COLUMN ADSORPTION OF POLLUTANTS FROM FISH POND WASTEWATER USING NANO-CLAY/SILVER DOPED CARBON NANOTUBES

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ABSTRACT

In this study, a Fe-Ni/Kaolin catalyst was used to produce carbon nanotubes (CNTs) in a chemical vapour deposition reactor (CVD). The produced CNTs were purified and functionalized, and combined with silver nanoparticles. The functionalized CNTs were applied to remove contaminants from fishpond wastewater using a column adsorption method with bed heights of 2, 3 and 5 cm. Likewise, a nanoclay filter was developed via a beneficiation method using sedimentation techniques to produce clay fractions, which were then purified, and a co-precipitation method to produce magnetite nanoparticles, which were then combined with the purified clay fractions. The developed nanoclay filter was used for continuous removal of dissolved solids, bacteria, and heavy metals from fishpond wastewater at a flow rate of 10mL/min. The standard water analysis procedure was followed to determine the level of pollutant removal, while heavy metals were analysed using an Atomic Absorption Spectrophotometer (AAS). The data were analysed using analysis of variance (ANOVA) to determine significant differences; the results were compared using a T-test, and the means of

significant differences were separated using Duncan's multiple range test. The percentage removal efficiency of the heavy metals was in the order: Cu 48 %, Zn 89 %, Fe 98 %, Mn 100 % and Total bacteria count (TBC) 95 %. The water quality indicators demonstrated the adsorbent's effectiveness in removing effluent. The ceramic water filter successfully removed colour, odour, and dissolved solids from the raw fishpond wastewater. It can be inferred from the analyses of the raw and treated fishpond wastewater samples that the developed nano-clay-based filter at a flow rate of 10mls/min and the nano-adsorbent at a column height of 5cm, used in a single purification process, are suitable for fishpond wastewater treatment.

Keywords*: Pollutants, wastewater, nano-clay filter, nanoparticles, fishpond.*

INTRODUCTION

Water pollution is a global challenge that is on the rise in both developed and developing countries; this, in turn, has greatly undermined economic growth and the physical and environmental health of billions of people (Javier *et al.*, 2017). Although global attention has focused primarily on water quality through use, this has stemmed from poor wastewater management, which has created serious water quality problems in many parts of the world, worsening the water crisis (FAO, 2016). The change in water quality or composition directly or indirectly as a result of both natural and human activities, such that it becomes unsuitable for domestic, agricultural, fisheries and other purposes for which it would otherwise be quite suitable in its uncontaminated state, is regarded as water pollution (Woodford *et al.*, 2015). These pollutants are usually pathogens, silt, and suspended solids, such as those found in soils, sewage materials, disposed food waste, cosmetics, automobile emissions, construction debris, and eroded river banks, as well as organic and inorganic chemicals (Akpan and Ajayi, 2016).

In fisheries, a rapid increase in fish farming has resulted in an increase in the discharge of wastewater to the surroundings and the environment at large and has led to the pollution of the environment, surface and underground water, and, in severe cases, algae bloom in surrounding water bodies, which is a serious environmental problem (Javier *et al.*, 2017). This kind of wastewater contains toxic indicators such as high pH, total dissolved solids, alkalinity, chemical oxygen demand, nitrate, phosphate, and heavy metals (Gautam *et. al*., 2014). The inability of bacteria to degrade heavy metals results in their accumulation in humans, plants, and other

organisms (Woodford *et al.*, 2015). Conventional water treatment processes such as distillation, chemical treatment, radiation, biofiltration, reverse osmosis, electrodialysis, and desalination are not completely effective in treating agricultural wastewater (Konda et *al.*, 2017). Some of these processes, such as distillation, require a great amount of energy input. Activated carbon is not efficient for nitrates, fluorides, microbes and heavy metals removal, while ultraviolet treatment is expensive and inactivated by living contaminants. Also, coagulation and flocculation are complex and less efficient process that requires continuous chemical input (Rashed, 2013). As a result, there is a need to develop an alternative approach to address the limitations of other treatment methods.

Conventional treatment methods for wastewater and heavy metal removal include ion exchange, chemical precipitation, membrane filtration, coagulation/flocculation, photocatalysis, biological treatment, and adsorption techniques (Gautam et *al.*, 2014). The ion-exchange treatment method involves a solid that can exchange cations or anions with the surrounding materials. Synthetic organic ion-exchange resins are commonly used in industry to remove heavy metals from wastewater effluent. Ion exchange cannot treat concentrated metal solutions due to frequent fouling of the matrix by solids and organics in wastewater. It is also non-selective and highly sensitive to the solution pH (Akpor *et. al.*, 2014).

Chemical precipitation is a widely used technique for wastewater treatment and is also utilised to remove heavy metals from inorganic-contaminated water due to its simplicity, convenient operation, and economical equipment requirements. In this process, suspended effluents settle as solid precipitate (Konda *et. al.*, 2017). These are then removed from the liquid phase by filtration. However, this method requires a large amount of chemicals to reduce the metal to a permissible level for discharge (Barakat, 2011). The drawbacks of chemical precipitation include its ineffectiveness in treating low concentrations of wastewater and the production of excess sludge that requires further disposal (Fu and Wang, 2011).

In the ultrafiltration process, high-molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules are removed. Despite its high efficiency, however, the major deficiency of this method is its high permeate reflux and membrane fouling (Guo *et. al.*, 2010).

The coagulation and flocculation method is complex and not economically viable; it is a less efficient process that requires a high chemical input, produces large amounts of sludge, and

results in large particle formation. Coagulation occurs when a coagulant is added to water, bringing suspended solids with similar charges in solution together by neutralising their charges and settling the particles (Prakesh et *al*., 2014). Photo-catalysis has been utilised to enhance the removal of heavy metals and organic pollutants that produce toxic by-products; its limited duration and limited applications are its major deficiencies (Asharaf et *al*., 2014). In biological wastewater treatment, the sensitivity of microorganisms to environmental factors is difficult to control, microbial cells are damaged, and the process is neither cost-effective nor time-efficient (Zare et *al*., 2018).

Carbon-based adsorbents are used for the removal of organic waste because they have high adsorption capacity for a wide range of organic and inorganic contaminants. Oxidised carbon nanotubes have high adsorption capacity for metal ions with fast kinetics. Their surface chemistry can be tuned to target specific contaminants. They are also useful for the regeneration and reuse of fish pond wastewater. Nanotechnology provides innovative solutions for water treatment. Numerous economic and scientific facts revealed that a shortage of water or its pollution can cause a severe decrease in productivity and death of living species (UNICEF, 2008). Contrarily, nano-remediation of wastewater via nanotechnology, in this respect, as defined by the U.S National Nanotechnology Initiative (NNI, 2001), is *"Understanding and control of matter at dimensions of roughly 1 to 100nm where unique phenomena enable novel applications*. Current research in nanotechnology offers the possibility of developing technically and economically viable alternative materials for wastewater treatment (Emir *et. al*., 2015). One practical technique used in nanotechnology applications for wastewater treatment is adsorption. It has been identified as one of the most efficient treatment techniques for removing organic, inorganic, and microbial pollutants from wastewater (Jiancheng et *al*., 2017). Adsorption technology offers significant cost savings, ease of application, greater availability, and improved efficiency (Zhang et *al*., 2015). Adsorption is one of the most practical, efficient and effective treatments for wastewater and heavy metals removal. This is because adsorption offers better performance in terms of process flexibility, ease of operation, design simplicity, cost-effectiveness, non-sensitivity to pollutants, and the absence of toxic substances in the treated effluent (Burakov et *al*., 2018a). Adsorption is a method of purifying water by attaching contaminants to a catalytic surface, the adsorbent. The adsorbents could be gel, clay, silica, sieves, and cotton fibre (Segneanu et *al*., 2013).

Nanomaterials are fabricated with features such as high aspect ratio, reactivity, tunable pore volume, and electrostatic, hydrophilic, and hydrophobic interactions, which are useful for adsorption, catalysis, sensing, and optoelectronics (Das et *al*., 2014). Nanotechnology-enabled processes are highly efficient, modular, and multifunctional, providing high-performance, affordable water and wastewater treatment solutions. Nanomaterials are durable and characterised by a high specific surface area (SBET). In other words, a large surface-to-volume ratio controls interactions with pollutants and/or bacteria (Qu et *al*., 2013). Nanotechnology-enabled processes for water treatment constitute major challenges to existing methods. Nanotechnology can also be applied to economically purify and utilise unconventional water sources. Nanotechnologies are advantageous for treating wastewater, as they eliminate contaminants and support recycling to produce purified water. This leads to reduced labour, time, and expenditure for the industry, thereby solving various environmental issues (Kanchi, 2014). The various limitations of the conventional treatment technologies, such as high cost or poor treatment efficiency, are what bring about the need to develop an alternative treatment method that will complement the existing ones. The adsorption method using a nano-adsorbent has been identified as an alternative treatment method for the efficient removal of heavy metals from wastewater (Lu & Astruc, 2018).

Adsorption is a surface process in which pollutants bind to a solid surface. It is a surface phenomenon that transfers atoms and molecules between phases. The treated wastewater produced from adsorption is usually of high quality (Sophia & Lima, 2018). There are two types of interactions that occur during adsorption between the adsorbent and adsorbate: physisorption (physical) and chemisorption (chemical) (Santhosh et *al*., 2016). Physisorption is reversible, nonspecific, and may form a monolayer or multilayer of adsorbate on the adsorbent. Chemisorption, on the other hand, is an irreversible, highly specific form of monolayer of adsorbate on adsorbent (Burakov *et. al*., 2018a). The flexibility, ease of application, non-production of toxic pollutants, and simplicity of the adsorption process make it a leading technology for wastewater treatment. The adsorption operation is of two types: batch or continuous. (Bankole et *al*., 2019).

Among the world's most important and useful industrial minerals, clay minerals are of great significance. Clay is used in a number of geological applications, such as stratigraphic correlations, indicators of depositional environments, and indicators of temperature for the

generation of hydrocarbons. In agriculture, clay minerals are a major component of soils and a determinant of soil properties. Clay minerals are important in construction, where they are a major constituent of brick and tile. Up to date, clay and clay-based minerals need improvement due to their utilisation and demand.

In times when technology was not at the core of human civilisation, clay minerals were used as an important material to produce a variety of products. Its softness, plasticity, porosity, tangibility, pliability, and climatic adaptability, all at an affordable cost, were viable characteristics that recognised its usefulness and led to the introduction of several products. Today, when nanotechnology is the hallmark of the scientific world, the contribution of clay minerals is clearly evident as highly useful fillers or additives in polymers to achieve desired effects. Therefore, this study applies nanotechnology to treat fish pond wastewater, addressing both water and environmental problems using a carbon nanotube/silver nanoparticle-based filtration system. Nanotechnology provides innovative solutions for water treatment.

MATERIALS AND METHODS

Chemicals and materials

The chemicals used in this study include: Iron (III) nitrate nonahydrate, nickel (II) nitrate hexahydrate, Iron (II) and Iron (III) chloride, and Silver nitrate. All the chemicals and reagents used in this study are of analytical grade, with purity ranging from 95 to 99%, and are used without further purification. The raw clay samples were collected from four different clay deposits in Nigeria for characterisation, including Afuze, Edo state; Ahoko, Kogi state; Ubakala, Abia state; and Wase, Plateau state.

Production of carbon nanotubes

The procedure described by Bankole *et al.* (2019) was adopted to produce the CNTs. A known weight (0.5g) was loaded into a quartz boat (120mm 15mm) at room temperature, and the boat was placed in the centre of the quartz tube. Heating in the furnace was carried out at 10 °C/min, and argon was allowed to flow over the catalyst for 90 min to purge the system of air before the reaction commenced. Once the temperature reached 700 °C, the argon flow rate was adjusted, and the acetylene flow rate was also introduced. The reaction was then allowed to proceed until

the 45-minute reaction time was reached. After which, the acetylene flow was stopped, and the furnace was allowed to cool to room temperature under continuous argon flow. The ceramic boat was then removed and weighed to determine the quantity of CNTs produced.

Purification and functionalization of carbon nanotubes with silver nanoparticles

For the purification of the raw CNTs, acid treatment was used as described by *Wang et al.* (2018). The synthesised carbon nanotubes were purified by acid treatment to remove iron, nickel, amorphous carbon, and other impurities likely introduced by the used catalyst. The HNO_3/H2SO4 acid mixture was used at a 1:3 ratios. The mixture was filtered to obtain a wet carbon nanotube residue, which was then dried in an oven at 100 oC for 48 hours. The obtained carbon nanotube was then analysed. The biosynthesis of silver nanoparticles was carried out in a dark room. A known weight of (Silver nitrate salt (AgNO3)) was prepared, and 95 mL of the solution was placed in a conical flask on a magnetic stirrer at 60 0C after which 5 mL of the plant extract was added drop by drop under continuous stirring. The solution begins to change from clear to dark brown, indicating the reduction of silver nitrate to silver nanoparticles. The surface Plasmon resonance of the sample was determined using a UV-spectrophotometer. To functionalize the carbon nanotubes, a known weight (0.1 g) of the carbon nanotubes was dispersed in 40 mL of silver nanoparticles, and the process was eventually scaled up. The mixture was then heated in a water bath shaker at 60 °C for 3 hours to enhance the dispersion of the carbon nanotubes within the silver nanoparticle blend. The blend was then filtered, and the pH was checked at approximately 7; it was then oven-dried at 120 °C for 12 hours (33).

Nano-clay production and characterization

Beneficiation was performed using sedimentation to produce clay fractions and remove excess non-clay impurities. The grounded samples were then sieved through a 150 μm sieve and stored in laboratory sample bottles until required for characterisation. The co-precipitation method was used to produce magnetite nanoparticles. FeCl3 (anhydrous) and FeCl.4H20 were used as ion precursor. The leaf with the highest phenol content, *Magnifera indica* extract, was used as a reducing agent. The ferron chloride (Fe3+) and Ferric chloride (Fe2+) salts were then combined

to obtain 100 mL of the precursor. The mixture was then used immediately to prepare various magnetite nanoparticle formulations to prevent oxidation of Fe2+ to Fe3+. The colour of the reaction changed instantly from golden yellow for the iron precursors and brown for the aqueous mango leaf extract to black. This shows the formation of magnetite nanoparticles. Samples were taken from each of the suspensions for UV-visible spectrum analysis. A known weight of the precursor volume was added to 20 g of activated clay. The mixture was then heated and stirred at 70 oC for 30 mins. The plant extract was also heated separately at 70 0C. After stirring the clay precursor for 30 minutes, 150 mL of the plant extract was added to the mixture. A black mixture formed instantly, indicating the formation of magnetite within the clay structure. The slurry was then dried in the oven. The dried sample was now washed with deionised water to remove excess plant extract from the synthesised composite. The washed sample was dried in the oven at 100 oC. It was thereafter calcined at 400 oC and 700 oC respectively. The dried samples were ground and stirred before characterisation.

Pond wastewater characterisation

Pond wastewater was collected from a commercial fish farm, Minna, Niger State, Nigeria. Immediately after collection, the wastewater was characterised. All analyses were carried out in accordance with standard methods for water and wastewater analysis. The inorganic composition method was determined using the American Public Health Association (APHA) method. Turbidity (Turbidity Meter), pH (a multi-parameter analyzer C3010), electrical conductivity (a multi-parameter analyzer C3010), dissolved oxygen (DO) (DO2 Meter), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total dissolved solid (TDS), alkalinity, the total amount of nitrate, calcium, magnesium, chloride, total bacteria count (TBC), total hardness and total alkalinity were determined using instruments by HACH, USA. All these analyses were carried out at the WAFT department laboratory, Federal University of Technology, Minna. Adsorption capacities of purified CNTs (P-CNTs), functionalized CNTs, and a nano-clay filter were investigated using a column adsorption process in wastewater treatment.

Colum adsorption analysis

The Nano-clay filter was immersed in deionised water for 2 hours to open the pores. It was then placed under a glass column, and the flow rate was set for 10 mL/min. Samples were then collected for water analysis using the atomic absorption spectrometer. Wastewater was passed at a flow rate of 10 mL/min through the nanoclay filter, and the partially treated water was further passed through a glass column packed with the adsorbent at heights of 2 cm, 3 cm, and 5 cm. The treated water was then collected in a beaker and analysed for the various physicochemical parameters and residual concentration of heavy metals.

Statistical analysis

The data from the physicochemical parameters and heavy metal tests before and after treatment using a nano-clay-based filter were analysed using analysis of variance (ANOVA) to determine significant differences. The results were also compared using a t-test, and $p < 0.05$ was considered statistically significant. While the means of significant differences were separated using Duncan's multiple range tests. The colour, odour, total bacterial count, and levels of some heavy metals, such as zinc, copper, iron, and manganese, were determined before and after wastewater treatment using the nanoclay filter.
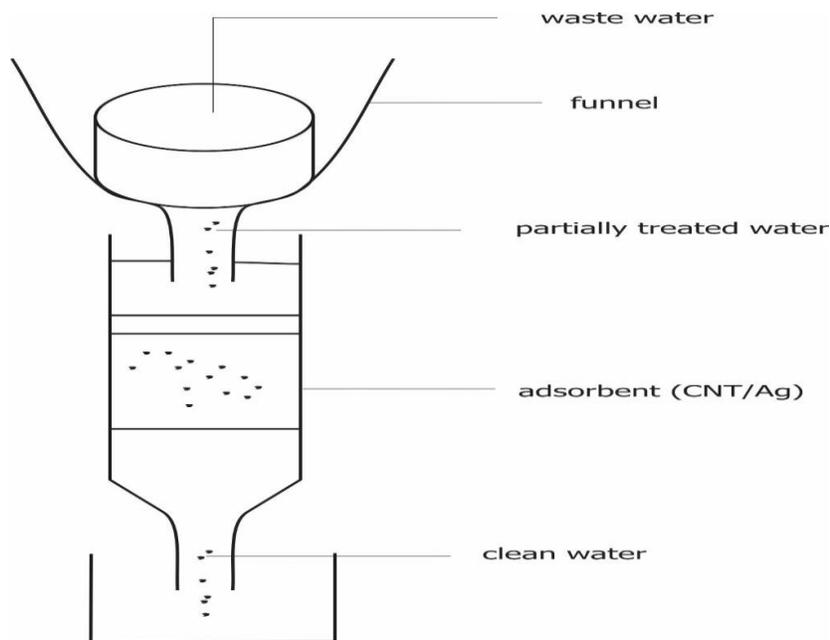
Figure 1: Schematic of Nano- Clay Based Filtration Process

RESULTS AND DISCUSSION

Physicochemical properties of fishpond wastewater

The physicochemical parameters of the fishpond wastewater were analysed, and the results obtained are presented in Table 1

. **Table 1: Physiochemical Parameters of Pond Wastewater before and after treatment**

Parameter	RAW	Nano-Clay	AgCNTs + Nano-Clay (2 cm)	AgCNTs + Nano-Clay (3 cm)	AgCNTs + Nano-Clay (5 cm)	WHO Limit
DO (mg/L)	3.07 ± 0.12^d	6.48 ± 0.39^b	4.50 ± 0.26^c	6.00 ± 0.34^b	8.00 ± 0.51^a	4.0–6.0
COD (mg/L)	124.20 ± 5.94^a	96.00 ± 5.99^c	88.00 ± 5.37^{cd}	112.00 ± 5.97^b	80.00 ± 4.23^d	10
BOD (mg/L)	1.00 ± 0.07^c	4.00 ± 0.09^b	6.00 ± 0.87^a	3.50 ± 0.17^b	3.50 ± 0.08^b	5.0–20
pH	6.91 ± 0.48^a	7.11 ± 0.45^a	7.08 ± 0.43^a	7.01 ± 0.42^a	7.06 ± 0.41^a	6.5–8.5
Conductivity (µS/cm)	464.00 ± 32.00^a	370.00 ± 23.26^b	365.00 ± 22.52^{bc}	353.00 ± 21.32^{bc}	332.00 ± 19.44^c	300–1500
Alkalinity (mg/L)	119.00 ± 8.00^a	77.00 ± 4.47^b	80.00 ± 5.20^b	83.00 ± 5.12^b	77.00 ± 4.23^b	50–100
Hardness (mg/L)	118.00 ± 9.00^c	145.00 ± 8.94^{bc}	155.00 ± 9.53^a	156.00 ± 9.38^a	138.00 ± 8.45	20
Calcium (mg/L)	35.74 ± 2.51^c	58.45 ± 3.66^a	26.49 ± 1.60^d	42.69 ± 2.67^b	33.64 ± 1.99^c	75–150
Chloride (mg/L)	4.84 ± 0.34^d	6.29 ± 0.39^c	8.22 ± 0.49^b	9.19 ± 0.55^a	9.67 ± 0.57^a	250
Magnesium (mg/L)	7.00 ± 0.50^c	0.54 ± 0.04^d	21.68 ± 1.31^a	12.46 ± 0.72^b	13.18 ± 0.78^b	50
Nitrate (mg/L)	3.26 ± 0.24^c	5.38 ± 0.33^a	5.17 ± 0.31^a	3.93 ± 0.24^b	3.90 ± 0.38^b	20–60
Phosphate (mg/L)	1.58 ± 0.11^a	0.62 ± 0.04^b	0.39 ± 0.03^d	0.43 ± 0.03^d	0.52 ± 0.03^c	0.005
TDS (mg/L)	0.78 ± 0.05^a	0.62 ± 0.04^b	0.50 ± 0.02^d	0.56 ± 0.03^c	0.46 ± 0.03^d	500–1000
TBC (cfu/mL)	86.00 ± 7.00^a	12.00 ± 0.89^b	10.00 ± 0.87^{bc}	8.00 ± 0.85^c	4.00 ± 0.85^d	10
Fe (mg/L)	0.812 ± 0.057^a	0.111 ± 0.008^c	0.136 ± 0.008^b	0.118 ± 0.008^{bc}	0.016 ± 0.009^d	0.30
Cu (mg/L)	0.072 ± 0.005^a	0.046 ± 0.003^b	0.037 ± 0.002^c	0.045 ± 0.003^b	0.038 ± 0.003^c	2.0
Mn (mg/L)	0.048 ± 0.003^a	–	–	–	–	0.1–0.5
Zn (mg/L)	3.490 ± 0.240^a	0.630 ± 0.035^b	0.540 ± 0.036^{bc}	0.510 ± 0.034^c	0.360 ± 0.025^d	3.0

Mean values with different superscript along the rows are significantly different (p<0.05) from each other

DO- Dissolved Oxygen; COD- Chemical Oxygen Demand; BOD-Biochemical Oxygen Demand; TDS- Total Dissolved Solid; TBC- Total Bacterial Counts; Fe- Iron; Cu- Copper

Mn- Manganese; Zn- Zinc

The column adsorption process results showed that dissolved oxygen was low for the raw wastewater (3.07), which could be attributed to decaying of organic matter, overfeeding of the fish, or unconsumed feed, high level of plankton turbidity, consumption of oxygen at night for respiration, the accumulation of waste or overcrowding in the culture medium (FAO, 2016a). A high oxygen level indicates that the pollution level in the culture medium is low. After treatment, it improved from 3 to 8 mg/L, which can be attributed to the removal of decaying organic matter and water agitation. The dissolved oxygen concentration in water ranges from 0 to 14 mg/L (Liu et al., 2016). The chemical oxygen demand (COD) indicates the presence of organic matter in a water body, and the major sources of COD are agricultural, industrial, and domestic activities. The COD of the raw wastewater (124 mg/L) exceeded the permissible limit, but after passing through the clay filter, it was reduced to 80 mg/L. The permissible discharge level for COD in effluents is less than 75 mg/l (Geerdink et. al., 2017). The BOD is inversely proportional to the DO. The best BOD value of 6 mg/L was obtained with a 2 cm adsorbent column height, and it falls within the standard limit (EPA, 2012). The pH of water can adversely affect the mobility, solubility, and toxicity of chemicals, increasing the risk of their absorption by aquatic organisms (Jaishankar et al., 2014). A pH below 2.5 causes irreversible damage to skin and organ linings, while outside the 6.5- range causes damage and corrosion to systems and pipes, thus increasing heavy metal toxicity in water (Campelo et al., 2017). The pH of the treated water ranged from 7.01 to 7.08, which is neutral and safe for aquatic organisms. The conductivity of the raw wastewater was 464 µS/cm, and it reduced to 332 µS/cm at a 5 cm column height of the adsorbent. Conductivity aids in determining water quality because an increase in conductivity indicates the presence of dissolved ions (Tiwari, 2015).

Alkalinity is a measure of water's buffering capacity. Water with low alkalinity is highly susceptible to pH changes. The alkalinity of the raw 119 wastewaters was reduced to 77 at 5 cm, which falls within the permissible limit. The total hardness of water is a measure of the quantity of divalent ions in water. High hardness could result from high magnesium concentrations with little or no calcium present (William, 2016). The hardness result falls within the standard permissible limit (Jaishankar et al., 2014). Although calcium concentrations increased, they remained within the permissible limits for all treatments. The chloride level increased in the treatments applied, but remained within the recommended limit of 250 mg/L (Gautam et al.,

2014). The nano-clay filter was effective in reducing the magnesium content of the raw wastewater, and the adsorbent treatment result also falls within the WHO water quality standard of 50 mg/L. Excessive nitrate concentrations can be harmful to humans and wildlife. The nitrate result falls within the permissible limit of 50 mg/L. The phosphate level of the raw 1.58 declined to 0.39 upon application of both the clay filter and the adsorbent. However, only the 2 cm adsorbent column height reaches the permissible limit of 0.50 mg/L, due to the presence of heavy metals (EPA, 2012). The total dissolved solids values obtained showed a reduction from the raw values and fell within the permissible limit (Jaishankar et *al*., 2014). All the treatments applied removed TDS from the wastewater, with the highest removal at 5 cm from the column base. The total bacteria count in the raw wastewater was 86 cfu/mL. In adsorption-based wastewater treatment, bacteria were effectively removed, especially with the application, which can be attributed to the growth-inhibitory and cell-death activities of the AgCNTs.

Adverse effects of iron include carcinogenic, intestinal damage, irritation of the respiratory tract, nausea, diarrhoea and death. (Gautam *et al*., 2014). The iron content of the wastewater falls within the permissible limit of 0.50 mg/L (Jaishankar *et al*., 2014) at 5 cm from the top of the adsorbent column. Similarly, high levels of copper in water could cause liver damage, irritation, insomnia, brain damage and diarrhoea (Barakat, 2011). The copper present in the wastewater was reduced upon contact with the filter and adsorbents; all treatments effectively reduced the copper content to a permissible level of 1.0 mg/L (Jaishankar et *al*., 2014). Moreover, manganese causes liver damage, pneumonitis, inflammation, neurotoxicity, and birth defects when it is present in water in excess of 0.50 mg/L (Gautam *et. al*., 2014). The clay filter and the different adsorbent heights effectively removed 100% of the manganese from the wastewater. Nevertheless, high concentrations of zinc (> 2.0 mg/L) in water cause depression, lethargy, neurological signs, cancer, nausea and zinc toxicosis (Barakat, 2011). The raw wastewater contained 3.49 mg/L of zinc, which decreased to 0.63 mg/L using the clay filter and to 0.63 mg/L at 5 cm of adsorbent column height. Overall, the clay filter shows an effective removal capacity and abilities for the treatment of fishpond wastewater so as to remove pollutants from it, although the developed adsorbent was also efficient, but not as efficient as the nano-clay.

Characterization of the Purified and Functionalized CNTS and Nano-clay filter
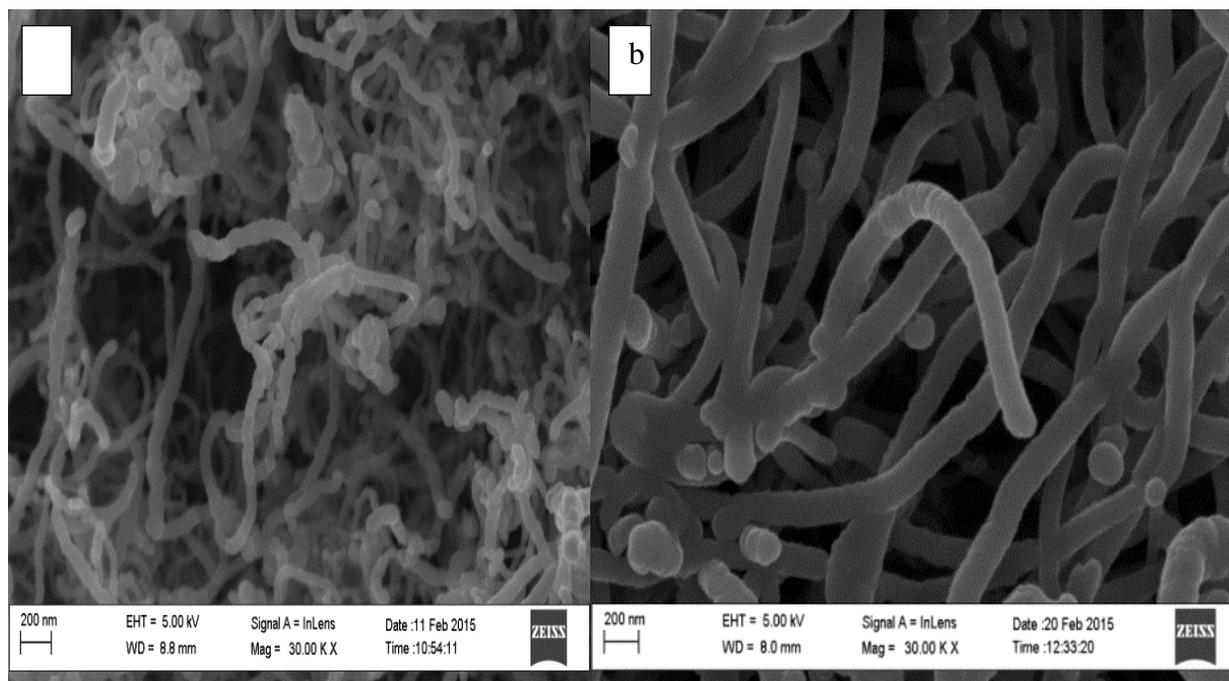
Fig 2: High resolution scanning electron microscope images of the (a) unpurified and (b)purified CNTs
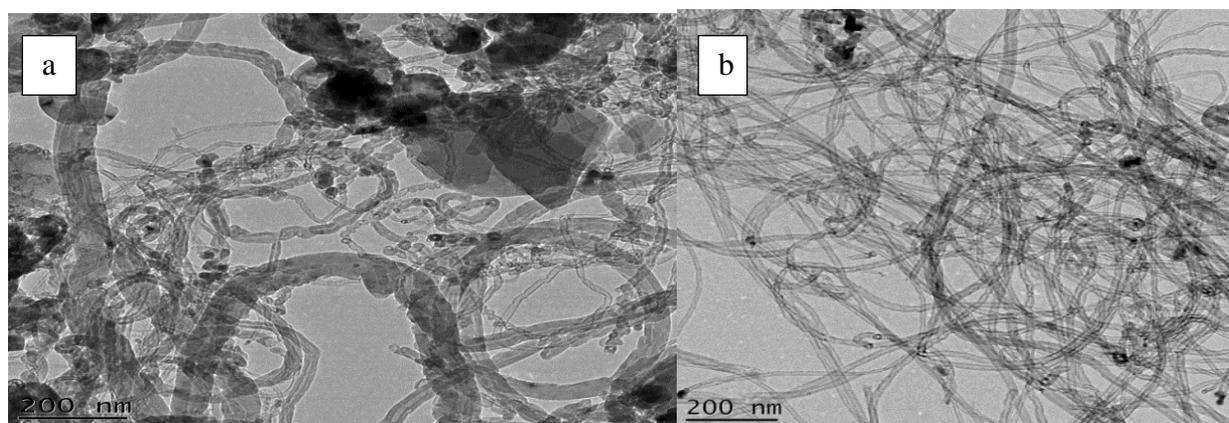
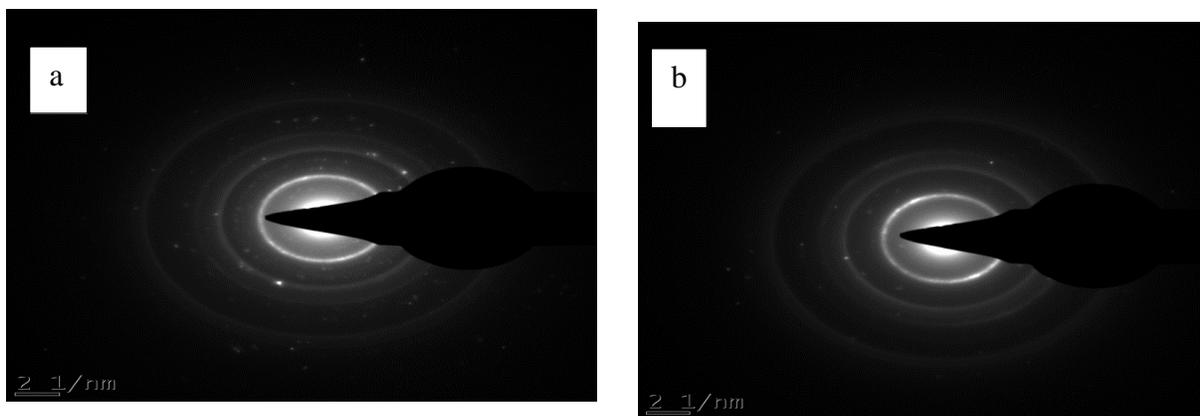**Fig 3: High resolution transmission electron microscope images of the (a) unpurified and (b)purified CNTs**

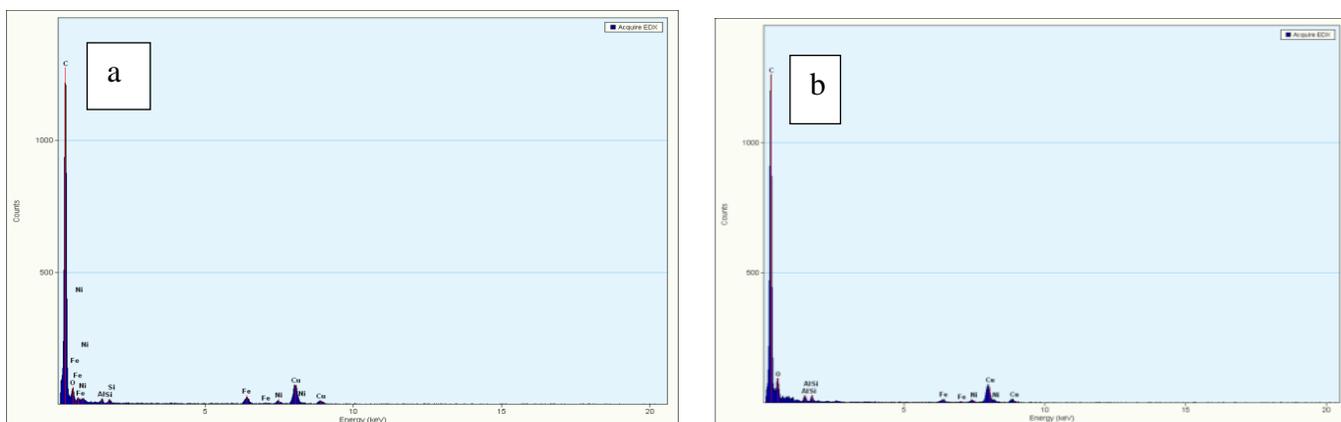Fig 4**: SAED of (a) unpurified and (b) purified carbon nanotubes sample**

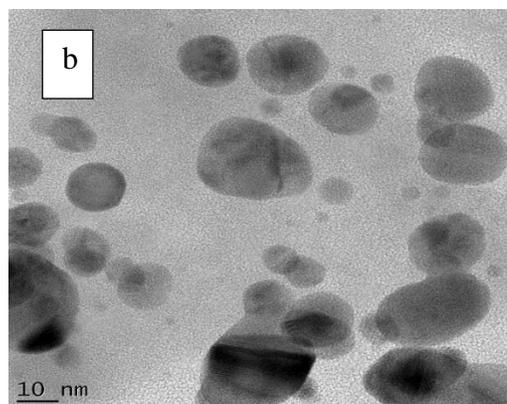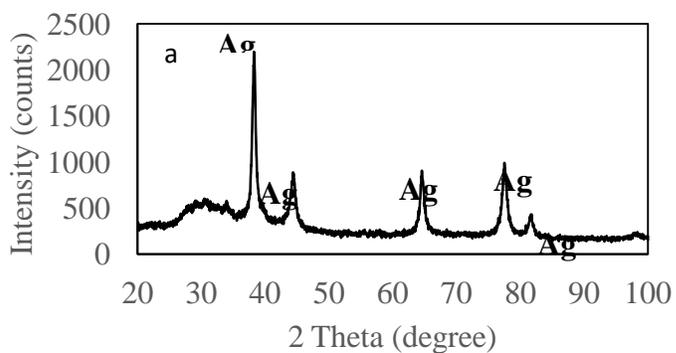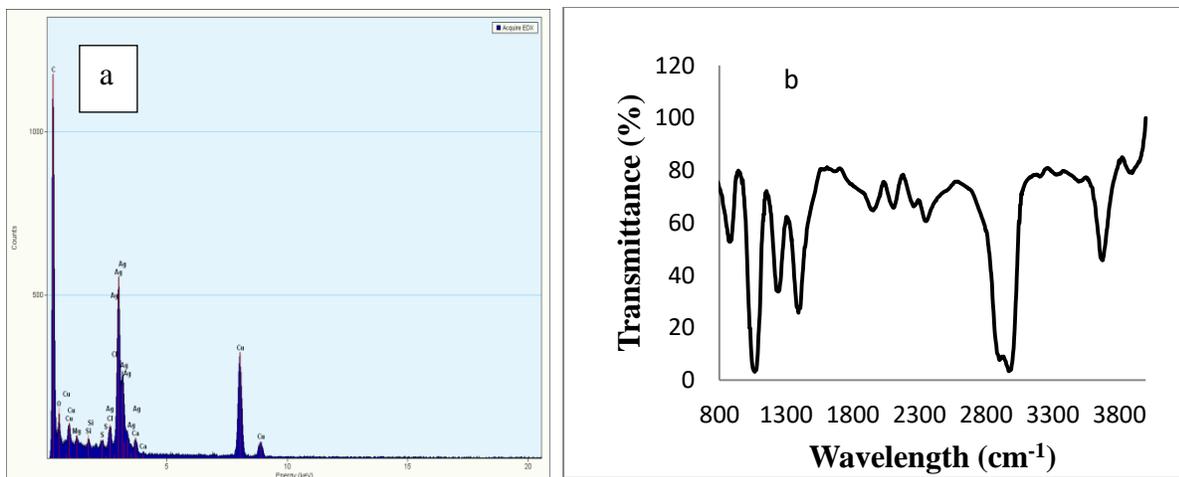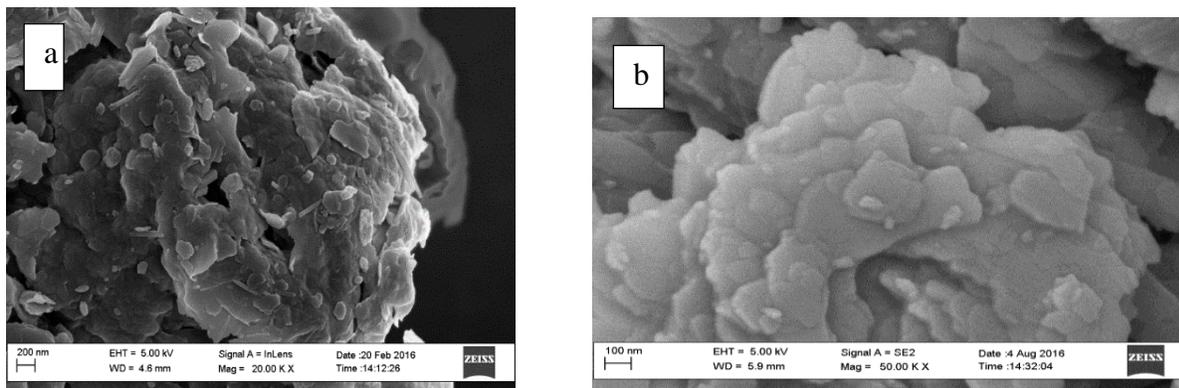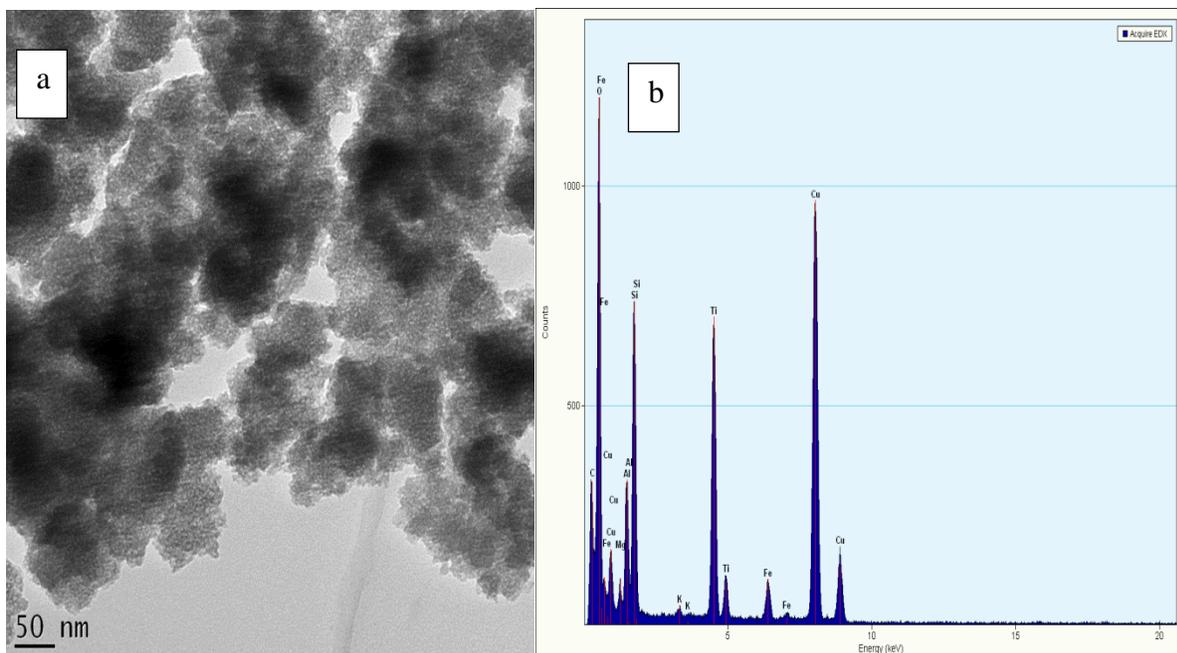**Fig 5: EDS spectra of (a) unpurified and (b) purified carbon nanotubes**

Fig 6: X-diffraction spectrum of AgCNTs and (b) Transmission electron microscope of AgCNTs

Fig 7: (a) EDS spectra of AgCNTs and (b) FTIR of CNTs with AgCNTs

Fig 8: Scanning electron microscope of (a) Raw and (b) beneficiated Afuze clay

Fig 9: Transmission electron microscope of Magnetite nanoparticle and (b) EDS spectra of Nano-clay magnetite nanoparticles

Fig 10: Pond wastewater sample before and after treatment using nano-clay and AgCNTs

The high-resolution scanning electron microscope image in Figure 2 shows the analysis carried out to determine the surface morphology of the unpurified and purified carbon nanotubes; the results indicate an interwoven tube-like structure for the unpurified carbon nanotube, whereas the purified carbon nanotube shows a clear tip bundle interwoven tube-like structure. The clear surface morphology of the purified CNTs indicates the effectiveness of the purification process. The TEM analysis, as shown in Figure 3, was performed to determine the shape, size, and purity of both unpurified and purified carbon nanotubes. The analysis of the unpurified sample shows the tubular shape of the graphite carbon with a metal catalyst and amorphous impurities on the CNT surface, while the purified CNTs show a significant removal of the metal catalyst and amorphous impurities, indicating the purification effectiveness. The selected-area electron diffraction (SAED) pattern of the unpurified and purified carbon nanotubes, shown in Figure 4, indicates white spots around the concentric rings. This shows that both are crystalline. However, the white spots on (b) appear to be more evident than in (a), which is due to the removal of metallic and amorphous impurities from the unpurified CNTs during the purification process. The energy-dispersive spectroscopy results in Figure 5 indicate that 96% carbon was identified in the unpurified carbon nanotubes, but this decreased to 94% in the purified carbon nanotubes. This reduction could be attributed to the loss of amorphous carbon impurities during the purification process. The elemental composition of iron and nickel particles obtained in the unpurified carbon nanotubes was also reduced in the purified carbon nanotube. This reduction in iron-nickel metal particles shows that the purification process was effective in removing metallic impurities.

The X-ray diffraction pattern, as shown in Figure 6, was used to study the phase structure of the silver nanoparticles and the diffraction peaks are shown. This result shows that the sample contains Ag+ ions, and the sharp, intense peaks indicate the crystalline nature of the silver nanoparticles. The XRD diffraction peaks show five sharp, intense peaks at 2θ angles of $38.32°$, $44.50°$, $64.59°$, $77.55°$, and $81.81°$. Similarly, HRTEM analysis was carried out in Figure 8 to determine the microstructure, morphology, and crystalline nature of the biosynthesised silver nanoparticles. The HRTEM image of the silver nanoparticle shows a spherical morphology and demonstrates bound particles, likely due to sonication, which is responsible for the sample's uniform dispersion.

The elemental composition of the silver nanoparticle was estimated using energy dispersive X-ray spectroscopy, and the spectra are shown in Figure 7. The major compositions of CNTs are 94 % carbon and 4.61 % oxygen. The 0.79% iron and 0.60% nickel were metallic impurities encapsulated within the CNTs' walls during the purification process. The CNT-Ag nano adsorbent has 80.6 % carbon, 6.5 % oxygen, 9.6 % silver and negligible 1.9 % and 1.4 % of iron and nickel. The absorption peaks corresponding to the functional groups formed during the reaction were analysed by FTIR. The appearance of definite peaks in the result can be attributed to the functionalization of carbon nanotubes with silver nanoparticles.

In the biosynthesis of silver nanoparticles via green synthesis, phytochemical screening of aqueous leaf extracts of *Carica papaya* and *Vitellaria paradoxa* was performed to detect flavonoids, tannins, and phenols. Based on previous research, plant extracts have been reported to be of great importance in the biosynthesis of metallic nanoparticles (Mamba *et. al.*, 2010). The compounds present are of great importance due to their reductive and antioxidant properties. It has also been reported that tannins can be used as reducing and stabilising agents for the synthesis of silver nanoparticles (Smith et *al.*, 2007). The adsorption peak at 420 nm for silver nanoparticles largely depends on temperature, silver nitrate concentration, and the volume of the extract. For this study, it was found that the optimum temperature for synthesising silver nanoparticles was 60 oC, concentrations of silver nitrate solution (0.001 M), and volume of extract (5 m/L) to obtain 419 nm for *Carica papaya* produced silver nanoparticles and 413 nm for *Vitellaria paradoxa* extraction.

The magnetite nanoparticles formed using *Magifera indica* show a distinct peak at 258 nm. This indicates the synthesis of a single-phase component, and this peak also falls within the range of peak formations for the synthesis of magnetite nanoparticles with plant extracts (Pattanayak and Nayak, 2013). In this study, the filter's performance was evaluated to determine its effectiveness in removing heavy metals at different flow rates. The raw wastewater from the fish pond, containing heavy metals such as iron, copper, manganese, and zinc, was passed through the filter at flow rates of 5, 10, and 15 mL/min. The study shows that each heavy metal in the pond wastewater was efficiently reduced, and the results indicate significant ($p < 0.05$) differences between the raw and treated wastewater. A flow rate of 10 mL/min was used for the column adsorption filtration process. This result is in line with that of a previous researcher (Egbosiuba, 2018) who used Ag-clay to treat industrial wastewater.

CONCLUSION

In conclusion, the development of the nano-adsorbent by doping carbon nanotubes with silver nanoparticles for the removal of effluents, and the production of magnetite nano-clay for the removal of dissolved solids, odour, colour, and heavy metals, was successful. The adsorbent was used in a column adsorption process, and the result shows the removal efficiency in the wastewater.

The ceramic water filter successfully removed colour, odour, and dissolved solids from the raw fishpond wastewater. It can be inferred from the various analyses conducted on the raw and treated fishpond wastewater sample that the developed nano-clay-based filter at a flow rate of 10mls/min and nano-adsorbent at a column height of 5cm in a single purification process are suitable for fishpond wastewater treatment.

REFERENCES

Akpan, D., & Ajayi, O. (2016). Adverse Effect of Water Contamination or Pollution to Human Health and Safety in the Nigeria Delta – Nigeria: An Environmental Case Study, *6*(10), 91–94.

Akpor, O. B., Ohiobor, G. O., & Olaolu, T. D. (2014). Heavy metals pollutants in wastewater effluents: Sources, effects and remediation. *Advances in Bioscience and Bioengineering*, 2(4), 37-43 https://doi.org/10.11648/j.abb.20140204.11

Asharaf, M.A., Balkhair, J.S., Ahmad, M., Akib, S., & Batol, S. (2014). Study of modern nano enhanced techniques for removal of dyes and metals. *Journal of Nanomaterials* Vol. 2014, Article ID 864914, 20 pages 2014.

Bankole, M. T., Mohammed, I. A., Abdulkareem, A. S., Tijani, J. O., Ochigbo, S. S., Abubakre, O. K. & Afolabi, A. S. (2019). Selected Heavy Metals Removal from Electroplating

Wastewater by Purified and Polyhydroxybutyrate Functionalized Carbon Nanotubes Adsorbents, Scientific Report, 9,4475, CVD method. *International Nano Letters,* 2 (23)

Barakat, M. A. (2011). New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry, 4*(4), 361-365 .https//doi.org/10.1016

Burakov, A. E., Galunin, E. V, Burakova, I. V, Kucherova, A. E., Agarwal, S., Tkachev, A. G., & Gupta, V. K. (2018a). Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes : A Review. *Ecotoxicology and Environmental Safety*, 148, https:doi.org/10.1016

Campelo, A., Raimundo, K., Faial, F., Feitas, C., Danielly, I., Oliveira, M.D, & Mendonca, R. (2017). Quality Index of the Surface Water of Amazonian Rivers in Industrial Areas in Para, Brazil.*MarinePollutionBulletin*,123(1-2),156-164,https:doi.org/10.1016/j.marpolbul.2017.09.002

Das, R., Ali, M.E., Hamid, S.B.A., Ramakrishna, S., & Chowdhury, Z. Z. (2014). Carbon Nanotube Membranes for Water Purification: *A Bright Future in Water Desalination*. Desalination 336, 97–109

Egbosiuba, T. C. (2018). Optimization, Characterization and Application of Carbon Nanotubes and Functionalized Carbon Nanotubes Prepared from Fe-Ni/AC Supported Catalyst for Industrial Wastewater Treatment.

Emir, Z., Zivko, V., & Ivan, H. (2015). Application of Nanotechnology in Wastewater Treatment. https://doi.org//10.14256/JCE.2165.2017

EPA. (2012). US Environmental Protection Agency: *2012 Edition of the Drinking Water Standards and Health Advisories*.2-6 https://doi.org/EPA 822-S-12-001

FAO. (2016). FAOSTAT. Database. http://faostat3.fao.org/ Rome, Food and Agriculture Organization of the United Nations

Fu, F, & Wang, Q. (2011). Removal of heavy metals ions from wastewaters: A review. *Journal of Environmental Management*.92,407-418.doi: 10.1016/j.jenvman.2010.11.011

Gautam, R. K., Sharma, S. K., Mahiya, S., & Chattopadhyaya, M. C. (2014). Heavy Metals in Water: Presence, Removal and Safety Contamination of Heavy Metals in Aquatic Media: Transport, Toxicity and Technologies for Remediation. *Royal Society of Chemistry*, (Chapter 1), 1-24

Geerdink, B., Sebastian, R., Hurk, V. Den, & Jacob, O. (2017). Chemical Oxygen Demand: Historical Perspectives and Future Challenges. *Analytical Chemical Acta*,1-11. https://doi.org/10.1016/j.aca.2017.01.009

Guo, H., Wyart, Y., Perot, J., Navleau, F., & Moulin, P. (2010). Low- pressure membrane integrity tests for drinking water treatment: A review. *Water research* 44(1), 4157. Doi:10.1016/j.watres.2009.09.032

Javier, M.S., Sara, M.Z., & Hugh, T. (2017). Water Pollution from Agriculture: A Global Review. FAO and IWMI. pp 3-11

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B., & Beeregowda, K. N. (2014). Toxicity, Mechanism and Health Effects of Some Heavy Metals. *Interdisciplinary Toxicology*, 7(2). https://doi.org/10.2478/intox-2014-0009

Jiancheng, S., Renlong, L., Haiping, W., Zuohua, L., Xiaolong, S., & Changyuan, T. (2017). Adsorption of Methylene Blue on Modified Electrolytic Manganese Residue: Kinetics, Isotherm, Thermodynamics and Mechanism Analysis. *Journal of the Taiwan Institute of Chemical Engineers*,0,1-9. https://doi.org/10.1016/j.jtice.2017.11.020

Kanchi, S. (2014). Nanotechnology for Water Treatment. *Journal of Environmental Analytical Chemistry.*1.e102 https://rehup.elsevier.com/B978-0-12-804300-   4.00002-2/ref0415

Konda, R. K., Michael, N., Farrah, S., Rajendra, P.P., Arijit, B., & Abraham J. D. (2017). Nanotechnology for Water Purification:Applications of Nanotechnology Methods in Wastewater Treatment..https://doi.org/10.1016/B978-0-12-804300-400002-2

Liu, C., Fiol, N., Poch, J., & Villaescusa, I. (2016). A New Technology for the Treatment of Chromium Electroplaiting Wastewater Based on Biosorption. *Journal of Water Process Engineering*,11,143 https://doi.org/10.1016/.2016.05

Lu, F., & Astruc, D. (2018). Nanomaterials for Removal of Toxic Elements from Water. *Coordination Chemistry Reviews*, 356, 147-164. https://doi.org/10.16/2017.11.

Mamba, G., Mbianda, X.Y., Govenda, P.P., Mamba, B.B., Krause, R.W. (2010). Application of Multiwalled Carbon Nanotube-Cyclodextrin Polymers in the Removal of Heavy Metals from Water. *Journal of Applied Sciences* 10(11):940-949, 2010

NNI. (2001). A report by the Interagency working group on Nanoscience, Engineering and Technology. Washington DC.

Pattanayak M.,& P.L. Nayak (2013).Eco-friendly green synthesis of iron nanoparticles from various plants and spices extract. International journal of plant, animal and environmental sciences.

Prakesh, N. B., Socken V., & Jayakaran P. (2014). Wastewater Treatment by Coagulation and Flocculation. *International Journal of Engineering Science and Innovative Technology* 3(2), 479. Retrieved from https:www.ijesit.com

Qu, X., Brame, J., Li, Q., & Alvarez, P.J.J. (2013). Nanotechnology for a Safe and Sustainable Water Supply: Enabling Integrated Water Treatment and Reuse. *Acc. Chem. Res*. 46, 834–843

Rashed, M. N. (2013). Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater. https://dx.doi.org/10.5772/54048

Santhosh, C., Velmurugan, V., Grace, A.N., & Bhatanger, A. (2016). Role of nanomaterial's in water treatment applications: A review. *Chemical Engineering Journal,* 306,116-1137 https://doi.org/10.1016/j.cep.2016.08.053

Sadaf, S., & Bhatti, H. N. (2014). Batch and Fixed Bed Column Studies for the Removal of Indosol yellow BG dye by peanut husk. *Journal of the Taiwan Institute of Chemical Engineers*, 45(2). https://doi.org/10.1016/j.jtice.2013.05.4

Segneanu, A. E., Orbeci, C., Lazau, C., Sfriloapa, Bandas, C. & Grozescu L. (2013). Wastewater Treatment Methods. doi: 10.5772/53755

Sophia, A., C., & Lima, E. C. (2018). Removal of Emerging Contaminants from the Environment by Adsorption. *Ecotoxicology and Environmental Safety*, 150, 1-17. https://doi.org/10.1016/j.ecoevn.2017.12.026

Smith, C. J., Shaw, B. J & Handy, R. D. (2007). Toxicity of single walled carbon nanotubes to rainbow trout, (*Oncorhynchus mykiss*): Respiratory Toxicity, Organ Pathologies, and Other Physiological Effects. *Aquatic Toxicology*, 82-94

Tiwari, S. (2015). Water Quality Parameters- A Review, *International journal* of *Engineering Science Invention Research & Development*, I (Ix), 319-324

UNICEF. (2008). *Unicef Handbook On Water Quality*.

Wang, W., Xie, H., Zhang, N., & Xiang, D. (2018). Sustainable Water Use and Water Shadow Price in Chinas Urban Industry. Resources, Conservation & Recycling," 128,489-498.https://doi.org/10.1016/j.resource.2016.09.005

Woodford, C.,Calhoun, Y., Seideman, D., & Woodford, C. (2015).Water Pollution in the environment. (pp. 1–13). https://doi.org/10.1007/b96279

William, A.W (2016). Understanding Water Hardness. Kentucky State University Extension Program. https://www.researchgate.net/publication/307122312

WHO. (2017). Guidelines for Drinking-Water Quality. *Fourth Edition*.

Zare, E., Motahari, A., & Silkripag, M. (2018). Nano Adsorbents Based on Conducting Polymer Nanocomposites with Focus on Polyaniline and its Derivatives for Removal of Heavy Metals Ions/ Dyes: A review. *Environmental Research*, 162, 173-195. Doi.org/10.1016/2017.12.025

Zhang, Z.,Pfefferle, L., & Haller, G.L. (2015). Characterization of Functional Groups on Oxidized Multi-Wall Carbon Nanotubes by Potentiometric Titration. *Catalysis Today*,1-7. https://doi.org/10.1016/j.cattod.2014.12.013

Zhang,]D., Yan, D., Lu, F., Wang, Y. & Feng, J. (2015). Copula-Based Risk Assessment of Drought in Yunnan Province, *China Natural Hazards*75:2199–2220. http://link.springer.com/article/10.1007/s11069-014-1419-6