Adsorption of some heavy metals from wastewater using fine sand and Zeolite

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ABSTRACT

In this study, successive columns containing different types of solid state materials were used to investigate the treatment efficiency of soya bean oil mill wastewater (soap stock) using heavy metals analysis. Soap stock is a liquid waste obtained from soya bean oil industry from the neutralization process which has several environmental issues due to its high amount of organic and inorganic pollutants. Soap stock emerges from the refining process when oil is treated with a dilute alkali solution separating the FFAs as soaps. In this present study, an attempt was made at treating the wastewater using successive columns containing different types of solid state materials. The wastewater was passed through successive columns of fine sand, Zeolite and Zeolite/fine sand composite.. This treatment method decreased the toxic concentration of heavy metals assessed which include Pb, Cu, Zn, Ni and Cd by mean percentages of 96.60%, 100%, 62.0%, 16.10% and 96.60% respectively. Most contaminants were removed in the Zeolite/sand composite column possibly as a result of ion exchange capacity in addition to high sorption affinity of Zeolite on its active sites. This simple Zeolite based method enable us to obtain environmentally friendly treated soya bean oil water that can be safely used for irrigation purposes.

INTRODUCTION

Wastewater obtained from edible refined oil processing industries is a major issue of environmental concern particularly in under-developed or developing countries. The waste streams that come out from such oil refinery create serious environmental problem such as great threat to aquatic life due to its high organic content and among other issues. Hence its treatment is essential prior to its disposal. The choice of effluent treatment method depends on the organic content present in the effluent and its discharge conditions (Rose et al, 2020). Vegetable oil effluent entering the sewer system consists mainly of fats, oils, greases (FOG), sulphate and phosphates resulting in both high inorganic and organic loading for the receiving wastewater works (Rose et al, 2020).

Edible oil industrial wastewaters usually come from the degumming, deacidification, deodorization and neutralization steps. In the neutralization step sodium salts of free fatty acid (soap stocks) are produced whose splitting through the use of sulphuric acid generates highly acidic and oily wastewaters. Its characteristics depend largely on the type of oil processed and on the process implemented that are high in chemical oxygen demand(COD), oil and grease, sulphate and phosphate content, resulting in both high inorganic as well as organic loading of the relevant wastewater treatment (Rose et al, 2020). Moreover, vegetable oil refinery wastewater is known to contain chemical compounds like phenol, heavy metals from bleaching earth, catalysts used in the hydrogenation process, oxidizable substances and fats and oils. Because of quantity and characteristic variations and complexity, wastewater treatment to meet the desired effluent standards is complicated, and the choice of

methods of wastewater treatment depends on many local conditions and therefore, cannot be standardized (Rose et al, 2020).

Different methods of treating edible oil mill wastewater have been reported, such methods include aerobic treatment, anaerobic digestion, reverse osmosis, electro dialysis, ultrafiltration and composting (Ahmaruzzaman, 2008) However, a cost effective and environmentally friendly method for the treatment of Oil processing Wastewater is not yet found. Building an effective treatment technology for oil processing Wastewaters is not economically feasible due to the cost implications. Recently, a zeolite based treatment method was developed for the treatment of olive mill wastewater which seemed to be a promising technology in the treatment of oil processing wastewaters (Ahmaruzzaman, 2008). This study adopts a similar zeolite based method in the treatment of soya bean oil mill wastewater known as soap stock. Adsorption has many advantages over the other processes of edible oil waste water because it has the characteristics of convenience, easy operation and simplicity in design. It has a wide application for removal of different pollutants. Other important advantages of this process include: low operation cost, high flexibility, simple design and operation, easy automation, lack of sensitivity to toxic pollutants and the capability of operation at very low concentration, environmentally friendly, less investment in terms of initial cost (Anagnostopoulos et al, 2013)

The most important criteria in adsorption processes is to find a low cost adsorbent that is widely available, having high adsorption capacity, possess rapid rate of removal and having low adverse effect on the treated

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water. Many adsorbents have been investigated reported for the treatment of edible oil wastewater but Zeolite has been proved to be more effective (Anagnostopoulos et al, 2012)

LITERATURE REVIEW

Edible vegetable oils are derived from the seed of such plants as soya bean, corn, palms, groundnut, olive tree, rapeseed/canola, linseed, cottonseed, castor, rice bran and sunflower. The oils are fatty acid esters of glycerol, commonly called triglycerides. The production of edible vegetable oils can be separated into two phases: extraction and refining (Anagnostopoulos et al, 2012)

.The oils are extracted from the seeds by mechanical or hydraulic pressing or solvent extraction. The crude oil that results from the extraction process must be refined to make the oil acceptable for edible purposes. There fining process removes components such as free (unesterified) fatty acids, phosphatides, unsaponifiable components such as sterols and tocopherols, carotenoids, chlorophyll (color), and metals (Anari al, 2010) Some by-products of low commercial value are obtained from vegetable oil refining processes. Important amounts of by-products such as soap stocks (SS), deodorizer fatty acid distillates (FAD) and acid oil (AO) are produced from the oil refining processes. These by-products are harmful to the environment if they cannot be used for any beneficial or industrial activity (Anari al, 2010).

Soap stock emerges from the refining process when oil is treated with a dilute alkali solution separating the FFAs as soaps. This wet lipid mixture is separated from the crude oil by centrifugation. It is generated at a rate of about 6 % of the input of oil entering the refining operation and its cost represents 1/10 of the refined oil cost. Soap stock is quite acidic, with pH values between3.50- 5.50.

This residual is also referred to as residual oleins (Auta et al, 2013). Neutralization process result in a by-product known as stock soap consist of the sodium soaps of free fatty acids (FFAs) present within the oil. Soap stocks always require subsequent treatment. The traditional method of treating soap stock is known as soap splitting. The soaps tock is split into fatty acids and water by acidification with strong acids usually H2S04. This is often considered an attractive solution because it is relatively simple (Auta & Bansal et al, 2009). Soap stock is the least valuable by-product from oil processing, and it is generated at a rate of about 6% of the volume of crude soya bean oil refined, amounting to as much as 0.8 million MT in the United States annually.

Typically, Soya bean oil mill wastewater is composed of the water from the tissue of the fruit, the water used for the various stages of oil production, soya pulp, mucilage, pectin, and oil, among other things, suspended in a relatively stable emulsion. Moreover, it contains toxic organic and inorganic compounds. In general, soya bean oil mill wastewater is characterized by an intensive violet dark brown to black color, strong specific soya oil smell, high degree of organic pollution (chemical oxygen demand (COD) of 220 g/L and biochemical oxygen demand (BOD) of 110 g/L), pH of 4.5-5.6, 45 g/L of organic compounds in total, high electrical conductivity (EC), high content of polyphenols (24 g/L), reduced sugars (60% of the dry weight), and high solid matter content (Bhatnagar & Borrega et al, 2013). Soya bean oil mill is an acidic effluent with a high nutrient content that can be used to fertilize soil; however, it is very rich in toxic phenolic compounds. In recent years, there has been increased attention directed toward finding the best methods to treat vegetable oil wastewater and toward recycling both the organic matter and nutritive elements in the crop production system. Some vegetable oil mill wastewater characteristics are favorable for agriculture, because this effluent is rich in water, organic matter, N, P, K, and Ca; however, other characteristics are unfavorable for agriculture, including the presence of phenolic compounds (Carro, L et al, 2010)

The atomic structures of zeolites are based on three-dimensional frameworks of silica and alumina tetrahedral that is, silicon or aluminum ions surrounded by four oxygen ions in a tetrahedral configuration. Each oxygen atom is bonded to two adjacent silicon or aluminum ions, linking them together, clusters of tetrahedral form boxlike polyhedral units that are further linked to build up the entire framework. In different zeolites the polyhedral units may be equidimensional, sheetlike, or chainlike. The aluminosilicate framework of a zeolite has a negative charge, which is balanced by the cations housed in the cagelike cavities (Chakrabarti, S, et al, 2008). Zeolites have much more open, less dense structures than other silicates; between 20 and 50 percent of the volume of a zeolite structure is voids. .Zeolites are safe, naturally occurring crystalline aluminosilicate that have a three-dimensional structure; aluminum, silicon and oxygen which are arranged in a regular structure of [SiO4]- and [AlO4]-tetrahedral units that form a framework with small pores (also called tunnels, channels or cavities) of about 0.1 - 2 nm diameter running through the material. In these small channels, solid, liquid and gaseous substances can be trapped. High ion exchange capacity, the molecular sieve properties and the relatively high surface area make zeolite a promising adsorbent media for treating effluent with different suspended solids (Dang et al, 2009) Zeolites have wide application as gas and odor filter, as a part of animal feed, and as ammonia removers from different wastewaters. The metallic ions sorbent behavior of natural zeolite has been also studied by several researches, and it has been recognized as a promising sorbent for heavy metals (Galá, J et al, 2013). Another characteristics of zeolite is their large surface area (20-50 m2/g by natural species, however above 1000 m2/g by synthetic ones). Both physisorption and chemisorption bounding may occur within the zeolite voids during the removal of pollutants. Zeolites, now-a-days can be used in almost all pollutants removal processes such as atmospheric, municipal or industrial wastewaters treatment and purification (Hansen, C.L et

al, 2007)

Heavy metals are also present in the soya bean oil mill wastewater. Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0. Most of the heavy metals are dangerous to health or to the environment. Heavy metals in industrial wastewater include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel (Ismail, B et al, 2013). The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the World Health Organization and Food and Agricultural Organization. Acute heavy metal intoxications may damage central nervous function, the cardiovascular and gastrointestinal (GI) systems, lungs, kidneys, liver, endocrine glands, and bones. Non-biodegradable contaminants pose a serious health and environmental hazard and removal of these wastes cannot be achieved using secondary methods (Jambulingam et al, 2007) Hence, tertiary/advanced wastewater treatment methods such as ion exchange, precipitation, membrane separation, electrolysis and adsorption can be used to remove these recalcitrant wastes. So far, a number of efficient methods have been developed for heavy metal removal. Some researchers has reviewed various methods for the removal of heavy metals such as chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation, flocculation and floatation. Generally, these processes are efficient in removing the bulk of metals from solution at high or moderate concentrations. However, chemical processes produce a large amount of metallic sludge, making metal recovery difficult (Jayarajan, M et al, 2011 & Johar, N et al, 2012). For these reasons, adsorption technology has gained a wider application due to its inherent low cost, simplicity, versatility and robustness. Adsorption is commonly used technique for the removal of metal ions from various industrial effluents (Khan, N.A et al, 2004 & Diez, V et al, 2012)

MATERIALS AND METHODS
Study Area
This research work was conducted in Makurdi town, the headquarters of Benue State. Makurdi town is the headquarters of Makurdi Local Government Area and capital of Benue State. The town is located between latitude 7°38'N - 7°50'N, and longitude 8°24'E and 8°38'E and 104 meters elevation. It is situated in the Benue valley in the North Central region of Nigeria. It is traversed by the second largest river in the country, the River Benue.

Collection and preservation of soap stock
Exactly 5 liters of fresh Soap stock was collected (using plastic container) at Seraph oil mills, Nigeria Limited, which is located at Km 7 Gboko Road Makurdi, Benue

State. The Soap stock was then transported immediately to Chemistry laboratory at Benue State University and was stored at room temperature prior to analysis.

Sample Digestion
The digestion method described by Anwar e tal (2014) was adopted with slight modification. 50mL of the sample was measured and transferred into beaker containing 10mL of concentrated HNO3. The sample was boiled slowly on a hot plate to 20mL. Another 5mL of conc. HNO3 was t hen added and heated until digestion was completed. The sample was filtered and transferred into 100mL volumetric flask and made to mark with distilled water. The digests was used for flame photometry and heavy metals analysis of the wastewater (Anwar, A et al, 2014)

Physical Precipitation of soap stock
Physical separation was carried out using glass cylinders with diameter 10 cm and length 20 cm. After 5 h of gravity separation, two kinds of suspended solids were observed: a floating part and a precipitated part. The floating part was decanted and the precipitate filtered using filter paper and a less turbid sample was obtained (Anwar, A et al, 2014).

Soya Bean Oil Mill Wastewater Treatment Using Successive Steps
The soya bean oil mill wastewater (Soap stock) was passed through three designed treatment steps, following physical separation. Each treatment consists of successive column containing different solid-state materials. The columns were made of transparent glass material with an internal diameter of 2 cm and a length of 20 cm. The columns were sealed from the bottom using two pieces of gauze fabric firmly held by strings and tape. The columns were packed with solid state materials to 15 cm height. The packing process was done in 5 cm increments to avoid segregation of particles. The columns were mounted vertically on a wooden holder in the laboratory. Each treatment system was replicated three times. The contact times between the soya bean oil mill wastewater and solid-state materials were 1 h for fine sand, 2 h for zeolite and 4h for the fine zeolite/sand composite. The physicochemical parameters used to evaluate the treatment efficiency for each method were pH, phosphate, turbidity, sulphate, nitrate and metal ions concentration (Anwar, A et al, 2014).

Characterization of Zeolite Y
Zeolite Y was synthesized and characterized using PXRD, EDS and FTIR. The PXRD used was a Bruker D8 Advance diffractometer operating with a copper X-ray tube, a monochromator with a Linx Eye detector. The PXRD data were collected using Cu Kα1 (1.5406A) radiation, over the 2θ range between 5 - 60° using a step size of 0.022° for 43 minutes. The EDS spectrum was produced on an EDAX Pheonix, EDX with a Carl Zeiss 1530 VP spectrometer. The samples were sprinkled onto

12mm aluminium stubs using "carbon sticky tabs". These were then gold coated using an Emitech SC 7640 gold/palladium sputter coater to reduce the static charges during the analysis. The PerkinElmer paragon 1000 FTIR spectrophotometer was used to collect FTIR data for the sample. The sample was prepared by making discs of a small amount of the sample (T 3 mg) in KBr and measurements were carried out over IR region of 1200-400cm-1 for the zeolite. A background spectrum was measured before the sample to compensate for atmospheric conditions around the FTIR instrument

Determination of heavy metals in soap stock using Atomic Absorption Spectrometry

The concentrations of heavy metals in the wastewater (soap stock) were analyzed before and after treatment to assess the decrease in concentrations of the pollutants using atomic Absorption Spectrometry

Zinc

Approximately11.24g of zinc oxide was dissolved in de-ionised water and diluted to 1L in a volumetric flask. 1 ppm, 2 ppm, 3ppm, 4 ppm and 5ppm solutions were made from the stock solution. The AAS was the calibrated at a

wavelength of 213.9 nm under lamp current of 5 mA using fuel acetylene (Diez, V. et al, 2012).

Lead

About 1.5g of lead nitrate Pb(NO3)2was dissolved in de-ionized water and diluted to 1L in a volumetric flask . 1 ppm, 2 ppm, 3 ppm 4 ppm and 5 ppm were prepared from the stock. The AAS was calibrated at 217.0 nm wavelength, spectra bond of 1 nm and current of 5 mA using acetylene and air as fuel (Diez, V. et al, 2012).

Nickel

About 4.0g of Ni (NO3)2.6H2O was dissolved in deionised water and diluted to 1L in a volumetric.1 ppm, 2 ppm, 3 ppm 4 ppm and 5ppm were prepared from the stock solution. The AAS was calibrated at 213.9 nm wavelength, spectra bond of 1 nm and current of 5 mA using acetylene and air as fuel (Diez, V. et al, 2012).

Cadmium

Exactly 2. g of cadmium nitrate was dissolved in 250 mL of de-ionized water and diluted to 1 L in a volumetric flask. 1 ppm, 2 ppm, 3 ppm, 4 ppm and 5 ppm were prepared from the stock solution. The AAS was calibrated
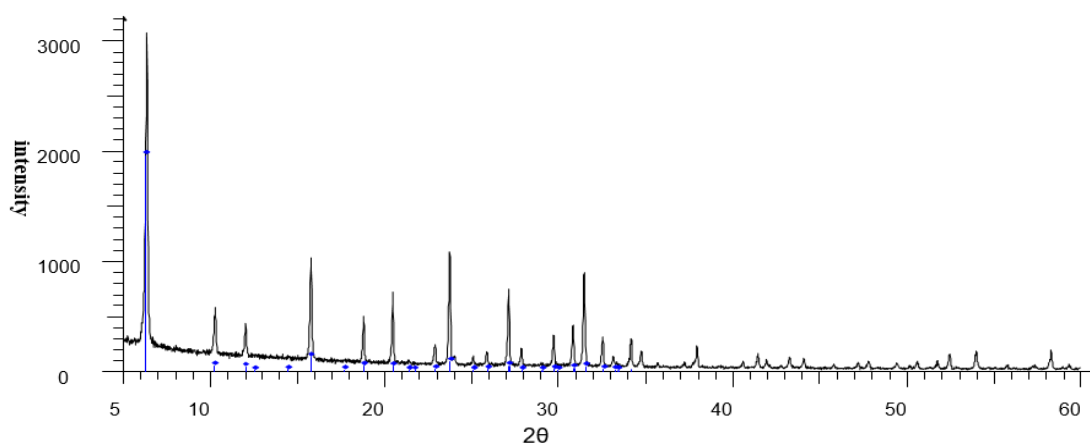
Table 1: Characterization data of fine sand using X-ray fluorescence spectrometer

Compounds/elements	% Weight
SiO2	92.49
Al2O3	7.44
Fe2O3	ND
CaO	0.06
MgO	0.09
K2O	ND

Key ND: Not detected

Table 2: Elemental composition of the synthesized Zeolite Y (EDS)

Elements	% Weight
0	48.7±0.07
Na	9.2±0.04
Al	11.5±0.0
Si	30.7±0.1
Si/Al	2.7

Figure 1: PXRD pattern for zeolite Y (experimental pattern) matched with the reference pattern 01-070-4285 (vertical tick marks), anhydrous formula ($Na_{54.91}Al_{56}Si_{136}O_{384}$).

at a wavelength of 228.8 nm at a spectra bond of 0.4 nm and lamp current of 3.5 mA using fuel acetylene.

Copper

1g of copper was dissolved in 25 mL of HCl. Few drops of nitric acid was added and diluted to 1 L in a volumetric

flask with de-ionzed water. 1 ppm, 2 ppm, 3 ppm, 4 ppm and 5 ppm were prepared from the stock solution. The AAS was calibrated at a wavelength of 309.3 nm and spectra band pass of 0.4 nm, lamp current of 10 mA using fuel acetylene and nitrous oxide.
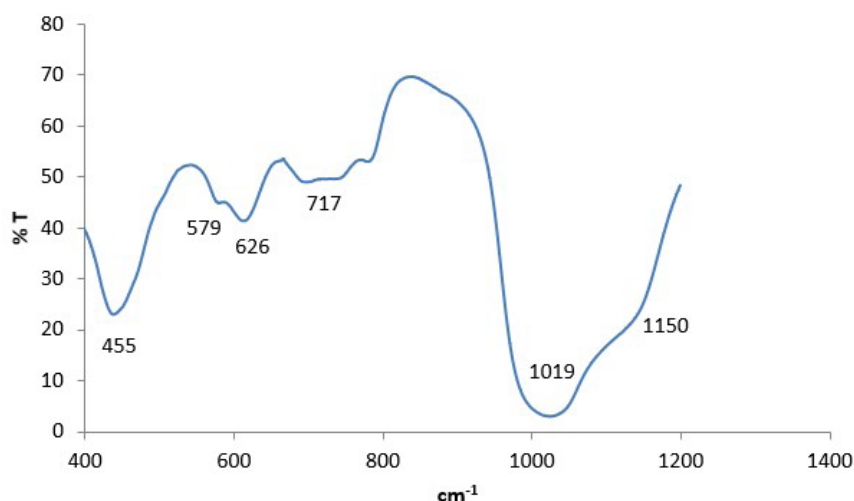
Figure 2: FTIR spectrum for the synthesised zeolite Y

Table 3: Heavy metals concentration in the soap stock Soya Bean Oil Mill before and after treatment

Heavy metals (mg/L)	Untreated wastewater	Physical pre-cipitation	Fine sand treatment	Zeolite treatment	Zeolite/sand treatment	FAO (2010)	EPA (2011)
Pb	0.7555±0.00	0.1475±0.00	0.103±0.00	0.0760±0.00	0.0260±0.00	0.5	0.01
Cu	0.2850±0.00	0.0350±0.00	0.0260±0.00	0.0050±0.00	ND	0.1	0.02
Zn	1.3505±0.00	1.1505±0.00	1.0725±0.00	0.5975±0.00	0.5135±0.00	1.0	0.5
Ni	0.0465±0.00	0.0355±0.00	0.0580±0.00	0.0400±0.00	0.0390±0.00	0.01	0.02
Cd	0.1455±0.00	0.0815±0.00	0.0195±0.00	0.0620±0.00	0.0270±0.00	0.01	0.02

Key: ND= Not detected

RESULTS AND DISCUSSION

Chemical composition of fine sand

The chemical composition of the fine sand used in this present study was determined by X-ray fluorescence spectrometer (ARL 9900 OASIS Model) as shown in (Table 1). Silicon dioxide was found to be the predominant oxide, 92.49%. Other oxides present were Al_2O_3 7.44%, CaO 0.06% and MgO 0.09%. The silicon to aluminum ratio of the fine sand used was 12.40. This characterization data obtained is in line with earlier investigation reported (Alluri et al, 2007).

PXRD

The PXRD data compared against the ICDD database for the theoretical phases showed good agreement that the targeted Zeolite Y was formed as clearly seen from the matched patterns (fig. 1).The PXRD patterns for the Zeolite Y was a single crystalline phase with high degree of crystallinity.

Synthesis of Zeolite Y
SEM-EDS

The elemental composition of zeolite Y was determined using energy dispersive spectroscopy (EDAX Pheonix model) as shown in (Table 2). The result revealed that Zeolite Y consist of 48 7% Oxygen, 9.2% Sodium, 11.2% Aluminum and 30.7% Silicon. The Si/Al ratio (2.7%) calculated was found to be in good agreement with the data obtained from PXRD (2.4%) as calculated from the molecular formula of the Zeolite Y ($Na_{54.91}Al_{56}Si_{136}O_{384}$).

FTIR

A broad band was observed in the region 1019 cm-1 which was attributed to the asymmetric vibrations of Si-O bridging and Si-O non-bridging bonds. The band in the range 717 cm-1 is due to the symmetric stretching of internal vibrations while the internal vibrations due to the bending of the T-O tetrahedra occurred between 455 cm-1. Vibrations of the double six rings (D6R) connecting the sodalite cages occurred between 579 cm-1 while that around 626 cm-1 is assigned to the symmetric stretching of external T-O linkages in the Zeolite. The band at 1150 cm-1 was attributed to the asymmetric stretching of external T-O linkages in the Zeolite respectively.

Adsorption of heavy metals

The results presented in table 3 showed a decrease in the concentration of heavy metals using the zeolite-based technique.

Lead

For the raw wastewater sample 0.7555±0.00mg/L was obtained, 0.1475±0.00mg/L for physical precipitation, 0.103±0.00mg/L for sand filter, 0.0760±0.00mg/L for Zeolite filter and 0.026±0.00mg/L for Zeolite/sand filter respectively. The decrease in the values could be attributed to the ion exchange and absorption affinity of the Zeolite material used. The values obtained were within that of maximum allowable concentration (MAC) limits by FAO (2011) and EPA (2016) for irrigation water with values ranging from 0.5 to 0.01mg/L (Babel, S al, 2003)

Copper
For the raw wastewater sample 0.285±0.000mg/L was obtained, 0.035±0.00mg/L for physical precipitation, 0.026±0.00mg/L for sand filter, 0.005mg/L for Zeolite filter and was less than the detectable limit using the Zeolite/sand filter. The decrease in the values could be attributed to the ion exchange and adsorption properties of Zeolite. The values obtained were within the maximum allowable concentration limits by FAO (2011) for irrigation water (Babel, S al, 2003)

Nickel
About 1.04465±0.00mg/L was obtained for the raw soya bean oil mill wastewater sample, 0.0355±0.00mg/L for physical precipitation, 0.058±0.00mg/L for sand filter, 0.040±0.00mg/L for Zeolite filter and 0.039±0.00mg/L for Zeolite/sand filter. The result shows a gradual decrease in the pollutant load from the raw wastewater to the final Zeolite/sand filter treatment, reducing the concentration within the maximum allowable limit of 0.2mg/L for agricultural water. Similar results were also reported for oil refinery wastewater treatment using the Zeolite and carbonaceous adsorbents (Kwon J.S et al & Muthukumaran et al, 2010)

Zinc
About 1.3505±0.00mg/L was obtained for raw soya bean oil mill wastewater sample, 1.1505±0.00mg/L for physical precipitation, 1.0725±0.00mg/L for sand filter, 0.5975±0.00mg/L for Zeolite and 0.5135±0.00mg/L for Zeolite/sand filter. These values are within the maximum allowable concentration limit of 1.00- 2.00mg/L for irrigation water. Similar works were also reported by some researchers on adsorption of heavy metals from water and wastewater using low cost adsorbents from agricultural by-products (Pitakpoolsil et al & Varga et al 2013)

Cadmium
For the raw wastewater sample, 0.1455±0.000mg/L was obtained 0.0815±0.00mg/L for physical precipitation, 0.0195±0.00mg/L for sand filter, 0.062±0.00mg/L for Zeolite filter and 0.027±0.00mg/L for Zeolite/sand filter. The value obtained at the Zeolite/sand composite filter is in accordance with the recommended values of 0.01-0.002mg/L by FAO and EPA (2011). Similar results were also reported on heavy metal removal of edible oil content in wastewater by advanced oxidative process (Aslan, S. et al 2001 & Chipasa et al 2009).

CONCLUSION
The treatment of soap stock was using successive steps that are raw wastewater, physical precipitation, sand treatment, Zeolite treatment and Zeolite/sand composite using solid state materials and testing the treatment efficiency using heavy metals analysis proved to be effective for edible oil effluent. This study found that the filtering abilities of Zeolite/sand composite works better

for soya bean oil mill wastewater treatment. The simple Zeolite-based method can be used for the soya bean oil mill wastewater treatment as an environmentally friendly and cost effective method. The treatment efficiency on the removal of heavy metals such as Zn, Cu, Pb, Ni and Cd using AAS gave a good heavy metal reduction from the wastewater.

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