on the longer basis by increasing the bed volume or through the reduction of the flow rate of filter, lower EBCT makes the adsorption process to be slow because of less effectiveness of the diffusion process of the effluent solution (Song et al., 2016). The spent GAC can leach contaminants by percolation into soils in groundwater; therefore their regeneration is favoured over disposal. Despite its effectiveness and wide range applicability, its use for research is limited considering the rate at which water is polluted. The use is limited because of its high cost of production and problem of regeneration (Ahmaruzzaman, 2011). Materials of similar composition which are cheap and readily available are rather used for research for the treatment of wastewater.

2.2 Application of Locally Sourced Adsorbents Materials

The presence of heavy metals in water is a major health and environmental concern to wastewater managers and the ecosystem. The increasing level of contamination and deterioration of water quality is a major problem that needs attention by water users. This is because of the increasing need of water for domestic and industrial activities. The major cause of heavy metal pollution of water is the problem of discharge of effluents from industrial and agricultural sources without adequate treatment before discharge (Zaghden et al., 2016). Several types of treatments methods for the removal of heavy metals from water range from chemical treatments to low cost bio-sorption. The chemical treatment method for wastewater could not achieve the expected result in the wastewater treatment guidelines (Ismail et al., 2014). The application of conventional treatment methods need higher treatment cost of operation, the treatment method tends to have incomplete removal or residual of water contaminants causing further treatment problems (Chiban et al., 2012). The study of the removal of wastewater pollutants using inexpensive adsorbents is becoming very popular for the treatment of industrial wastewater. The low cost adsorbents used for adsorption purposes were waste products from industry, agriculture, and domestic wastes which are easily accessible and abundant in supply. Adsorbents are classified based on uses for gaseous phase application such as air purification and solvent extraction. The second classification of adsorbents is for liquid phase treatment. (Yang and Jiang, 2014).

The common adsorbents for the removal of water pollutants are agricultural wastes such as eggshells, agave bagasse, Maize cob, coconut shell (Foo and Hameed, 2010; Paranavithana et al., 2016; Velazquez-Jimenez et al., 2013). There are emerging adsorbents from mineral composition such as the treatment of heavy metals and organic pollutants using the activated cow bone powder (Latiff et al., 2015, Adeleke et al., 2016) The composition of most natural adsorbents for the treatment of wastewater contains calcium carbonate ($CaCO_3$), which can be very effective to adsorb heavy metals (Ismail et al., 2014). The use of agricultural waste products most especially materials containing lignocellose are very effective for the removal of metals in aqueous solution (Elhafez et al., 2016). Agricultural wastes such as rice husk, palm fruit shell, fruit seed, coconut shells and fruit peels can be used for adsorption purposes (Malik et al., 2016; Raval et al., 2016). These agricultural wastes are referred to as low-cost on the basis of their abundance in supply and the ease of getting the materials from the industry, agricultural areas and food processing production (Afroze et al., 2016). The application of composite adsorbent nowadays is recognized as modern and advanced technology in the adsorbent preparation techniques. The composite media can improve adsorption capacities significantly because of the physical and chemical characteristics of combining materials. They can also enhance the physical and chemical properties such as surface area, pore arrangement, functional group, and mechanical stability (Wang et al., 2014). The surface of composite adsorbent is proven to be effective for the removal of organic and inorganic compounds (Abbas et al., 2016; Orge et al., 2017). There are reported works on the use of composite adsorbent in wastewater treatment. Some of the researches include the use of sodium alginate/sodium-rectorate (SA/Na + REC) nano-composite for the adsorption of dyes and carbohydrate polymer. Hosseinzadeh and Khoshnood (2016) studied the removal of Congo red dye from aqueous solution (Sayğılı, 2015), the use of hydroxyapatite composite for the reduction of Co (II) and Eu (III) (Sheha et al., 2016), magnetic composite was applied for the removal of heavy metals (Reddy et al., 2013) while the use of zeolite-activated carbon as composite adsorbent was studied for the adsorption of acid orange 7 (Lim et al., 2013). Similarly, the application of bentonite bio-char composite for the removal of ammonium from fish tank was investigated by Ismadji et al. (2016), the use of carbon-mineral composite for the treatment of landfill leachate was studied by Halim et al. (2010a).

Wastewater treatment using adsorption is valuable for the treatment of varieties of wastewater with less economic implication, no requirement for land availability. It has no maintenance cost and produces quality effluent of treated wastewater. Adsorption is applicable for different categories of wastewater ranging from low, medium and high strength wastewater. Some of the commonly used adsorbent includes coconut shell adsorbents, zeolite and mineral enriched adsorbent materials.

2.2.1 Coconut Shell Adsorbent

Coconut shell is widely used for the production of GAC of high quality. It is widely used as an adsorbent because it is inexpensive and mostly available in developing countries such as Malaysia and Indonesia. Coconut shell activated carbon is usually prepared from coconut shell by heating at 700 °C, crushed coconut shells is modified with $ZnCl_2$. The resultant char is activated in steam or air at 900 °C. The carbon obtained has surface area of 800 m^2/g having very high adsorption capacities. The kinetics and equilibrium adsorption study of ammonium ion activated carbon prepared from coconut shell was studied by Boopathy et al. (2013), it was observed that the activated coconut shell carbon (ACSC) showed the highest removal efficiency at pH 9, temperature of 283k and contact time of 120 minutes. The optimum adsorption was obtained on a multilayer surface and intraparticle diffusion. The combination of heated coconut shell with acid can be effective for the adsorption purposes. Coconut shell treated with acid and coated with chitosan has better binding surface area for Zn (II) (Amuda et al., 2007). The adsorption efficiency of the coated coconut shell was well fitted in Langmuir and Freundlich isotherm (Amuda et al., 2007). Activated carbon coconut coir was used to adsorb Cr (VI) in the aqueous solution (Chaudhuri et al., 2010). The influence of contact time, adsorbent dosage and pH on the coconut coir activated carbon affected the removal of Cr (VI), Cu (II), and Cd (II). The application of 8 g/L of activated coconut coir carbon was used to adsorb 20 mg/L of concentration of Cr (VI) at 100% adsorption efficiency. The adsorption capacity of coconut coir activated carbon was proven to be better adsorbent than commercial activated carbon for the adsorption of Cu (II) and Cd (II), which fitted very well to Langmuir isotherm (Chaudhuri et al., 2010). The application of coconut husk in a study observed that the pH of solutions has great influence on the adsorption process (Abdulrasaq and Basiru, 2010). In their study, they observed that 50 mg/L removal of Fe (III), 50 mg/L Cu (II), and 10 mg/L Pb (II) were adsorbed at pH 5. The adsorption capacities were close to 90%. Also, coconut husk adsorbent for the removal of Fe (III) and Cu (II) were fitted to the Frendlich isotherm with $R^2 = 1$. Their conclusion was that Fe (III) and Cu (II) removal was due to their chemical bonding. Additionally, Pb (II) had better adsorption in Langmuir isotherm. The metals were also well-fitted to the second order kinetic due to chemisorption (Abdulrasaq and Basiru, 2010).

2.2.2 Bone Activated Carbon Adsorbent

The bone charcoal has the composition of carbon and minerals in the form of calcium carbonate ($CaCO_3$), it has the composition of hydrated calcium phosphate, hydroxyapatite (HAP) resulting in the formation of insoluble calcium phosphate when used as interface between the adsorbent and the adsorbate (AbdulRahman et al., 2016). This usually occurs at some certain temperature and is dependent on the nature of the adsorbate (Moreno-Piraján et al., 2010). However, the characteristics of the adsorbent have been explored in areas of wastewater treatment. Previous literature showed that activated carbon from cow bones is widely known to be used for the removal of color from sugar (Moreno-Piraján et al., 2010). The removal of organic solutes using cow bone carbon is still very rare in research phase in the treatment of POME. Cow bones were activated in the study of Adeleke et al. (2016) for the reduction of manganese and for the reduction of organic pollutants (Adeleke et al., 2016) in palm oil mill effluent (POME). The surface of activated cow bone powder is hydrophobic in nature and can be applied for the adsorption of organic solutes in high strength wastewater such as POME (Adeleke et al., 2017a,b). It has been reported that oxides of aluminum, calcium and phosphorus provide hydrophobic behavior to the composite material (Ito et al., 2013). These elements are the major components of cow bones. Calcium and phosphorus when added to anodized surfaces usually have contact angle in the range of 90 degrees, this indicates hydrophobicity (Yoshihara et al., 2010). When calcium oxide dissolves in water, it forms calcium carbonate which has tendency of forming an alkaline precipitate in the adsorbate (Adeleke et al., 2017a,b). Adsorbent enriched in CaO, raises the pH of the solution to at least 10, creating in the process a medium whereby excess calcium ions can react with phosphate to produce insoluble precipitate known as hydroxyapatite (Boanini et al., 2010). The characteristics of activated cow bone media for effective adsorption of heavy metals is due to presence of hydroxyapatite (Adeleke et al., 2016). Hydroxyapatite interface is recognized as good adsorbent for cationic exchange of various metals concentration in aqueous solution (Dong et al., 2010), which is known to have high degree of irreversible fixation of bone char through chemisorption by the precipitation of metal ions (Vareda et al., 2016). Cow bone is capable of removing heavy metals such as Cu (II), Mn (II), Fe (II), and Ni (II) and also organic compounds (Moreno-Piraján et al., 2010), and it was applied in the removal of lead ions (Cechinel and de Souza, 2014). A study using bone charcoal for the removal of Cr (III) in wastewater was conducted, the bone charcoal was obtained from bovine (Dahbi et al., 2002). The study on the bone charcoal showed that the removal of Hg (II) from the use of camel bone charcoal was due to the ion exchange of the mineral composition (calcium and phosphate components) (Hassan et al., 2008). The influence of pH on the metal removal affects the adsorption properties of the activated carbon. (Demirbas et al., 2004). The application of bone adsorbent as component of a composite material has the potential of showing the characteristics of activated carbon in the composite (Adeleke et al., 2017a,b). Materials are combined as composite adsorbent based on their effectiveness for the remediation of the target pollutants.

2.3 Composite Adsorbent

Several researches have been documented on the development of single adsorbents for range of pollutant removal in wastewater or in aqueous solution. There is increasing interest in regards to developing an adsorbent comprising of different single adsorbents with varying properties to form a composite adsorbent. Some of these compounds include zeolite, fly ash, bentonite, activated carbon, chitosan, montmorrillonite. The significance of the use of composite adsorbent is to enhance adsorption of wastewater. The materials used in developing the composite are identified based on their hydrophobic and hydrophilic properties (Kamarudin et al., 2015). The combination of different materials as composite has shown to possess better sorption of wastewater (Szychowski and Pacewska, 2012). The foremost research effort on carbon-mineral adsorbent was reported by (Leboda, 1992). In his findings, he concluded that mechanical mixing and carbonization of organic substances either physically or chemically bonded with the surface of mineral adsorbent. Hence, catalytic activities and adsorption of water pollutants were achieved. After his documented research effort, researchers began to explore different materials for developing composite adsorbent. Some of the researches conducted using composite adsorbent for wastewater treatment include the research effort of Velmurugan et al. (2015) on the use of magnesium and coconut shell activated carbon as composite for the removal of heavy metal ions in aqueous solution. The conclusion of their research was that the magnesium composite had a greater adsorption of Pb (II) > Cd (II) > Co (II) > Zn (II) and without the magnesium composite the removal was Zn (II) > Cu (II) > Co (II) > Pb (II) > Cd (II). Also, Ai and Jiang (2010), studied the effect of AC/ ferrospinel composite for the removal of dyes. They observed adsorption of methyl orange (MO) and Basil fuchsin (BF) were well fitted to the Langmuir model, the adsorption capacities were recorded as 95.8 and 101.0 mg/g for MO and BF respectively. Sandeman. (2011) investigated and made comparative evaluation of the effectiveness of activated carbon, PVA hydrogels and PVA/AC composite for the removal of cationic methylene blue (MB), anionic methyl orange and Congo red (CR) from aqueous solution. Their conclusion was that the interactions with the ACs or PVA/AC available for adsorption as well as its structural and textural characteristics influenced adsorption capacity. Singh (2010) developed coconut shell carbon-iron oxide composite adsorbent, the optimum conditions of adsorption were achieved at concentration of 240 mg/L, temperature 50°C, pH 8.5 and adsorbent dosage of 1 g/L. The Langmuir model observed maximum adsorption efficiency of crystal violet (CV) at 81.70 mg/g. In the investigation of Adeleke et al., 2017a,b, composite adsorbent was developed from hydrophobic and hydrophilic adsorbent materials for the reduction of COD and NH_3-N from POME. Activated carbons are hydrophobic in nature in the aqueous solution and has the potential to adsorb non-polar solutes such as COD. Similarly, zeolite is a good example of hydrophilic adsorbent material and have the propensity to adsorb polar molecules such as NH_3-N. (Adeleke et al., 2016). However, the use of low cost adsorbents as a replacement for commercial activated carbon has brought new dimensions to the treatment of high strength wastewater such as POME. It has also provided greater opportunities in improving ways of water management. The removal efficiency of the pollutants on the adsorbent material is optimally reduced by combining the adequate ratio of the optimal conditions of adsorbent parameters. The effectiveness of a composite adsorbent for the reduction of solutes in wastewater is influenced by the optimal mixing ratio of the combining materials.

2.3.1 Optimization of Operating Conditions for the Adsorption Process

The optimization of operating parameters has been widely reported in the literature to determine the adsorptive capacity of the prepared adsorbent. The method of optimization of adsorption parameters can be achieved by combining the ratio of adsorbent of similar characteristics in terms of the removal efficiency of the target pollutants. In the study of the removal of high strength color from semiaerobic stabilized landfill leachate using limestone and activated carbon. The mixing ratio of 40 cm^3 of carbon-zeolite were used for the batch adsorption of leachate (Aziz et al., 2010). Similarly, adsorbent mixing ratio of 40:0, 35:5, 30:10, 25:15, 20:20, 15:25, 10:30, 5:35, 0:40 was adopted by volume of dosage of limestone and activated carbon in Aziz et al. (2011). The optimum removal efficiency of color (88%) was achieved using the mixture of limestone (35 cm^3) and AC (5 cm^3) (Aziz et al., 2011). The optimum ratio of 25:15 by volume of limestone- GAC was achieved at 58% removal efficiency of NH_3-N (Hussein et al., 2007). Similarly, the optimum mixing ratio for the removal of COD and NH_3-N from leachate was achieved at 150 rpm, pH 6 and 120 minutes contact time (Daud et al., 2017). Furthermore, the optimum mixing ratio of 150 rpm, pH 7 and 120 minutes was adopted for the adsorption of manganese from POME (Latiff et al., 2015). For effective adsorption of solutes, adsorbent materials are combined based on their behavior in the adsorbate. Halim et al. (2010a) classified adsorbents on the basis of their potentials to adsorb solutes in the polar and nonpolar phase of the adsorbate. They classified limestone and zeolite as hydrophilic materials and also activated carbon and rice husk carbon as hydrophobic materials. (Halim et al., 2010b). The description of the combining ratio can be illustrated in Table 2-1.

A parameter under fixed condition of other parameters can be used for optimization purposes. However, in real life application, investigating a parameter under fixed condition of other parameters may not comprehensively determine the nature of the adsorption process. The use of conventional approach in the study of adsorption, whereby a process is investigated by maintaining other parameters at a fixed condition may not be suitable to determine the combined effect of other parameters (Ravikumar et al., 2005). The operating parameters

Table 2-1 Combination of Adsorbent Material

Hydrophilic/Hydrophobic Ratio cm^3/Particle Size
0–40
5–35
10–30
15–25
20–20
25–15
30–10
35–5
40–0

to investigate the nature of adsorption can be suitably expressed by investigating the impact of multiple parameters simultaneously for adsorption purposes. The central composite design (CCD) of the response surface methodology (RSM) can achieve this purpose. RSM was used in the work of (Sahu et al., 2009) to establish the relationship of the adsorption of Cr (VI) using 25–30 designed experimental runs. The variables considered were represented in coded values as temperature (X_1), pH (X_2), initial concentration (X_3), and adsorbent dosage (X_4). Song et al. (2016) used 15–20 run of CCD experimental design to investigate the adsorption capacity of magnetic composite material under operating parameters of initial temperature, pH and initial concentration on the adsorption. In addition, Hu et al. (2013), investigated the effect of operating parameters of pH, initial concentration and temperature on the adsorption of Cu on graphene oxide composite using RSM. Debnath et al. (2015) analyzed the optimization of the adsorption of Congo red using lignocellulose composite adsorbent. The analysis of the effect of the operating parameters of pH and initial concentration combined was observed to be antagonistic. It was also observed that the effect of the combined operating parameters of initial concentration and temperature was synergistic while the effect of pH and temperature was reciprocal. In the study of Alkhatib et al. (2015), experiment of the optimization of the removal of color after the conventional treatment of POME was conducted using RSM. The operating variables used were the contact time, pH and the adsorbent dosage. The highest adsorption efficiency of 89.95% was obtained after the experimental output.

The application of RSM for multiple parameters makes the interpretation of the mechanism of adsorption, treatment process and application of models to be comprehensive. Hence, the use of RSM is a very valuable tool for optimization purposes.

2.3.2 Linear Optimization and the Preparation of a Composite Adsorbent

In the process of the preparation of the composite adsorbent, batch adsorption study under fixed conditions are usually conducted at different optimum ratio. In the study conducted by Adeleke et al. (2016), operating parameters at fixed condition of contact time of 105 minutes, 150 rpm shaking speed and pH 7 were used for the batch adsorption study to investigate the removal of pollutants of POME from the prepared adsorbent. Since the adsorbent materials were of different weight by dosage, to determine the right volume of the dosage by weight occupied in the POME, the dosage of each adsorbent used was evaluated using the bulk densities of the particle sizes of the starting materials (Adeleke et al., 2017a,b). This was obtained at predetermined volumes from density–mass relationship of the adsorbents.

The optimum condition of the hydrophobic-hydrophilic ratio was used to determine the optimum condition by percentage of the starting materials that will be mixed with the OPC. The optimum condition in this case is defined as the best mixed ratio that gives the best removal efficiency of the parameters at the lowest application of OPC, which served as the binder. All experiments to be optimized should be run in triplicate and the average recorded to reduce the unexpected variability of expected outcomes. The stages for the determination of the optimum condition used to prepare the composite are as follows: By the selection of the optimum particle size of the single adsorbents in a sequence batch study. By the determination of the optimum ratio of the hydrophobic media and the hydrophilic adsorbent under separate classification. The classification of adsorbent materials was based on the potential to adsorb nonpolar solutes in the adsorbate and also the ability to adsorb the polar solutes in the aqueous medium. This can be obtained using the contact angle experiment. The process of the preparation of composite adsorbent in the study of Adeleke et al., 2017a,b is presented in Figs. 2-1 and 2-2.

The volume of the adsorbent-binder ratio for the preparation of a composite adsorbent is defined by the adsorbent ratio that gives optimum reduction of the solutes in the adsorbate at minimum binder ratio. This is influenced by the porosity volume of the adsorbent is a very valuable parameter in fixed bed column adsorption for effective column design. An illustration of the fixed bed column. Other parameters that determines the nature of the

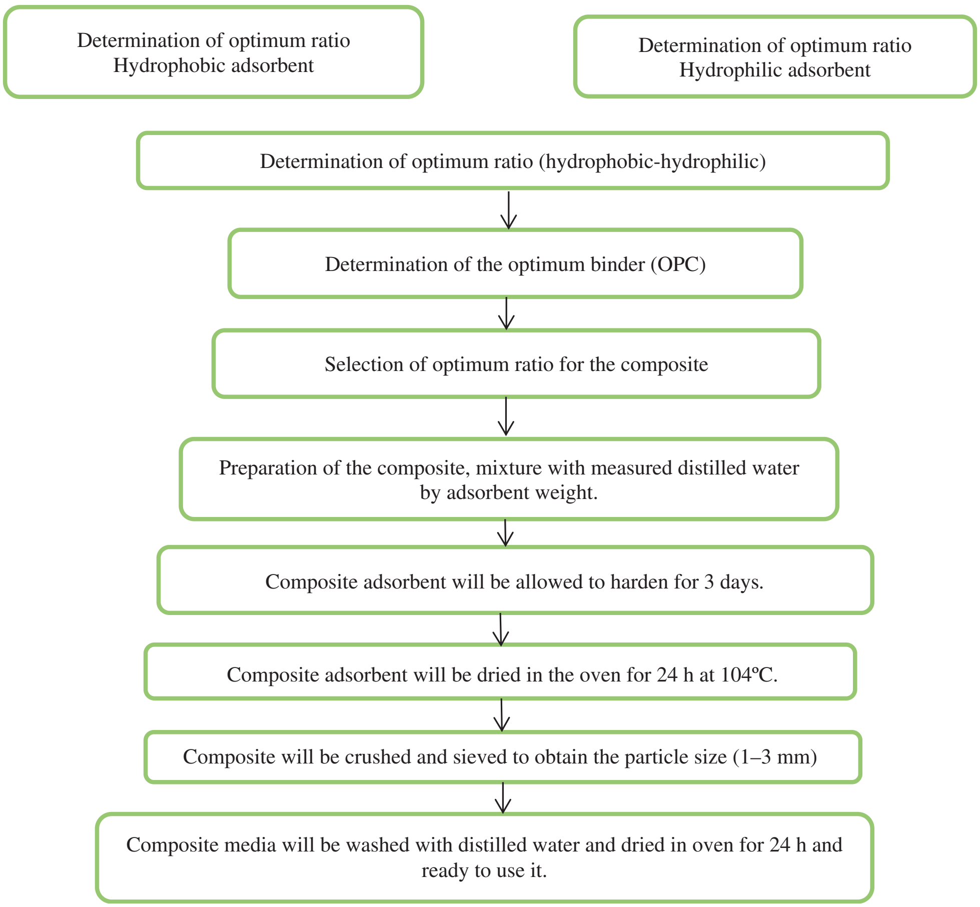

FIGURE 2-1 Preparation of composite adsorbent.

FIGURE 2-2 Preparation of composite adsorbent.

adsorption process includes the morphology of the adsorbent, the chemical composition of the adsorbent materials and also the point of which the adsorbent material is electrically neutral known as the point of zero charge of the adsorbent. The point of zero charge in relation to the pH of the adsorbate is used to determine whether the adsorbent surface is negative or positive. It is known that a negative surface has strong potential to engage in cationic adsorption of solutes in the adsorbate while a positive surface of adsorbent is known to be suitable for the adsorption of anionic adsorption in the adsorbate. The surface characteristics and pore size distribution of the adsorbent material is mostly determined by the Brunauer Emmet Teller (BET) analysis. The BET classifies adsorbent based on shape, pore, and sizes including both internal and external structures. The transport and diffusion mechanisms within the adsorbent pores and on the surface determines the nature of adsorption. This is determined by the nature of the concentration gradient. The chemical composition of an adsorbent is determined by the energy dispersive X-ray spectroscopy (EDX) or the application of the X-ray flourescence used for the characteristics of adsorbent material in the excited state to determine the elements and chemical compounds present in the adsorbent. The functional groups, cationic exchange capacity and the types of bonding of the solutes to the adsorbent are other chemical characteristics that defines the suitability of the adsorbent material for the attachment of solutes on the adsorbents. The description of some of the characteristics of adsorbent materials is described below.

2.3.3 Contact Angle Measurement

The contact angle measurements were conducted on the starting materials using Pendant drop penetration time test. The pendant drop test was used to investigate the interfacial tension on the starting materials when in contact with fluid. The curvature of the drop is known as Pendant drop penetration and is determined by the balance between the interface and the gravitational forces (Sarmadivaleh et al., 2015). This is expressed in Young–Laplace equation as:

$$\Delta PP = Y\left(\frac{1}{R1} + \frac{1}{R2}\right) \tag{2.1}$$

$$\Delta pk - \Delta PP = z\Delta pg \tag{2.2}$$

Where,

Y is defined as the interfacial tension
$R1$ and $R2$ are the radii of curvature of same point on the curved surfaces.
ΔPP is the pressure difference between the deionized water and the adsorbent at a random point p on the interface z.
Δpk is defined as the pressure difference between the deionized water and the adsorbent at height point of drop when $z = 0$.
Δp is the difference of the density between the deionized water and the adsorbent
g is the acceleration due to gravity.

In application, the deionized water is filled in to the cell through the needle at a constant flow rate using a high precision syringe pump. The deionized water forms a drop at the bottom of the needle and dropped on the surface of the adsorbent. Two additional drops are added to the surface of each starting material. The whole process is captured with a standby camera to measure the contact angle. The obtained contact angles of the materials are used to determine and classify the adsorbents on the basis of their hydrophobic or hydrophilic characteristics.

2.3.4 Bulk Density

Bulk density determines the weight of adsorbent by volume of the sample. Bulk density increases with decrease in porous surface of the adsorbent. Activated carbon is known to have a porous surface of around 3000 m^2/g. Due to the large specific surface area and porous surface, activated carbon has lower bulk density. The measured dry weight is divided by the saturated volume to obtain the bulk density by the equation below.

$$\text{Bulk density} = \frac{\text{Dry weight of adsorbent (g)}}{\text{Volume of sample (mL).}} \tag{2.3}$$

2.3.5 Porosity Volume

Saturation method is mostly used to determine the porosity volume of the adsorbent. The porosity volume is much applicable for the determination of composite adsorbent in a continuous fixed column. In the case of fixed bed adsorption, water-saturated composite samples are introduced into the column until equilibrium concentration was achieved (Alonso et al., 2005). Saturation in a fixed column experiment is performed according to the packed column. An example of a fixed bed column adsorption is illustrated in Fig. 2-3.

In the study of Halim et al. (2010b), porosity volume experiment was conducted by filling the composite sample to maximum height of the column. The volume of the sample was

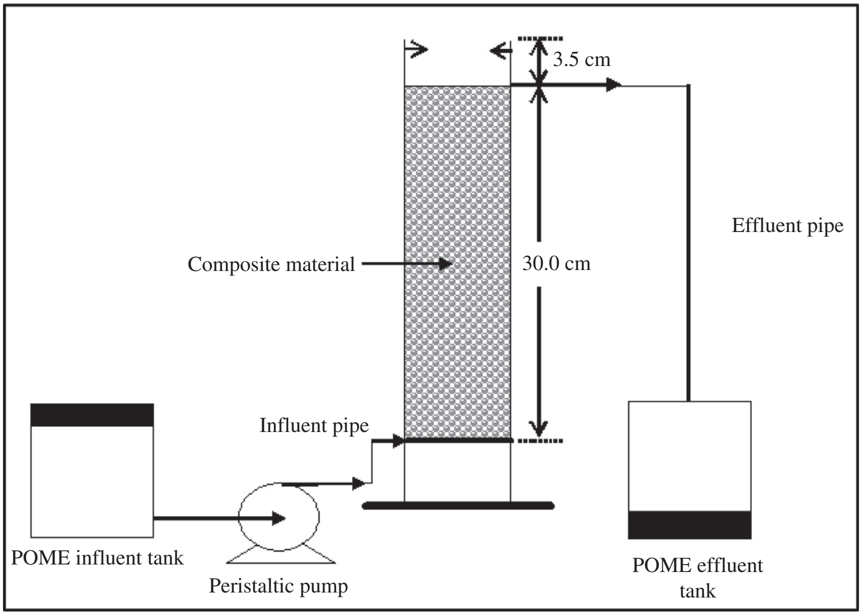

FIGURE 2-3 Column for fixed bed adsorption.

measured and recorded. A separate beaker was filled with deionized water containing more than the water needed to saturate the sample. The volume of the deionized water used at the saturation point was recorded. The volume of water used is the difference between the total volumes of water before saturation. This gives the pore volume of the sample. Therefore;

$$\text{Porosity } (Pt) = \frac{\text{Porevolume } (Vp)}{\text{Totalvolume } (Vt)} \tag{2.4}$$

Where total volume = solid volume (Vs) + pore volume (Vp)

2.3.6 Morphology Study

The surface morphology of the prepared adsorbent showing the textural and the pore size arrangement of the adsorbent are usually observed to determine the porosity and structure of adsorbent. The microstructure of the adsorbent is determined from the micrograph obtained from the scanning electron microscopy (SEM). In order to determine the rate of diffusion of the adsorbent and transport within the pores and on the surface of the adsorbents, the images of the adsorbent is obtained before and after the treatment of the batch adsorption. The images are obtained by scanning accelerated electron beam by the collection and recording of the secondary beam and backscatter electrons. To obtain a clear image, the micrograph is captured at high resolution and at a very clear and visible magnification. This is achieved by bombarding electrons on the surface of the sample particles.

The morphology of composite adsorbent for the treatment of POME in the study of Adeleke et al. (2017a,b) is illustrated in Fig. 2-4

The samples are usually coated with gold or platinum target to enhance the conductivity of the adsorbent materials before the bombardment.

2.3.7 Brunauer Emmet-Teller (BET) Surface Area

The BET surface analysis is conducted on the adsorbent to determine the surface area, pore volume and the pore size distribution of the adsorbent particle. The study is mostly determined by the N_2 adsorption/desorption using a micrometric ASAP 2000 system. The nitrogen adsorption-desorption on the sample is placed under vacuum at equilibrium time interval to remove moisture content from the solid surface. The analysis of the surface area, pore volume, and size of the composite is obtained from the plot of the relative pressure against the quantity adsorbed.

2.3.8 Chemical Characterization of Adsorbent

The chemical characterization focusses on the elemental composition and chemical compounds of the adsorbent materials and also the functional groups on the active sites of the adsorbent. Acidic surface have the potential for cationic exchange due to the presence of carboxylic compounds on the surface of the adsorbent. Elemental analysis of the prepared

(A)

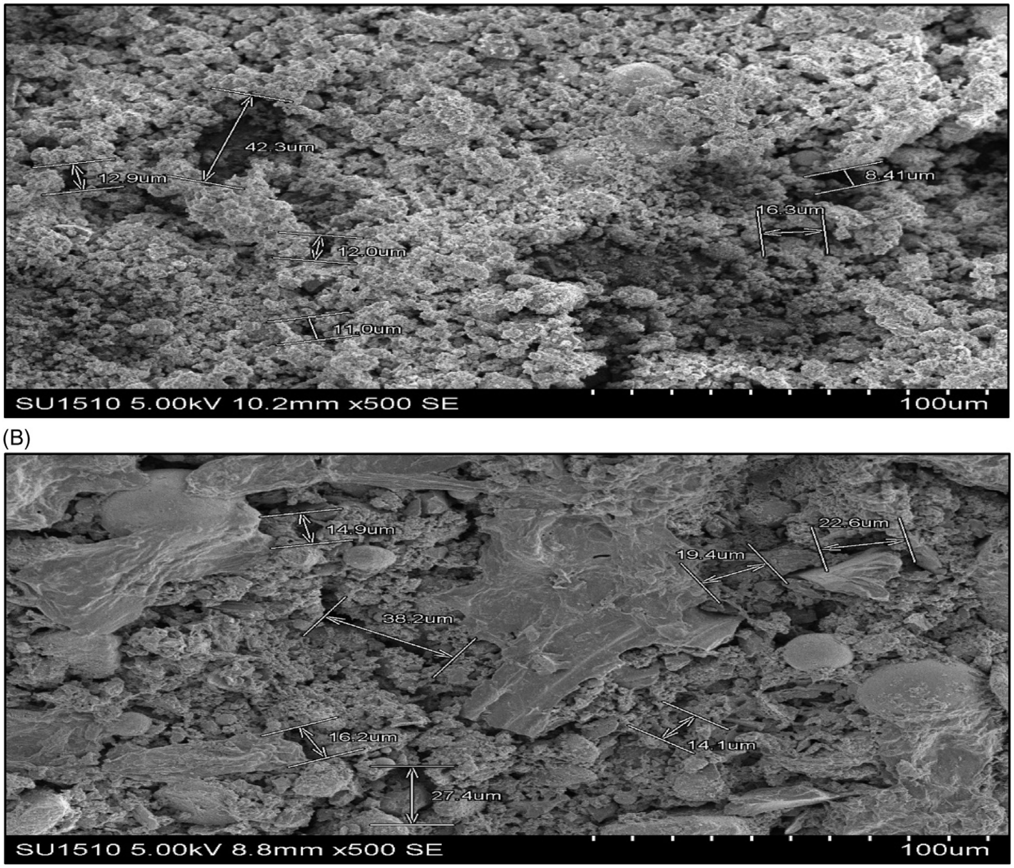

FIGURE 2-4 (A) Morphology of composite before batch treatment. (B) Morphology of composite after batch adsorption.

adsorbent materials can be achieved using the energy dispersive X-ray (EDX) incorporated in SEM (JOEL-JSM 6400). Prior to the investigation, adsorbent materials are coated to enhance the conductivity of the adsorbent material in order to achieve better resolution of the microstructure of the adsorbent and to avoid the accumulation of electrostatic charge. Some of the materials used for coating to enhance the conductivity of the sample includes gold, platinum, chromium, and tungsten. The coating material on the surface is usually conducted at low-vacuum sputter coating or by high vacuum evaporation. The images produced by SEM is as a result of the interaction between electron beams of the samples obtained at various depths. The images are transmitted in form of signals. Some of the most common types of signals produced by SEM includes the secondary electrons, back-scattered electrons and transmitted electrons. Nonconductive sample to be analyzed by the SEM obtain charges when scanned by the electron beam can result to improper scanning of the material. The elemental compositions of the adsorbents were achieved as percentage atomic contents in the adsorbents. This was used to determine the heavy metals before and after the batch adsorption study. The emission of secondary X-rays from an excited material involves the bombardment with high-energy X-rays. This is achieved by the radiation of the element at different electronic orbitals by the removal of the electron inside the orbitals by an energetic photon which is provided by a primary source of radiation. For the excitation of the atoms, a source of radiation with sufficient energy is needed to expel tightly held inner electrons. X-ray transmitters in the range of 20–60 kV are used to obtain atomic information of the excited material.

2.3.9 Functional Group on Adsorbent

Fourier transform infrared irradiation (FT-IR) is an analytical procedure of obtaining the functional groups on the surface of an adsorbent material which is obtained at high spectra resolution. The effectiveness of the FT-IR spectroscopy is determined by the extent at which adsorbent material adsorbs light at a specified wavelength. FT-IR is used for the identification of the chemical bonds in a molecule by the production of infrared absorption spectrometer. FTIR is applicable to analyze the functional groups of the irradiated adsorbent materials. The powdered form of the adsorbent materials is dried in the oven at 105°C usually with silicon carbide. The dried sample is placed on the translucent crystal plate, the manual bench-press is adjusted and placed on the sample to ensure light compaction until the spectrometer detected the functional groups on the adsorbents. The scan of the adsorbent is done for within a few seconds to achieve better sensitivity. The spectra are mostly in the range of 400–4000 cm^{-1} (Model Perkin Elmer FT-IR-2000, US).

2.3.10 Point of Zero Charge

The point of zero charge (pH_{pzc}) determines the point at which the interfacial region of a material is electrically neutral. When the pH of the system is lower than pH_{pzc}, the medium is said to be acidic because acidic water donates protons more than the hydroxide group. In the process, the surface becomes positively charged, which implies that there is high tendency for the attraction of ions. Conversely, when the pH of the system is higher than the pH_{pzc}, the surface tends to be negatively charged occasioned by the attraction of cations and repulsion of the anions. The pH of the Pzc is mostly obtained by the acid-base titration. Another common technique is described in the study of Cechinel and de Souza (2014). The experiment to determine the pH_{pzc} of activated cow bone adsorbent was carried out using the 11 point pH measurement as adopted by Cechinel and de Souza (2014). 0.025 g of adsorbent weight of material was placed in a 250 mL conical flask, 25 mL of deionized water was added to each of the flasks at different initial pH conditions. The pH was adjusted using 0.1 M NaOH and HNO_3. The samples were agitated at 120 rpm for 24 hours at 25°C. At the end of the contact time, the final pH of each of the samples was measured. A plot of the final pH against the initial pH was obtained from the obtained values. The point at which the plot of the final pH intersects with the plot of the initial pH value was recorded as the pH_{pzc}.

2.3.11 Analysis of Cation Exchange Capacity

The ammonium acetate saturation (AMAS) method is widely conducted to determine the CEC of the adsorbent media which is often used to explain the mechanism of adsorption. This was achieved by the saturation of the ammonium acetate (NH_4OAc) solution. About 5−10 g of each of the adsorbents are put in a 250 mL flask. 100 mL of NH_4OAc is added to each of the conical flask and shaken thoroughly for 1 hour after which the sample is shaken at 150 rpm for 24 hours. The samples are filtered with 2.5 μm (Whatman no. 42) using the vacuum pump by applying light suction until a clear filtrate is obtained and discarded. The sample is washed with ethanol to remove excess saturating solution. The solution is allowed to completely filter through the flask with light suction after which the supernatant is discarded and cleaned from the flask. Each of the samples is washed with 25 mL of 1 M KCl. At this stage, the sample is discarded and the filtrate transferred to a 250 mL volumetric flask. A Nessler colorimetric test is conducted to test for NH_4-N in the filtrate at 420 nm. A blank sample is prepared according to the Nessler method to adjust the spectrophotometer in order to obtain the reading of the sample for the evaluation of the CEC.

The CEC is evaluated as:

$$\text{CEC}\ (\text{meq/g}) = \frac{0.1\ \text{L}}{14} \times \frac{1}{\text{weight of sample (g)}} \times \text{conc}\ \text{NH}_4{}^{+}\ (\text{mg}/L) \tag{2.5}$$

2.4 Optimization of Process Parameters

The optimization of process parameters in adsorption process can be processed either by the conventional method by the optimization of operational parameters under fixed condition in terms of other parameters. The other method involves the optimization of multiple variables for the prediction of response parameter. One of the commonly used method is by applying response surface methodology (RSM). The two forms of optimization method was adopted in the study of (Latiff et al., 2015, Adeleke et al., 2017a,b). Linear optimization, which is conventionally used in literature, was adopted for the determination of the optimum condition of the particle size and ratio of adsorbent used for the preparation of the composite adsorbent in terms of the removal efficiencies of COD and NH_3-N (Latiff et al., 2015). A typical example of the combining ratio of the adsorbent parameters using linear optimization is illustrated in Table 2-1. The other form of optimization of the process parameters was achieved using the RSM, to investigate various variables and factors of adsorption and the efficiency of the prepared composite for the treatment of the pollutants of POME (Adeleke et al., 2017a,b). Two responses of COD and NH_3-N were also used for the optimization purpose. This was adopted because COD is the most critical parameter of raw POME (40,000-100,000) mg/L (Cheng et al., 2015). Also, the concentration of NH_3-N in water bodies may result to the eutrophication effect in the flora and fauna (Boyd, 1947). The linear optimization is conducted under fixed condition of pH 7, contact time 105 minutes, shaking speed 150 rpm. The factors used for the optimization is determined under fixed condition. Batch adsorption study or fixed bed column adsorption can be for the optimization of experimental factors.

2.5 Batch Adsorption Experiment

Batch adsorption experiments is conducted to obtain information about the uptake of parameters. Adsorption experiments is investigated using 250 mL Erlenmeyer flask with a stopper. 100 mL of the POME at different weight of adsorbent dosage are put in the flasks and placed in the isothermal water-bath shaker (Haake Wia Model, Japan) for the predetermined period of contact time. The water bath has a temperature controller adjustable from 25 to 100 ± 1 rpm. The adsorbent dosage used for the adsorption study can either be quantified in terms of weight or volume of the adsorbent. In the case of volume of adsorbent, it is evaluated from the bulk density of the adsorbent material. Prior to the investigation of the adsorption efficiency of the adsorbent for the uptake of the parameter, the solutions is filtered using 0.45 μm Whattman filter paper to obtain the residual concentration of the treated effluent. The analysis of COD from the residual concentration of the filtered sample is known as soluble COD. The analysis of each of the parameter of the wastewater characteristics is based on the standard methods. The amount of the adsorption of the adsorbate at equilibrium contact time qe (mg/g) is evaluated according to Eq. (2.6) and the removal efficiency is measured according to Eq. (2.7).

$$qe = \frac{(\text{Co} - Ce)v}{w} \tag{2.6}$$

$$\text{Adsorption efficiency} = \left(\frac{\text{Co} - \text{Ce}}{\text{Co}}\right) \times 100 \tag{2.7}$$

Where,

Co is the initial liquid–phase concentration of adsorbate (mg/L)
Ce is the final liquid–phase concentration of adsorbate (mg/L)
v is the volume of solution (L)
w is the weight of the adsorbent (g)

2.6 Optimization of the Process Parameters Using Central Composite Design

The optimization of process parameters is used to determine the best condition of the operational factors that can be suitable to achieve the effective treatment efficiency of the adsorbent materials. One of the most comprehensive method of optimizing the parameters of adsorption is by the use of RSM, which is widely applied in varieties of wastewater such as the domestic, agricultural, municipal and industrial effluents. RSM was applied to the study of Adeleke et al. (2017a,b) for the treatment of organic pollutants of POME. The effect of six factors (independent variables) which included pH (x_1), shaking speed (x_2), contact time (x_3), particle size (x_4), initial concentration (x_5) and adsorbent dosage (x_6) were investigated for the removal of COD (y_1) and NH_3-N (y_2)which were the response parameters. The central composite design (CCD, expert 6.0.10) method was used to determine the number of experimental analysis to be evaluated for the optimization of the variables and responses. This was conducted using the Design Expert software to analyze the evaluated data for the first order response surface equations of the model. The significance of the six variables on the adsorption process was analyzed using the analysis of variance (ANOVA, $P < .05$). The significance of the adjusted coefficient of determination (R^2 adj) was for the checking of the fitness of the linear model. The interactions between the factors and their effects on the reduction of both organic solutes could have a synergistic or antagonistic effect on the investigated responses. The results of the prediction of the interaction of the variable factors for the reduction of the responses can be presented and visualized using three-dimensional graphical representation of the system behavior, called RSM.

2.6.1 Experimental Design Using the Central Composite Design

The central composite design (CCD, expert 6.0.10) method is used to determine the number of experiments to be evaluated for the optimization of the variables and responses. The minimum, intermediate, and maximum values of each variables are labeled as −1, 0, and +1, respectively. This is illustrated in Table 2-2.

In the study of Adeleke et al. (2017a,b), optimization of process parameters of composite adsorbent was conducted using 85 experimental analyses considering 6 operational variables to investigate the optimum condition that gave better removal efficiency of the response factors, a central composite design (CCD) design expert 6.01 consisting of six independent variables was used in order to get the optimal conditions for the removal of COD and NH_3-N from POME by a composite adsorbent using response surface methodology. Eighty-five runs [nine (9) center points and eleven (11) extra points)] were conducted in order to cover the possible combinations of operational factors and their effect on the reduction of the investigated responses. Batch adsorption experiments were performed in a random and with triplicate in order to reduce the unexpected variability effects for the observed responses. The results revealed that the investigated factors significantly influenced the reduction of COD and NH_3-N and was better than the conventional method of optimization. The effective of reduction of the organic parameters of POME would lead to improve characteristics of the treated effluent before discharge.

Table 2-2 Experimental Design for the Optimization of the Response Factors

		Level		
Factor	**Symbol**	**Low (−1)**	**Middle (0)**	**High (+1)**
pH	x_1	4	7	10
Shaking speed (rpm)	x_2	50	175	300
Contact time (h)	x_3	2	13	24
Particle size of composite (mm)	x_4	1	2	3
Initial concentration of composite (dilution factor)	x_5	100	300	500
Adsorbent dosage (g/L)	x_6	65	95	125

Moreover, in the optimization process, the optimum operation for the reduction percentage of parameters are usually varied with each factor separately and as combined factors. The combination of factors could either be synergistic by influencing the reduction of the response parameter or antagonistic by reducing the efficiency of the treatment process. To determine the effectiveness of the treatment process, the efficiency of the adsorbent materials is evaluated using the reduction percentage from the relationship between the initial concentration and the residual concentration of the investigated response parameter. The effectiveness of the adsorption process is determined from the Eq. 2.7.

2.6.2 Development of Regression Model for the Response Parameters of the Adsorbent

The regression coefficients is the numerical index used to quantify the reduction percentage of the investigated parameter with the consideration of the interaction of the variable factors and the effect on the adsorption process. The variable factors for the prediction of the response parameter can be quantified from the linear, quadratic and cubic function of the CCD, the coefficient of the model in terms of the operating parameters is used to predict the regression equation of the prediction of the model. The F-value is used to determine the suitability of the model for the prediction of the response factors while the *P*-value ($P < .05$) shows the significance of the model at confidence level of 95%. The response is satisfactorily predicted when there is high coefficient of *F*-value in terms of the standard error. The ability to determine the aptness of the model is usually with respect to the standard error, a low value of standard error in relation to the *F*-value signifies that the model is sound and effective for the prediction of the response parameters. However, a low value of the standard error observed in Table 3-5 in relation to the *F*-value signified that the model was effective for the prediction of the reduction of the COD and NH_3-N in terms of the operating conditions (Adeleke et al., 2017a,b). A typical result of regression coefficient and their significance of the linear, quadratic and cubic model for the reduction of parameters of POME is illustrated in Table 2-3

The optimum operation for the reduction percentage was varied with each factor separately and also as a combined factor. The reduction percentage which is the dependent variables was calculated according to Eq. (3.4). The evaluated data was analyzed using the analysis of variance (ANOVA, $P < .05$). The independent factors which included pH values (4−10), shaking speed (50−300 rpm), contact time (2−24 h), particle size (1−3 mm), initial concentration of POME (100−500 dilution factor) and adsorbent dosage (65−125 g/L) were selected in order to examine the comprehensive factors which might have effects on the reduction of COD and NH_3-N. The calculation of the regression coefficients of the linear and quadratic, as well as the interaction between the factors in the model, was conducted to explain the variability of the experimental data. The effect of each independent factor was considered significant at *P*-value $< .05$ which is equivalent to 95% of the confidence level. The results found that five examined factors have a positive significant linear effect on the reduction of COD, while time has a negative significant effect which means that the increase of time affects or reduces the efficiency of the adsorption process. In contrast, three factors including pH and adsorbent dosage and initial concentration have positive effect on NH_3-N. pH and initial concentration was observed not significant on the reduction of NH_3-N except the adsorbent dosage which positive effect reduced the NH_3-N concentration in the POME. Also two factors of contact time and particle size of the adsorbent have a negative significant effect on the removal of NH_3-N. As the contact time increases, adsorption decreases depending on the behavior of the surface.

Also, the size of adsorbent is dependent on the rate of adsorption. The solute molecule is expected to readily penetrate pores of the smaller diameter than larger pore spaces. As a result, adsorption capacity increases with a decrease in particle diameter (Li et al., 2016). The quadratic effect of the pH is significant but the quadratic effect of particle size of the composite is not significant on the reduction of both COD and NH_3-N. Also, the quadratic

Table 2-3 Regression Coefficient and Their Significance of the Linear, Quadratic, and Cubic Model for the Reduction of COD and NH_3-N From POME by Using Central Composite Design

	Coefficient		Standard Error		F value		*P*-value	
Term	**COD**	**NH_3-N**	**COD**	**NH_3-N**	**COD**	**NH_3-N**	**COD**	**NH_3-N**
Model	**68.923**	**52.166**	**0.890**	**1.389**	**14.094**	**6.497**	**< 0.0001**	**< 0.0001**
X_1	1.682	0.636	0.414	0.647	16.469	0.966	0.000	0.333
X_2	1.013	− 0.700	0.414	0.647	5.975	1.170	0.020	0.288
X_3	− 2.399	− 1.804	0.414	0.647	33.503	7.775	< 0.0001	0.009
X_4	1.872	− 1.794	0.414	0.647	20.414	7.691	< 0.0001	0.009
X_5	1.850	0.357	0.511	0.797	13.129	0.200	0.001	0.658
X_6	1.948	2.246	0.414	0.647	22.088	12.050	< 0.0001	0.002
X_1^2	0.889	1.667	0.272	0.425	10.645	15.349	0.003	0.001
X_2^2	− 3.313	3.691	0.272	0.425	147.821	75.274	< 0.0001	< 0.0001
X_3^2	− 2.349	− 1.292	0.272	0.425	74.326	9.223	< 0.0001	0.005
X_4^2	0.955	0.914	0.272	0.425	12.274	4.612	0.001	0.040
X_5^2	-0.541	5.418	0.738	1.152	0.537	22.118	0.469	< 0.0001
X_1X_5	1.725	0.893	0.352	0.549	24.038	2.645	< 0.0001	0.114
X_2X_3	2.902	4.897	0.352	0.549	68.051	79.496	< 0.0001	< 0.0001
X_2X_4	− 1.426	− 0.059	0.352	0.549	16.439	0.012	0.000	0.915
X_2X_5	− 0.860	− 1.355	0.352	0.549	5.981	6.088	0.020	0.019
X_2X_6	− 1.251	− 1.391	0.352	0.549	12.652	6.418	0.001	0.017
X_3X_4	− 3.104	− 0.289	0.352	0.549	77.849	0.276	< 0.0001	0.603
X_3X_6	− 0.686	1.881	0.352	0.549	3.799	11.734	0.060	0.002
X_4X_5	− 0.954	0.417	0.352	0.549	7.356	0.577	0.011	0.453
X_5^3	0.096	− 1.300	0.319	0.497	0.091	6.831	0.766	0.014
X_6^3	− 0.055	− 0.351	0.112	0.175	0.243	4.013	0.626	0.054
$X_1X_2X_4$	− 0.258	− 1.273	0.352	0.549	0.540	5.374	0.468	0.027
$X_1X_2X_6$	− 1.022	0.128	0.352	0.549	8.444	0.054	0.007	0.817
$X_3X_5X_6$	− 0.768	− 0.086	0.352	0.549	4.760	0.024	0.037	0.877
$X_4X_5X_6$	0.829	− 0.737	0.352	0.549	5.550	1.799	0.025	0.190

effect of speed and time is not significant for the reduction of COD, but the quadratic effect of the shaking speed and the initial concentration is significant to the reduction of NH_3-N. The synergistic effects of the examined factors investigated in the study was based on ANOVA analysis. In the case of COD reduction, the results of the analysis revealed that pH factor has a positive significant synergic effect with an initial concentration of composite ($P < .05$) but not significant for the reduction of NH_3-N. The shaking speed factor exhibited a positive significant synergic effect with time which improved the reduction of both organic pollutants investigated in the POME. Also a negative significant effect of the synergic of initial concentration and particle size of the composite and also the shaking speed and initial concentration have negative impact on the reduction of both pollutants. Meanwhile, the negative effect of the synergic between the shaking speed and initial concentration is not significant to the reduction of both COD and NH_3-N similar to the cubic effect, the effect of the shaking speed and the adsorbent particle size is not significant for the reduction of COD but influenced the removal of NH_3-N. In the case of the contact time and particle size, a negative effect for the reduction of COD concentration was observed but significant for NH_3-N. A case of contrast was observed for the contact time and adsorbent dosage where there was negative effect on COD but positive effect on NH_3-N to the adsorption process. The combined effect of pH, shaking speed and particle size was significant for the reduction of COD but significantly decreased the efficiency of NH_3-N. Both the negative effect of pH, speed and adsorbent dosage on COD and positive effect on NH_3-N is not suitable for the adsorption process. The negative effect of the contact time, initial concentration and the adsorbent dosage is not suitable for the reduction of COD but suitable for the reduction of NH_3-N concentration in the POME. The effect of the particle size, initial concentration and adsorbent dosage is significant for the reduction of COD but not significant for the reduction of NH_3-N. The prediction of the reduction of the investigated pollutants of POME can be represented through the numerical coefficient of the regression model.

The second-order model describes the significant relationship between the reduction of COD and NH_3-N and selected factors in terms of coded factors as given by Eqs. (2.8) and (2.29).

$$\begin{aligned} y_1 = &+ 68.92 + 1.68x_1 + 1.01x_2 - 2.40x_3 + 1.87x_4 + 1.85x_5 + 1.95x_6 + 0.89x_1^2 - 3.31x_2^2 - 2.35x_3^2 \\ &+ 0.95x_4^2 + 1.72x_1x_5 + 2.90x_2x_3 - 1.43x_2x_4 - 0.86x_2x_5 - 1.25x_2x_6 - 3.10x_3x_4 \\ &- 0.69x_3x_6 - 0.95x_4x_5 - 1.02x_1x_2x_6 - 0.77x_3x_5x_6 + 0.83x_4x_5x_6 \end{aligned} \tag{2.8}$$

$$\begin{aligned} y_2 = &+ 52.17 - 1.80x_3 - 1.79x_4 + 2.25x_6 + 1.67x_1^2 + 3.69x_2^2 - 1.29x_3^2 + 0.91x_4^2 + 5.42x_5^2 + 4.90x_2x_3 \\ &- 1.36x_2x_5 - 1.39x_2x_6 + 1.88x_3x_6 - 1.30x_5^3 - 0.35x_6^3 - 1.27x_1x_2x_4 \end{aligned} \tag{2.9}$$

Where y_1 and y_2 are the responses for the reduction percentage of COD and NH_3-N respectively. The summary of the analysis of variance (ANOVA) for the quadratic model represents the significance of the prediction of the model, It was noted that the regression model for the reduction of response parameters was significant at a confidence level of 95% ($P < .05$) with determination coefficients (R^2 adj) equal to 0.892 and 0.776 for COD and NH_3-N respectively, indicating the aptness of the model. The ANOVA of the response surface quadratic model

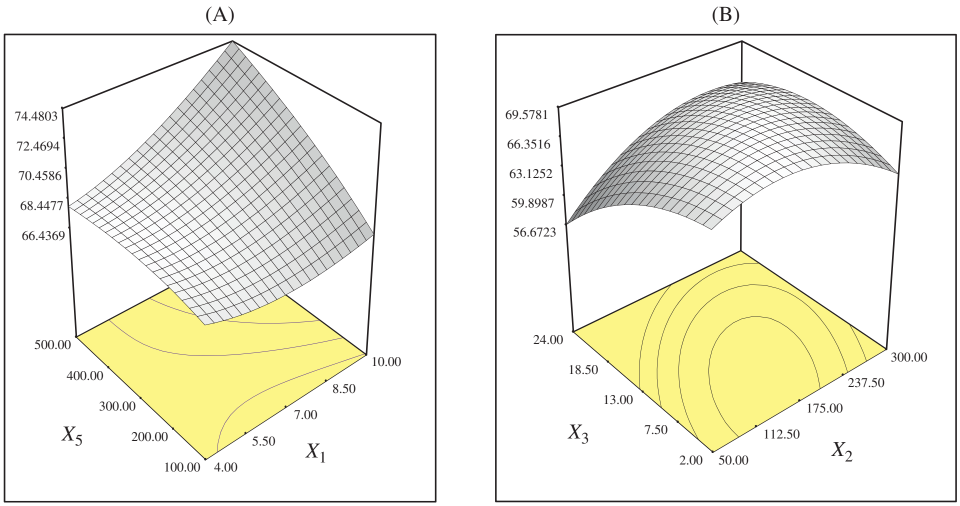

FIGURE 2-5 (A) Interaction between pH and initial concentration of composite. (B) Interaction between shaking speed and time.

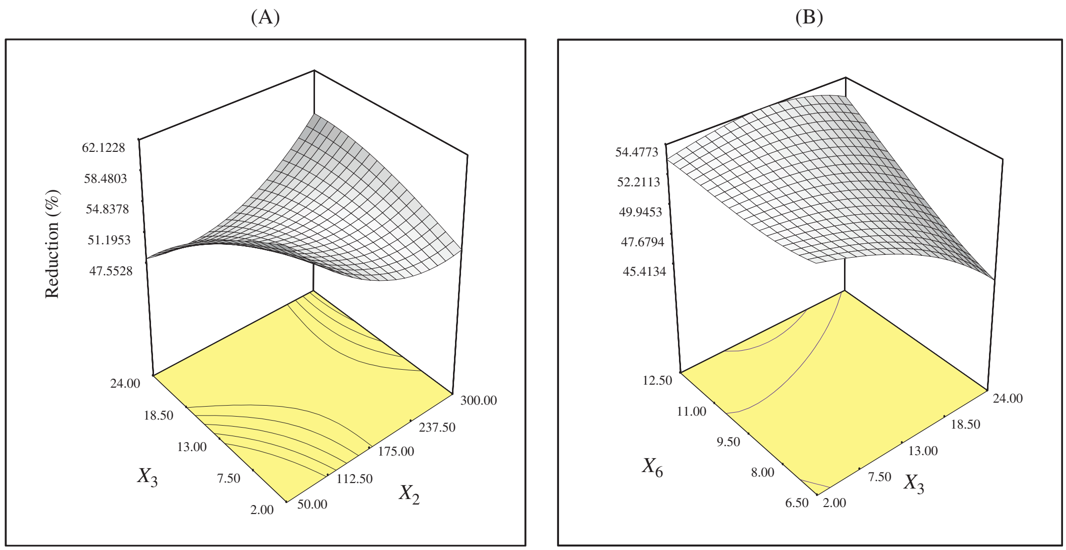

FIGURE 2-6 (A) Interaction between shaking speed and time. (B) Interaction between time and adsorbent dosage.

for the reduction of response parameters from POME on natural composite The strong significant ($P < .01$) interaction between shaking speed and time as well as between time and adsorbent dosage strongly enhanced the reduction of COD and NH_3-N from POME by 74.48% and 69.56% (Fig. 2-3A and B) and 62.12% and 54.48 % (Figs. 2-5A and B, 2-6).

From the result obtained from the optimization process, the use of a single parameter in the adsorption, in terms of other fixed parameters, may not be suitable to optimize operational conditions. The ability to reduce experimental trials that are required to express multiple trials and interactions makes RSM a better optimization technique. The experimental design tool such as RSM has been proven to be very effective with a statistical model in understanding the interaction among the optimized parameters. The use of RSM has been widely applied in the literature, for example in the study conducted on cationic dye by (Azzaz et al., 2016), shoe waste by (Iqbal et al., 2016) and peat (Rosli et al., 2017). The condition for the best operation of adsorption process was performed based on the results obtained from the screening of independent factors which revealed the possible direction for maximizing the adsorption process of the adsorbent material. The optimal operation parameters of the adsorption process for the reduction of the organic pollutants of POME was recorded at pH 10, 50 rpm of shaking speed for 2 h and by using 3 mm of composite particle size and 125 g/L of the adsorbent dosage of the treated sample of POME (Adeleke et al., 2017a,b). The use of activated carbon-peat composite have promising potential for the treatment of POME (Rosli et al., 2017). The observed and predicted reduction of COD and NH_3-N were 89.60% versus 85.01% and 75.61% versus 74.04%, respectively. Under these conditions, the independent factors exhibited strong interactions with 95% confidence level for both COD and NH_3-N reduction.

2.7 Conclusion

Conventional methods for the treatment of POME may not be effective for low concentration of the effluent. Similarly, the cost of the treatment process and routine maintenance of bioreactor is not economical including open ponding system which requires large land mass. However, adsorption is more applicable for the treatment of effluent at low concentration although the efficiency of the treatment process depends on effectiveness of the adsorbent material. The effectiveness of the adsorption process is influenced by the nature of the adsorbent materials and the characteristics of the adsorbents such as the pore size, functional group, surface morphology, bulk density including the hydrophobic and hydrophilic behavior. Low cost adsorbents are synthesized as activated carbon for the treatment of POME as a replacement for the commercial carbon. The combining ratio of adsorbent materials determines the reduction of POME characteristics, adsorbent parameters are more comprehensive and better optimized to achieve effective reduction of response factors using response surface methodology. The application of regression model from the central composite design can perform optimization of operational parameters of wastewater better than the conventional linear optimization techniques.

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