FEDERAL UNIVERSITY OF TECHNOLOGY MINNA

PUBLIC LECTURE

Theme:

Human Exposure to Carcinogens and Associated Health Risks: "My Concern and Contributions to Reducing Disease Burden in Nigeria"

By

ENGR. DR. SADEEQ ABUBAKAR MOHAMMED
(PhD, FIMC, CMC, R.Eng, MNSE, MNIAE, MIUSS)

18th November2021

Engr. Prof. A.A. Balami
Courtesy of Engr. Dr. Sade
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Preamble

The scarcity of freshwater resources being currently experienced in water stressed and most developing countries has prompted millions of smaller communities to depend on wastewater for agriculture, drinking, bathing and fishing. In this context, the treatment option of textile and tannery wastewater containing heavy metals and dyestuffs used for agriculture is the subject of interest in this research. However, this concept can be applied to other industries with similar pollution index. Release of these micro-pollutants into the water bodies especially surface water has been an issue of concern amongst researchers due to the health risks associated with such carcinogens (heavy metals) when found in the food chain. Although, conventional wastewater treatment technologies exist; however, they are inefficient at much lower concentrations, design process is complex and are usually very expensive. As such, the essence of this study is to devise a simple, efficient, affordable and reliable technology for wastewater treatment using low cost adsorbents. Hydrochar of low cost biomass wastes that include eggshell, rice husk, coconut shell, coconut peat and lemon peel were used to treat industrial wastewater, which brought the concentration level below the WHO/FAO standard. This implies that there is hope for the treatment of water and wastewater used for crop irrigation in Nigeria.

From the analysis of the batch I sorption data, coco-peat (CP) has proven to be a novel sorbent for the removal of Cr(VI) and Pb(II) ions from contaminated wastewater. The adsorption efficiency of these metal ions by CP is over 90%, eggshell (ES) was able to remove nearly 100% of Fe(II) and Cu(II) and coconut shell CS is good for decolouration of the wastewater. Optimisation using response surface methodology (RSM) was further used to analysis batch I sorption data, which shows that adsorption of heavy metal ions attain optimum at pH9 and 2 h of contact time. Four different kinetic models as well as adsorption isotherms were used for the validation of the sorption data and R^2 determined. A good correlation shows R^2 is 1 or approaches 1. The Pseudo-second kinetics and Elovich kinetic models best described the sorption kinetics of the metal ions. The R^2 for Fe(II) adsorption by eggshell hydrochar is 1, which is the same as that obtained from the reference adsorbent (bonechar). Of the four adsorption isotherm used, Langmuir fit and Dubinin – Radushkevich models were able to fit the sorption data very well with high R^2 values compared to the reference adsorbent (BC).

The column studies found that when the hydrochars were arranged in layers Cr(VI) not only being reduced to concentration of 0.210 mg/L but also converted to Cr(III), Cu(II) of 0.0657 mg/L, Fe(II) of 0.708 mg/L and Pb(II) of 0.626 mg/L in the final filtrate after the second column. Yet another method that explored mixing the hydrochars together, resulted in final filtrate containing Cr(VI) being converted to useful Cr(III) which was measured as 0.182 mg/L, Cu(II): 0.190 mg/L, Fe(II): 0.224 mg/L and Pb(II): 0.540 mg/L. A special test was carried on chromium to determine which specie is present in the filtrate after adsorption. Findings from that test reveals that the chromium is Cr(III). The inference drawn here is that the hydrochars were able to convert Cr(VI) to Cr(III) during chemical reaction.

In conclusion, applying this innovation to treat wastewater used for crop irrigation in Nigeria and other developing countries with similar environmental issues, has help in decolourising the dye in wastewater and significantly reduce the concentrations of heavy metal ions below the acceptable limits issued by the Food and Agriculture Organisation (FAO) and World Health Organisation (WHO) for irrigation water. "A Healthy Nation is a Wealthy Nation"

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INTRODUCTION

Water is a finite resource that is essential for the sustenance of life, agriculture and industry. Studies have shown that there is a general decline in the amount of freshwater resources worldwide, but the severe impact is mostly experienced in developing and water-stressed countries (FAO/WHO, 2006; Hamilton *et al.*, 2007). Currently, about one-third of the world's population live in water-stressed countries and by 2025 it is expected to rise up to two-thirds (UN-Water, 2007). Water scarcity may limit food production and supply, as about 70% of all freshwater withdrawals go to irrigated agriculture (≈ 2800 km^3 of freshwater/year) (UN-Water, 2012). The use of wastewater in developing countries has emerged as an important option to augment the perennial scarcity of freshwater resources. Agricultural productivity in developing countries is lower due to water scarcity which is also observed to affect the expansion of crop production.

The economic contribution of farmers in developing countries is now hamstrung by the scarcity of water resources and this is observed to affect not only the expansion of crop yields but also economic growth and quality of crops and vegetables produced by the farmers (FAO/WHO, 2009). As a consequence of freshwater scarcity, millions of global farming communities now depend on wastewater for domestic and agricultural activities (Raschid-Sally and Jayakody, 2008). Wastewater stems to provide a great deal of relieve to farmers for year-round production of crops. The use of wastewater for agriculture permits the cultivation of wide range of crops in multiple cycles, thereby promoting potentials for high yields. Hence, competition for this scarce resource spans between agriculture and industry.

Wastewater reuse in agriculture has a historical precedence and this practice has to increase in the near future (Ensink and Van Der Hoek, 2009). Reuse of wastewater for agriculture constitutes a low-cost and sustainable process, which if carried out under controlled conditions, could rejuvenate soil with organic matter and nutrients for enhanced crop production (Qadir *et al.*, 2007, Jiménez *et al.*, 2010). Additional benefit of wastewater reuse for agriculture is that, it is a cost-effective source of irrigation water to hot and dry climates (Hamilton *et al.*, 2007; Jimenez and Asano, 2008). Conversely, poor management of wastewater can lead to the introduction of contaminants such as heavy metals, dyes, pharmaceutical residues and pathogenic organisms which is eventually released through food chain and ends in humans (Drechsel *et al.*, 2009; Fatta-Kassinos *et al.*, 2011).

Notably, farmers exposed to prolonged contact with contaminated wastewater and the consumers of crops irrigated with untreated wastewater are likely to suffer a wide range of diseases that include

cancer, cardiovascular and neurological illnesses (Fatta-Kassinos *et al.*, 2011). Scholars were able to establish an epidemiological link between consumption of food crops irrigated with untreated wastewater and individual or communal illnesses (Blumenthal and Peasey, 2002; FAO/WHO, 2006; Ensink and Van Der Hoek, 2009). Studies have shown how these illnesses leads to the reduction in life expectancy (WHO, 2006), with worst-hit in developing countries.

Municipal wastewater when combined with untreated industrial wastewater that is indiscriminately discharged into an adjoining river is particularly a threat not only to humans and animals but also to the environment. In fast-growing cities of many developing countries, wastewater infrastructure is non-existent, inadequate or obsolete. For instance, the city of Jakarta, with a population of 9 million, generates 1.3 million m^3 of sewage daily, of which less than 3% is treated. In Nigeria, Ademoroti et al. (1992), reported that about 75% of the wastewater generated by textile and tannery industries are discharged directly into nearby rivers, streams or lagoons (surface waters), 15% into surrounding bushes and 10% into drainage and gutter systems without treatment (Ademoroti *et al.*, 1992; Adebayo *et al.*, 2007). It has been reported that about 42% of all the textiles industries in Nigeria are sited in Lagos (Apapa, Illepeju, and Ikeja), while 27% are in Kano (Bompai, Challawa, and Sharada), 20% in Kaduna (Kakuri, Kaduna South) and the remaining 11% are distributed in cities such as Aba, Onitsha, Asaba, and Ado-Ekiti (Ademoroti *et al.*, 1992). On the other hand, the northern parts of Nigeria (Kano, Kaduna, Maiduguri) have the largest tannery industries (NBS, 2010).

The characteristics of textile and tannery wastewater (composition and concentration) in Nigeria is similar to those found in other developing countries (Akan *et al.*, 2009; Bello *et al.*, 2013; Bichi *et al.*, 2013; Halim, 2013; Sorsa *et al.*, 2015). The effluents from these industries contain reagents such as carboxylic acids, alkalis, dyes, sodium bisulphate, soda ash, hydrogen peroxide, dextrin-starch, gums and resins, waxes, surfactants, dispersing agents, soaps and heavy metals (Holkar *et al.*, 2016). The presence of these kinds of pollutants in irrigation water and agricultural soils above their recommended thresholds has been a concern due to their pervasive health accumulative and impact both ecological systems and public health (FAO/WHO, 2006; Ensink and Van Der Hoek, 2009).

There are documented reports showing varying concentration levels of heavy metals and organics in textile and tannery wastewaters; indiscriminately discharged into surface waters in Nigeria and many other developing countries (FAO/WHO, 2006; Ensink and Van Der Hoek, 2009; Sorsa *et al.*, 2015). Regrettably, these types of wastewaters are currently being used for agricultural irrigation in Nigeria (Oke *et al.*, 2006; Akan *et al.*, 2009; Dan'Azumi and Bichi, 2010; Bichi *et al.*, 2013)..

Policymaking bodies such as Food and Agriculture Organisation (FAO) and World Health Organisation (WHO) have been exploring modalities in safeguarding humans from excessive exposure to micro-pollutants present in wastewater used for crop irrigation. The adoption of water quality guidelines issued by the joint action of the FAO and WHO for agricultural practices worldwide is desired; but in reality, its implementation is hard to achieve practically particularly in developing countries (Chang *et al.*, 2002). This is usually due to the following reasons: 1) poor infrastructure and wastewater treatment facilities; 2) non-compliance and policing of rules and regulations governing wastewater discharge; and 3) expensive costs for modern wastewater treatment facilities.

Problem Statements

Industrial production requires large volumes of water and as such generate corresponding amounts of polluted wastewater. Wastewaters from industries are known to compose a wide range of chemicals including heavy metals, dyes/pigments, pharmaceutical residues, automobile and electronic wastes etc. The presence of these substances in wastewater used for crop irrigation poses a very serious public health risk due to their pervasive accumulative impact (FAO/WHO, 2006).

1. **Wastewater Generation from Textile and Tannery Industries:** Figure 1 illustrates textile and tannery operations and how the

generated wastewater from these industries are indiscriminately discharged into the adjoining River Jakara in Kano Nigeria. This river is predominantly used for raising a variety of farm produce through wetland (Fadama) irrigation. The humans and animals are usually at the receiving end of this poor irrigation practice.

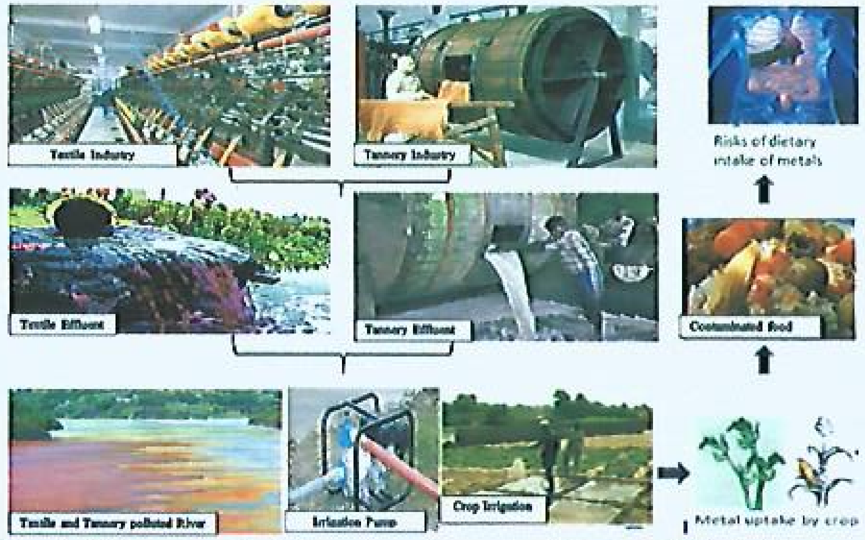

Figure 1: Pathways through which organics and inorganics pollutants enter biological tissues

2. **Discharge from IBB Specialist Hospital into River Chanchaga and surrounding farmlands:** The indiscriminate deposition of biomedical solid wastes opposite the entrance gate of IBB specialist hospital is a taboo. Regrettably, some destitute were found scavenging such biomedical waste for items; hence exposing themselves to adversity. Further, it was observed that whenever it rains, the storm water that falls on the biomedical wastes seeps through the vegetation and discharge into the surrounding farmland on which both leafy and non-leafy vegetables, sugar cane, maize and others are cultivated. (See plates 1- 6). Also from the rear of IBB Specialist hospital, one may see how an open rectangular drainage meant to convey wastewater from the hospital is directed into river Chanchaga that supplies Minna Municipality with drinking water.

Plate 1 Gold leading failure of Chanchaga bridge

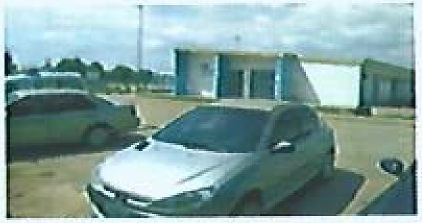

Plate 2 IBB Specialist Hospital Minna

Plate 3 [illegible]

Plate 4 Liquid waste discharged into River Chanchaga

Plate 5 Liquid waste discharged into River Chanchaga

Plate 6 Minna Municipal Water Supply

3. **Wastewater Generation from Dana Pharmaceutical Industry in Minna:** Dana Pharmaceutical Industry is located along Shiroro Dam Road Maitumbi, Minna. Although, the establishment of this industry in Minna have comparative advantages because it is a source of revenue for the State and provides job opportunity for the locals; however, our safety and that of the environment cannot be compromised. Plates 7 - 12 depicts environmental apathy resulting from the unhealthy situation the residents of Anguwan Dana are been confronted with, which has become a threat to their agricultural soils. The land behind the industry is fast degrading and a large portion of the viable agricultural soil been lost to gully erosion resulting from indiscriminate discharge of pharmaceutical wastes (liquid) into our water ways.

Plate 7 Entrace Gate to Dana Pharmaceuticals In Minna

Plate 8 Toxic wastes discharged through the canal

Plate 9 Dana decided to deceive the public by indicating that it is rainwater drain

Plate 10 Emergency of gully erosion due to toxicity of Dana effluents Soil loss Toxic wastes

Plate 11 Teenagers exposed the Dana Dana Effluents causing sick lesions, irritation and cancer

Plate 12 Cultivation of hot pepper and tomatoes with such wastewater flowing through TRADOX to discharge at [illegible]

The toxic wastewater from Dana pharmaceutical industry discharges into another river containing other micro-pollutants resulting from illegal/uncontrolled mining of Gold by artisans in

Anguwan Dana. The river containing these pollutants now flow in-between the Legislative Quarters of the 3-Arms Zone and PDP Secretariat. The river then splits its flow, with the first flowing through General Muhammad Inuwa Wushishi Housing Estate and Tradoc (Army Barrack Minna) to connect River Chanchaga through Lapai-Gwari (where massive irrigation activities and fish farming takes place). While the other segment of the river flows to discharge at Chanchaga, which can be seen directly from the rear of the IBB specialist hospital. The upper fringes of that river are densely cultivated with a variety of crops.

Release of pharmaceutical and personal Care Products into our waterways

Pharmaceutical and personal care products (PPCPs) consist of the prescribed and nonprescribed drugs while the personal care products (PCPs) are used to improve the quality of human life. These PPCPs consist of organic compounds such as antibiotics (erythromycin, sulfamethoxazole, trimethopr), antiallergic (loratadine), antacid (cimetidine, ranitidine) hormones, analgesics and anti-inflammatory (codine, hydrocodene, paracetamol, tramadol), endocrine disruptors. It is well known that these pharmaceuticals are metabolised by the host and are subsequently excreted into the environment via urine and faeces while the PCPs enter the environment through direct or indirect metabolisation pathways (see Figure 2). The occurrence of these PPCPs in Nigerian water bodies was found in the range of 75 – 129 ug/L (Ogunbanjo, *et al.*, 2020), indicating high concentration of pharmaceutical residue in the wastewater samples. Similarly, there are documented studies reporting that the concentration of PPCPs present in the Indian water bodies was the world's highest ever recorded (Xu *et al.*, 2017; Mutiyar and Mittal, 2013). Some of the PPCPs are toxic even at low concentrations while others persist and bioaccumulate in the environment, thereby increasing the toxicity. Moreover, continuous exposure to these PPCPs results in hormonal imbalance and cancer in humans (Xu *et al.*, 2017). Furthermore,

release of these pharmaceutical residues into our food chain could lead to endocrine hormonal disruption. There is prevalence rate of fibroids cases among young adult ladies or women in Nigeria. For instance, according to Elugweraonu, *et al.* (2013), from 2008 to 2012, in Edo State, a total of 4,536 case files were reviewed, among which 896 tested positive for uterine fibroid; given a prevalence rate of 19.75. The authors further reported that the year 2012 recorded the highest incidence of uterine fibroid (23.59), followed by the year 2008 (23.36), 2009 (19.78), 2011 (18.91) and 2010 (14.56) respectively. That study revealed that women within 26 – 35 years were significantly affected in all the years under study, with an incidence rate of 66. 96, while older women (>35) and those younger (>26) presented an incident rate of 29.58 and 3.46 respectively.

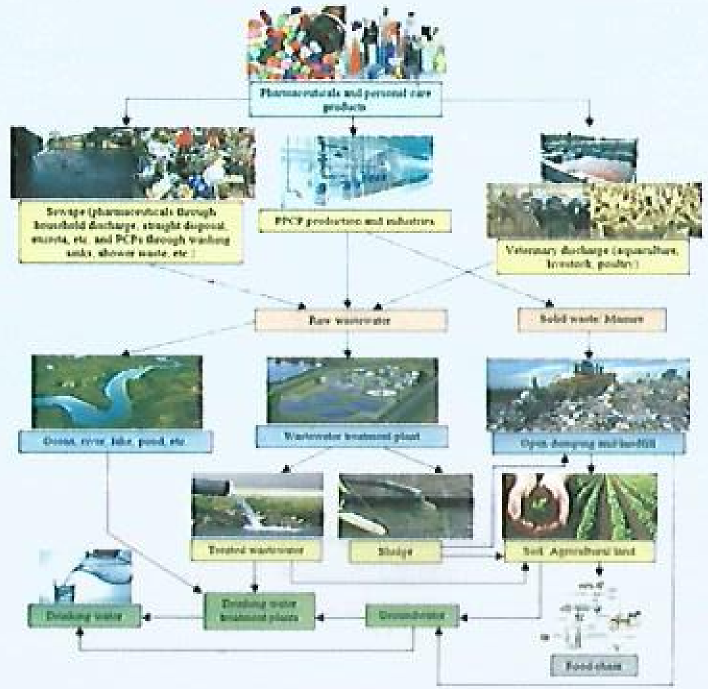

Figure 2. Sources, environmental fate and transport of PPCPs. PPCPs, Pharmaceuticals and personal care products.

5. Actions of CBN and NISEPA against the inhabitants of Zhenuko Village, Maikunkele

Zhenuko is village that is 1 km away from Maikunkele, it is located on Lat(9° 40' 57" N; 6° 28' 6" E) along Beji-Zungeru Road in Bosso Local Government Area. The Central Bank of Nigeria (CBN), find it convenient to burning their shredded mutilated currency on their open land. The inhabitants are predominantly peasant farmers and completely ignorant about the Chemistry of heavy metals on

Figure 3 Mutilated money burnt in the open and dispersed via agents of erosion

Secondly, Zhenuko has been made Minna dumping site, where all manners of wastes are brought without considering the plight of the inabitants who suffer a wide range of illness. Furthermore, because the average peasant farmers in Minna and its environs cannot afford inorganic fertilizers due to provocative cost, so they resolve to opting for heterogeneous dumpsites (chemically contaminated soil) as organic manure to raise their crops.

Now surmise to the above narrations, it is evident that IBB specialist Hospital, General Hospital Minna, Dana Pharmaceutical Industry, Niger Stte Environmental and Protection Agency (NISEPA) and CBN all offends Section 20 of the 1999 Constitution of the Federal Republic of Nigeria, which gives the basis of environmental policy. Pursuant to that Section 20 of the Constitution, the State is empowered to protect and improve the environment and safeguard the water, air and land, forest and wildlife of Nigeria.

Separation technologies

The conventional wastewater treatment technologies that are used for the removal of heavy metals and Pharmaceutical and Personal Care Products (PPCP) Care from industrial wastewaters include: chemical precipitation, ion-exchange, coagulation, evaporation recovery, electrochemical, membrane filtration, adsorption using granular activated carbon (GAC), and industrial by-products like nano-sized materials (metal oxides) (Amarasinghe and Williams, 2007; Acheampong *et al.*, 2015). The MF and UF membranes are used only for pretreatment while nanofiltration, reverse osmosis, and MBRs have shown an effective PPCP removal. The removal efficiency of PPCP by membrane filtration is governed by hydrophobicity and charge while in MBR, the PPCP removal is influenced by flux, membrane permeability, and fouling. However, a wider application of most of these technologies is not only limited by the complexity in designs, but also the high cost of procurement, operational and maintenance. In addition to these limitations, the techniques other than adsorption convert the pollutant into a secondary toxic wastes which require additional costs for treatment (Annadural *et al.*, 2002,

Saka *et al.*, 2012). Furthermore, apart from adsorption using GAC, all the conventional methods mentioned above have been found to be ineffective in removing metal ions in dissolved solutions below 100µg (Geetha and Belagali, 2013).

Recent research on sorption of organic and inorganic pollutants from wastewater using low-cost biomass wastes has been reported (Azouaou *et al.*, 2010; Zhao *et al.*, 2016). Biomass wastes have emerged as promising alternatives to the commercial activated carbon and industrial by-products (e.g. zeolite and metal oxides)/nanomaterials which are quite expensive for wastewater treatments (Azouaou *et al.*, 2010; Ahmaruzzaman, 2011). The use of low-cost materials for adsorption has the following advantages: the design technique is simple for adoption; agricultural wastes can be converted into a useful resource, the biomass can be sourced locally, it is cheap and environmental-friendly, the production technique is sustainable and it can be easily reproduced. Thermal pretreatment of biomass as in the case of GAC has been reported to improve adsorption potential.

Hydrothermal Carbonisation

Hydrothermal Carbonisation (HTC) is a thermochemical pathway, in which biomass is heated between 180 – 300 °C in a closed autoclave vessel operated under saturated pressure (usually 20 bar) for a period of 2 – 6 hs to produce a carbonaceous solid, called 'hydrochar'(Funke and Ziegler, 2010; Sevilla *et. al.*, 2011). In 1913, a German Chemist named Friedrich Bergius developed a method termed HTC for transforming cellulose materials into coal through a process called coalification (Bergius, 1913). This concept was later adopted to carbonise biomass in water at a temperature range of 150 – 350 °C to produce coal (Berl and Schmidt, 1932). There is renewed interest in the production of hydrochars from organic materials as a method of reducing CO_2 emissions by combustion (Libra *et al.*, 2011). The advantage of HTC over pyrolysis is that the former is operated at lower temperatures to convert wet feedstocks into carbonaceous solids at relatively high yield with less energy requirement for drying compared to the latter (Peterson *et al.*, 2008; Sun *et al.*, 2011). In addition, the HTC process is not limited to biomass with a low moisture content, but open to a variety of agricultural wastes (Titirici *et al.*, 2007; Libra *et al.*, 2011).

Carcinogens and their mode of dispersion into the environment

What are Carcinogens?.

A carcinogen is a specific chemical or physical agent that has the ability to cause cancer in individual or a population exposed to that agent. It could also mean any substance with the potentials to cause cancer. Exposure carcinogen may occur through food consumption, air, a product we use, occupational exposure and through chemicals in foods and drinks (Valavanidis, *et al.*, 2009). These substances work by interacting with a cell's Deoxyribonucleic Acid (DNA) and inducing genetic mutations. Interestingly, some carcinogenic agents are associated with increasing the risk of developing specific type of cancer. For instance, exposure to asbestos, particularly to workers in industrial setting has been linked to the development of a specific type of lung cancer called *mesothelioma*. Hence, once the source of carcinogen has been identified, some specific measures to reduce the incidence of specific cancers associated with carcinogens, Apart from asbestos, other well-known carcinogens are: heavy metals (arsenic, nickel, cadmium, mercury, vanadium, Radon); organics (vinyl chloride, benzidine, benzene); pharmaceuticals: (antibiotics, hormonal stimulants, analgesics, endocrine disruptors, Formaldehyde). This may act alone or in combination with another carcinogen to cause to cancer.

Health risks due to human exposure to carcinogens

Some studies have linked various diseases to human exposure to heavy metals and metalloids. The hazards include mutagenicity, carcinogenicity, and teratogenicity (Tong *et al.*, 2000, Galadima and Garba, 2012). Mutagenicity is the alteration of genetic structure, which does not always cause disease whereas carcinogenicity causes damage to specific regions of the genome and always results in disease. Carcinogenic substances get into the biological system through inhalation, ingestion and contact with skin. Teratogenicity is a specific

Heavy Metals and their Occurrence in the Environment

Heavy Metals and their Occurrence in the Environment

What are heavy Metals?

Heavy metals (HMs) are natural components of the earth crust. An element is regarded as heavy metal when its atomic weight greater than 23 and density exceeding 5 g/cm^3. Their occurrence in environmental media (soil, water and air) can be through natural or anthropogenic processes (Chen, 2012). Their mode of dispersion varies from one region to another, with spatial variations often based on their background concentrations (Khlifi and Hamza-Chaffai, 2010). The natural mobilisation processes involved are flooding, geochemical weathering and/or volcanic activity (Figure 4). Anthropogenic processes are human-induced activities which include mining and ore smelting operations, domestic and industrial solid waste disposal, urban runoff, wood processing, application of lubricants on agricultural machinery and discharges from untreated municipal sewage and industrial wastewater (Tchounwou *et al.*, 2012) (See Figure 5).

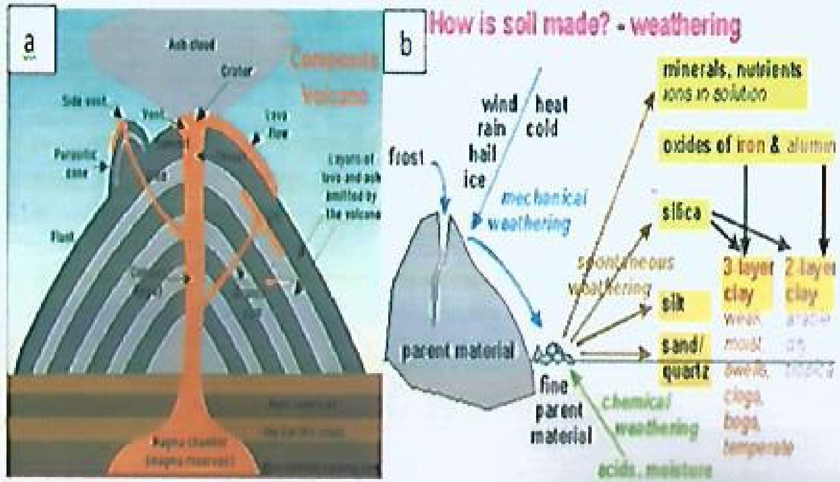

Figure 4 Schematic description of natural pollution (a) volcanic eruption and; (b) Rock weathering

Anthropogenic Sources: Mining and ore smelting operations, domestic and industrial solid waste disposal, urban runoff

Figure 5. Anthropogenic process leading to release of heavy metals into the environment

Ailments resulting from prolonged exposure to heavy metals include cancer, retarded growth, physical, muscular, and neurological degenerative processes that mimics Alzheimer's and Parkinson's diseases, with reduced or damaged mental functions (Türkdoğan *et al.*, 2003) (see plate 13-16). Other health risks include skin lesions, bone diseases and cardiovascular and renal dysfunctions (Calderon, 2000; Tong *et al.*, 2000). A well-known case study of bone disease was reported from Japan Osteomalacia otherwise known as *Itai-Itai*; a sickness characterised by softening and/or shrinking of the bones. The disease was traced to the consumption of rice produced from fields irrigated with water diverted from a river contaminated by cadmium (Järup and Alfvén, 2004; Takijima *et al.*,1973). As noted earlier, Lăcătuşu *et al.* (1996) linked reduced life expectancy of the inhabitants in Romania by 9-10 years from consumption of vegetables irrigated with wastewater containing Cd, Cu and Pb (see also Table 1). In another study, Zhuang *et al.* (2009) reported that inhabitants of about 83 villages in Dabaosham, China suffered from oesophageal and liver cancer due to consumption of rice cultivated on heavy metal polluted soils from irrigation with untreated industrial wastewater.

Problems with cadmium are widely reported because of its common use in industry (e.g. battery, galvanising and dyeing). Exposure to high levels of Cd, have been shown to increase urinary dysfunction. Damage to soft tissues such as kidneys, testicles and liver, destruction of red blood cells and high blood pressure (Nordberg, 2009; Siu *et al.*, 2009; Honda *et al.*, 2010). Since Cd is in the same periodic group to Zn, some enzymes also absorb it thereby altering enzyme function causing diseases (Kayode *et al.*, 2011). Cd can become lethal above 0.001 mg/L recommended threshold (FAO/WHO, 2006).

On the other hand, Copper (Cu) and its compounds are more common naturally and found in ores as chalcopyrite ($CuFeS_2$) and are mobilised through natural process; it is released by wash-off into the environment through storm water. Other sources of copper in the environment include smelting, metal electroplating, alloying, plumbing, production of battery, fertilizers, paints and dyes (Jiaping, 2012). Although, Cu is beneficial to humans, plants and animals; it can also be very toxic when ingested beyond its recommended threshold of 0.2 mg/L (FAO/WHO, 2006). Symptoms of Cu toxicity are severe irritation of the nose, mouth and eyes, headaches, dizziness, vomiting, diarrhoea and widespread capillary damage, brain damage, hepatic and renal damage as well as depression (FAO/WHO, 2001).

Chromium (Cr) is another element commonly found in effluent of electroplating, painting, dyeing and tanning processes. The element also exist in natural ores known as chromite and can be released into the environment (OSHA, 2007). Chromium exist in two oxidation states, the trivalent [Cr(III)] and hexavalent [Cr(VI)] chromium ions (Jiaping, 2012). Trivalent chromium is a trace nutrient or enzyme cofactor that is beneficial to humans and animals; while, hexavalent chromium is carcinogenic and mutagenic to life (Abdulsalam *et al.*, 2014). The recommended thresholds for Cr(VI) in drinking water, irrigation water and food crops are 0.05 mg/L, 0.10 mg/L and 0.10 mg/kg respectively (FAO/WHO, 2006). However, the treatment of Cr(VI) ions in irrigation water by low cost adsorbents is the subject of interest in this study.

Lead (Pb) is also toxic and found in ores as galena or leads-sulphide (PbS) which is weathered and the metal released into the environment. Pb can also be found in industrial products such as dyes, paints, solder, stained glass, lead crystal glassware, ammunition, ceramic glazes, jewelry and batteries. The presence of this metal in the environment especially through food chain can result in nerve, brain and kidney damage (Chen, 2012). The permissible Pb concentration is 5.0 mg/L in irrigation water and 0.05 mg/kg in food crops which is frequently difficult to meet in many areas of the world (FAO/WHO, 2006).

Plate 13 Effect of Chromium toxicity on a native of Hazaribagh, Bangladesh

Plate 14 Effect of arsenic toxicity on a native of Bangladesh

Plate 15 Effect of arsenic toxicity on palms due to ingestion of arsenic in Bangladesh

Plate 16 A child suffering neurological disorder due to lead poisoning in Zamfara, 2010

Human Exposure to Pharmaceutical and Personal Care Products

Pharmaceutical and personal care products (PPCPs) consist of the prescribed and nonprescribed drugs while the personal care products (PCPs) are used to improve the quality of human life. The production and consumption of PPCPs are increasing worldwide owing to the augmented population. These PPCPs consist of organic compounds such as antibiotics, hormones, analgesics, endocrine disruptors, and UV-filters used in sunscreen. It is well known that these pharmaceuticals are metabolized by the host and are subsequently excreted into the environment via urine and feces while the PCPs enter the environment through direct or indirect metabolization pathways. These PPCPs, either in parent form or as a metabolite conjugate, are then released in the surface water and groundwater, thereby polluting them. A varied concentration ranging from ng/L to µg/L of these PPCPs was found in water bodies across the world. An example of surface water pollution is that from Dana Pharmaceutical Industry in Maitumbi-Minna.

Mobilisation pathways of micro-pollutants into humans

Figure 6 shows the complete range of pathway-linkages from farm-to-fork for potential toxins. The question posed in this brief is whether carbon-enriched materials (hydrochars) derived from waste biomass can serve as adsorbents for these types of pollutants and reduce their public health impact through poor crop irrigation practice.

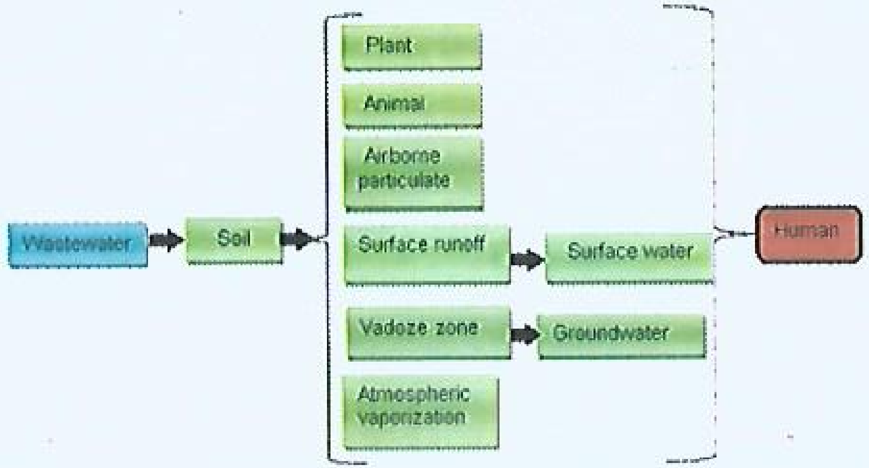

Figure 6. **Pathways through which wastewater pollutants reach humans**

Heavy metals in agricultural soils and irrigation water

Prolonged use of contaminated wastewaters (especially those from industries) on agricultural soils often increases the risks of bioaccumulation of hazardous metals (Li *et al.*, 2006). In these circumstances, the soil acts as a reservoir of metals, and plays a vital role in attenuating the influence of toxins biodiversity (Sardar *et al.*, 2013). Prolonged exposure of agricultural soils to heavy metals and/or synthetic organic compounds can lead to poor quality of crops and reduced yields

(Tchounwou *et al.*, 2012). The more soluble the metals are in soils the wider their dispersion. Solubility depends on soil type, nature of metal, speciation, water quality and pH (Covello and Merkhoher, 1993; Jan *et al.*, 2010). Studies on bioaccumulation of heavy metals in agricultural soils and their uptake by crops, in developing countries, have been extensive; reviewed examples of these include: Nigeria (Iyaka and Kakulu, 2012; Opaluwa et al., 2012), India (Krishna and Govil, 2004, 2007; Udayakumar *et al.*, 2014), China (Huamain *et al.*, 1999; Wong *et al.*, 2002), Iran (Maleki *et al.*, 2014). Therefore, strategy to reduce this human exposure to heavy metals via the food chain requires more affordable treatment techniques.

Similarly, a study conducted in Taoyuan, Taiwan revealed that over 100 ha of paddy rice fields were contaminated by Cd and Pb due to illegal discharges of untreated industrial wastewater, used for crop irrigation (Chen, 1991). Findings from that study revealed a mean concentration of Cd in soil of 378 mg/kg and Pb up to 3,150 mg/kg (Chen, 1991). These concentrations are in many times greater than the recommended thresholds of 4 mg/kg for Cd and 84 mg/kg for (Pb) in soil (FAO/WHO, 2006). These findings by Chen (1991) are consistent with similar studies carried out in Nigeria (Awode *et al.*, 2008, Idris *et al.*, 2015), India (Krishna and Govil, 2007), Bangladesh (Sarker *et al.*, 2015), Pakistan (Nazir *et al.*, 2015) and Romania (Lăcătuşu *et al.*, 1996). These studies have all confirmed that the prolonged use of industrial wastewaters on agricultural soils results in bioaccumulation of heavy metals to a level above the FAO and WHO recommended threshold limits. Table 3 presents an international reference guide, issued to provide protection against the hazards of soils and crops contamination by heavy metals. These threshold limits are subject to periodic review as new information is gathered (Giller *et al.*, 1998). Periodic monitoring, evaluation, reconditioning and remediation are also proscribed, to ensure that the concentration of combined metals, in soils, do not exceed the recommended thresholds limits (Yadav, 2010).

Plants Exposure to Heavy Metals and Phytotoxicity

Different plants have varying resistance to heavy metals toxicity; but the most rapidly growing crops such as vegetables are usually the most susceptible. The most obvious phytotoxic effect, easily observed, is chlorosis or leaf discolouration resulting from Fe-deficiency due to the chelation with or Cd-induced interaction (Das *et al.*, 1997). Chlorosis retards plant growth, and often leads to the browning of root tips and leaves, and in severe cases plant death (Guala *et al.* 2010; Yadav, 2010). In order to alienate the toxic effects of metals to crops, metal-chelating agent like ethylenediamine tetra-acetic acid (EDTA) is used to bind metal ions to soils. However, plant absorption of the chelating agent is a potential health risk especially to humans and animals that consumes such plants (Means and Alexander, 1981). Therefore, wastewaters used for crop irrigation need some forms of affordable treatment options.

Some studies have reviewed the various concentrations of heavy metals in crops grown with untreated wastewater in Nigeria and other developing countries. In Nigeria, Batagarawa (2000), analysed moss plant collected within the vicinity of textile and tannery industries in the Kano metropolis and observed that Cu concentration ranged between 1.74 - 11.54 mg/kg, Pb (10.38 - 154.64 mg/kg) and Zn (11.40 - 87.34 mg/kg). Only Cu was below the 40 mg/kg FAO/WHO recommended threshold limit. Based on the Pb concentration range stated above, the magnitude is observed to be an order greater than the 0.3 mg/kg recommended threshold limit; while, Zn was also in excess of the permissible 20 mg/kg (FAO/WHO, 2001; Islam *et al.*, 2007). The inference drawn from these analyses implies that the crops produced within this geographical location of Kano State, Nigeria are polluted and therefore unsafe for consumption. In Romania, Lăcătuşu *et al.* (1996) measured concentrations of Cd, Cu, Pb and Zn in vegetables produced using untreated industrial wastewater. Table 1 presents the concentrations of various heavy metals in both fresh and dried vegetables. The concentration of heavy metals is rather alarming; all except Cu were found to be above the FAO/WHO recommended limits. Regrettably, the Romanian societies (Baia Mare and Copsa Mica inhabitants) exposed to vegetables grown on metal contaminated soils were reported to have a decreasing life expectancy by 9-10 years and also suffered a wide range of clinical problems (Lăcătuşu *et al.*, 1996).

Table1: Mean concetration of heavy metals in edible portion of vegetables grown with untreated industrial wastewater in *Romania lacatusu at al., (1996)*

Vegetable	Cd		Cu		Pb		Zn	
	A	B	A	B	A	B	A	B
Fresh vegetables (mg/kg)								
Carrot	0.23	0.03	1.20	1.20	0.89	5.46	9.46	9.71
Potato	0.09	0.07	1.40	1.40	0.43	0.26	7.08	8.23
Tomato	0.09	0.06	1.05	0.60	0.28	0.13	5.10	2.80
Cucumber	0.05	-	0.60	-	0.35	-	5.00	-
Dry vegetables (mg/kg)								
Lettuce	6.70	4.90	13.80	11.80	68.30	119.00	301.00	121.00
Parsley	2.10	2.20	11.10	10.80	36.40	53.00	225.00	85.00
Onion	1.70	1.80	4.10	3.00	4.00	2.00	145.00	29.00
Beans	1.00	-	7.20	-	7.80	36.00	144.00	-
Cabbage	8.50	-	3.80	-	15.20	51.20	844.00	-
Dill	-	3.00	-	3.00	-	-	-	167.00
Garden Orache	-	4.70	-	7.00	-	-	-	197.00
(FAO/WHO, 2001)	**0.20**		**40.0**		**0.30**		**20.00**	

A is for crops from Copsa Mica and **B** from Baia Mare

Table 2 is a summary sheet compiled to show various concentrations of heavy metals found in crops produced using untreated or partly treated industrial wastewaters in some developing countries. A possibility of providing a remedial solution to this problem is to use some readily available cheap biomass wastes to remove micro pollutants from wastewater; hence, this forms the basis of this study.

Table 2: Concentrations of heavy metals in vegetables produce with industrial wastewater in developing countries (mg/kg)

S/N	Sample location/Country	Cd	Cr	Cu	Ni	Pb	Irrigated crops	Reference
1	Affected farming communities around Dabaoshan mine, China	0.230 - 0.320	-	0.960 - 2.180	-	0.100 - 0.180	Eggplant	Zhuang et al. (2009)
		0.050	-	0.760 - 0.790	-	0.060 - 0.070	Tomato	
		0.050 - 0.070	-	0.850 - 0.610	-	0.050 - 0.090	Pepper	
2	Irrigation sites around Huludao City industrial layout, Northeast China	0.036	-	0.970	-	0.017	Tomato	Zheng et al. (2007)
		0.055	-	1.650	-	0.008	. Pepper	
3	Crop field near an industrial area, Jiangsu, China	0.088	0.170	0.780	-	0.011	Eggplant	Cao et al. (2010)
		0.046	0.130	0.660	-	0.011	Pepper	
4	Agricultural soil irrigated with wastewater from smelting plant in Beijing, China	4.800	548.060	18.400	-	78.200	Pepper	Wang et al. (2003)
		3.590	439.450	17.210	-	51.640	Eggplant	
5	Polluted irrigation sites in Sahre Rey, Iran	0.170	-	27.530	0	1.430	Eggplant	Bigdeli and Seilsepour (2008)
		0.010	-	39.990	0.030	1.940	Tomato	
		0	-	21.800	0	1.560	Pepper	
6	Irrigation sites in Varanasi city, India	0.400	0.750	7.500	0.750	0.500	Tomato	Singh et al. (2010)
		0.500	0.500	6.500	0.500	0.400	Eggplant	
7	Sewage-irrigated soil, along the Musi River, India	-	1.100	0.700	3.100	3.000	Eggplant	Chary et al., (2008)
8	Crop field around Anpara TPP (UP), India	-	0.300	4.600	0.310	0.410	Eggplant	Tripathi et al. (2009)
9	Polluted irrigation sites around Akaki River, Ethiopia	0.115	4.910	13.210	2.210	-	Tomato	Prabu (2009)
		0.180	5.550	17.210	5.380	-	Pepper	
10	Contaminated farmland irrigated with River Challawa, Kano, Nigeria	0.850	10.400	7.560	4.660	11.330	Pepper	Awode et al. (2008)
11	Jankara irrigation sites, around Jankara industrial layout, Kano	0.130	0.180	0.450	1.680	0.260	Eggplant	Akan et al. (2008)
		0.110	0.210	0.330	2.320	0.230	Tomato	

Table 2Continued

S/N	Sample location/Country	Cd	Cr	Cu	Ni	Pb	Irrigated crops	Reference
12	Alau dam and Gongulon irrigation sites, Maiduguri, Nigeria	0.09 ± 0.01	46.88 ± 0.85	0.48 ± 0.01	11.66 ± 0.09	0.69 ± 0.03	Tomato, pepper , eggplant okra	Uwah et al. (2011)
13	Maiduguri, Nigeria	0.48 ± 0.02	52.00 ± 2.58	-	-	-	Carrot	Uwah (2009)
		0.04 ± 0.01	90.50 ± 2.22	-	-	-	Waterleaf	
14	Polluted soils around Korangi, Paskistan	0.900	0.500	29.400	6.800	11.400	Tomato	Raza (2005)
15	Irrigated fields in Harare, Zimbabwe	1.500	11.000	80.000	3.800	5.100	Tomato	Muchuweti et al. (2006)
		2.750	5.000	85.000	3.100	2.800	Pepper	
16	Soil affected by treated wastewater at Assamra irrigation site 40 km North-east of Amman, Jordan	0.02	0.071	0.173	-	0.610	Eggplant	Al-Nakshabandi et al. (1997)
17	Agricultural fields near the non-ferrous metal works, Plovdiv, Bulgaria	0.002 - 0.013	-	-	-	0.070 - 0.120	Tomato	Angelovaa et.al. (2009)
		0.004 - 0.041	-	-	-	0.110 - 0.220	Pepper	
		0.003 - 0.032	-	-	-	0.090 - 0.150	Eggplant	
18	Soils affected by highway runoff, municipal and industrial discharges, Kayseri, Turkey	0.430	-	37.380	4.600	7.200	Eggplant	Demirezen and Aksoy (2006)
		0.620	-	37.060	1.800	5.300	Pepper	
		0.410	-	32.600	3.100	9.700	Tomato	
19	Regulatory Organisations	0.020-0.200	-	5.000	0.200	0.500-1.000		*FAO/WHO standard
		0.010	0.100	0.200	0.200	5.000		**WHO/EU standard
		0.010	-	0.060	0.050	0.010		***FEPA-Nigeria standard

Relationship between dietary intake of heavy metals and life expectancy

Regrettably, despite technological advancements, life expectancy in developing countries still remains low. For instance, Central African Republic has the lowest life expectancy in the world (53 years), Nigeria (55 years), Cameroon (59 years), Ghana (60 years) etc. Ironically, in Japan life expectancy is 30 years longer. Figure 7 and Figure 8 respectively displays the average life expectancy in Nigeria compared to other countries. Figure 8 illustrate cancer to be among the leading causes of Death in the State and Nigeria at large.

In order to quantify these health risks: Models like Quantitative Microbial risk assessment (QMRA) and Quantitative Chemical Risk Assessment (QCRA) models were developed.

* The models can be used to evaluate and quantify the magnitude of disease burden for a population.

* The unit of measurement, that allows for a quantification of both death and disability due to disease, is called DALY (disability adjusted life year): being equivalent to one year of "healthy" life lost.
* Understanding the true burden that pollution can have for global health is very important for futuristic plans.

Figure 7 Life expectancy in developing and developed countries

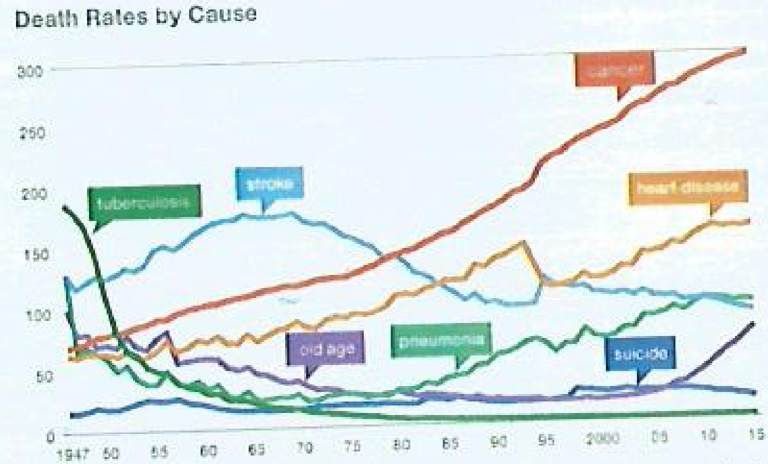

Figure 8. Displays death rate over a given time period

Table 3 is a summary of the rate at which people in the state died as a result of various circumstances. The recent are attributed to ill health. The youths who the future leaders are now ill due to various ailments that could be considered as avoidable.

Table 3 Reported Death Rate in Minna from 2006 to 2021

YEAR/ MONTH	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2021	2021
Jan	58	63	81	75	70	62	39	96	75	54	69	68	**	48	64	61
Feb	69	68	69	78	58	71	53	94	81	57	77	53	93	58	38	56
Mar	76	59	86	78	83	64	69	114	96	98	121	79	74	67	77	62
Apr	86	70	76	57	71	74	74	93	94	96	73	93	63	87	69	83
May	66	72	89	76	63	94	53	102	70	90	91	53	29	52	57	60
Jun	70	91	74	64	80	84	62	105	91	61	83	54	33	68	51	64
Jul	82	75	80	80	89	63	68	93	16	78	66	57	51	60	36	79
Aug	74	71	75	61	71	42	72	95	24	70	54	57	60	66	55	63
Sep	81	84	73	59	128	54	88	97	81	79	57	67	48	81	54	75
Oct	82	93	91	84	70	88	79	97	74	99	94	87	53	69	61	60
Nov	67	63	84	72	73	74	71	102	68	81	88	70	56	86	63	
Dec	64	89	80	108	32	94	88	78	Strike	108	64	90	56	58	46	
G/TOTAL	875	1,448	958	892	888	862	816	1,166	770	971	937	826	693	800	671	663

Concentrations of constituents in textile and tannery wastewaters

Production in both tanneries and textile industries requires a large amount of water; also discharging effluents containing both organic and inorganic pollutants. Unlike organic pollutants, which are susceptible to biodegradation, the inorganic pollutants such as heavy metals are non-biodegradable and usually have a long decay and mobile half-life especially in biological tissue . Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) are the most international standard parameters that determine the degree of organic pollution in wastewater (Siyanbola *et al.*, 2011). *Wynne et. al.* (2001) examined textile effluents and also noted a very high saline content and colouration which contributed to a rise in BOD, COD and TOC. The authors further linked the presence of metals, dyestuff and salt compounds to inhibiting microbial activity which in severe cases caused failure in the biological treatment system. Although all the three parameters; organic carbon, colour and metals are crucial in wastewater treatment; studies into removal of these biological contaminants from wastewater are limited. Hence, this study aims to investigate the potential of adsorption using biomass wastes/and their produced hydrochars to reduce the concentrations of heavy metals, COD and TOC in textile and tannery wastewater to target the FAO/WHO standards. Unfortunately, BOD requires extensive time, although useful to determine degradability ratios; but was not considered in this study. Plate 17 (a) to (f) illustrate the kind of wastewater used for crop irrigation along the fringes of river Jakara in Kano.

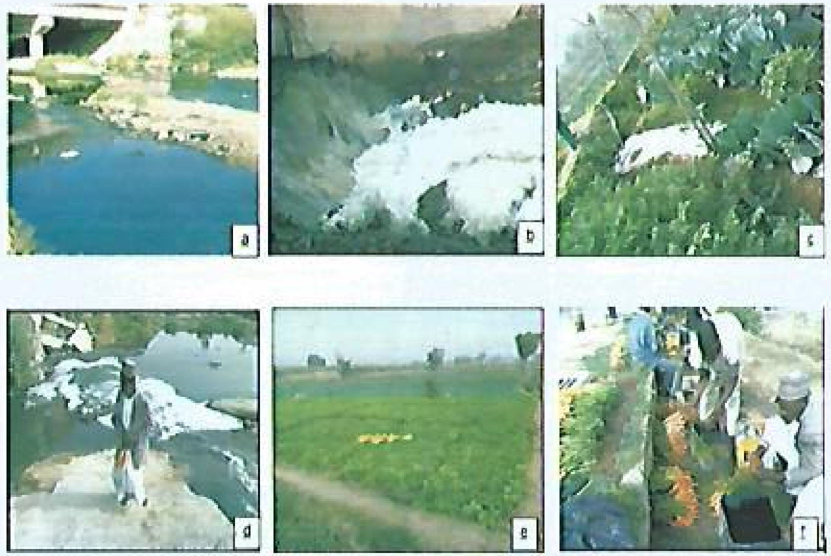

Plate17 (a) and (b) are outlets of raw effluent from textile and tannery industries; (c)and (d) contaminated Challawa River diverted into irrigation field; (e) irrigated spinach, cabbage and carrots; (f) vegetables ready for sale

Table 4 is a summary of these reviewed papers with the concentrations of metals found in textile and tannery wastewaters. The concentrations of metals in this type of wastewater follow a similar trend for both Nigeria and other developing countries. Summary of the data presented herewith suggests total concentrations of metals in textile and/or tannery wastewater from the various countries ranges between 0.1 – 5.0 mg/L and 6.0 – 10 mg/L respectively.

Review of several literatures on this subject has shown that there is no simple, affordable and sustainable water treatment facility in Nigeria designed for the removal of heavy metal ions and organics from wastewater streams used for agriculture. This research gap informed my decision for undertaken this research. Hence, the purpose of this work is to develop a simple technique using readily available biomass materials to provide some remedial solutions to surface water pollution originating from textile and tannery industries in Nigeria, which can be applied elsewhere with similar characteristics. The review generally indicates that the concentration of metals in textile and tannery wastewaters exceeds their recommended threshold limits for discharge into surface waterbodies.

Table 3 Concentration range of heavy metals in textile and tannery polluted rivers used for agriculture in some developing countries

Industry	Location/Country	(mg/L) Cr	Cu	Fe	Pb	Method of Metal Analysis	Reference
TE	Kaduna, Nigeria	0.24-0.70	2.20 - 4.50	2.72 3.70	1.12 - 1.90	AAS	Ohioma, et al.(2009)
TE	Kaduna, Nigeria	0.50 - 2.13	1.16 - 5.14	0.45 - 2.14	-	AAS	Yusuff and Sonibare(2004)
TA	Kano, Nigeria	1.02 - 1.56	0.14 - 0.34	0.16 - 1.23	0.23 - 1.92	AAS Unicom 969	Akan et al. (2007)
TE and TA	Kano, Nigeria	-	1.16 - 5.14	0.45 - 2.14	-	AAS	Akan et al. (2009)
TE and TA	Challawa/Sharada Kano Nigeria	3.33 - 5.79	0.82 - 1.51	3.53 - 8.12	0.67 - 3.10	AAS	Bernard and Ogunleye (2015)
TE and TA	Kano, Nigeria	2.54 - 9.11	0.25 - 2.00	0.22 - 3.66	1.22 - 3.22	AAS	Akan et al. (2008)
TE	Oshodi-Lagos, Nigeria	0.30 - 0.44	0.25 - 0.33		-	AAS	Ademoroti, et al. (1992)
		0.40 - 0.80	0.25 - 0.30		-		
TE	Ikeja-Lagos, Nigeria	0.09 - 0.75	0.09 - 0.18	0.960 13.21	0.47	AAS	Adebayo, et al. (2007)
TE	Ikorodu-Lagos, Nigeria	0.06 0.56	0.10 - 3.21	0.59 - 2.87	0.75	AAS	Siyanbola et al. (2011)
TE	Penshawar, Pakistan	1.05 - 1.86	0.07 - 5.14	1.08 - 3.11	-	AAS	Imtiazuddin (2012)
TE	Chatta and Chrial Canals, India	0.01 - 0.06	0.01 - 0.05	0.11 - 1.54	0.02 - 0.22	AAS	Gupta, et al. (2015)
TA	Kamatoli, Dhaka Bangladesh	0.23 0.70	0.48 - 0.86	-	0.05 0.07	AAS	Das et al. (2010)
TA	Buriganga, Dhaka, Bangladesh	0.95 - 1.87	0.06 - 0.12	-	0.01 - 0.09		
Regulatory organisations		0.10	0.20	5.00	5.00		FAO/WHO (2006)
		0.10	0.06	0.20	0.01		FEPA (1992)

TE - Textile; TA – Tannery; FEPA – Federal Environmental Protection Agency of Nigeria

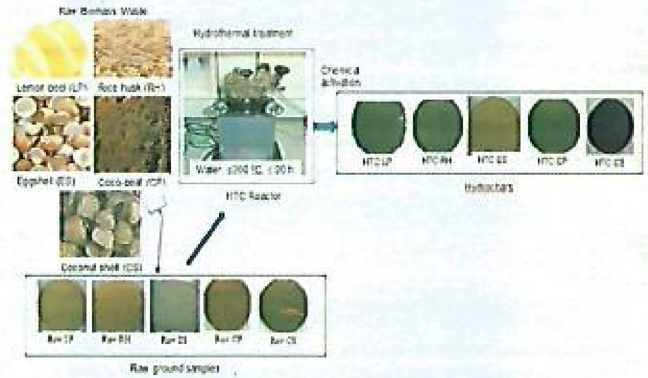

Figure 9. A graphical illustration of the hydrothermal carbonisation process

My Contributions

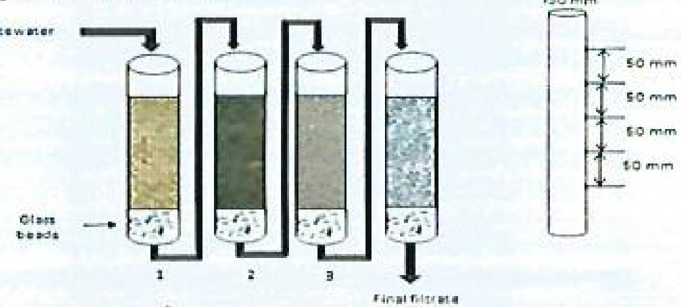

Figure 10: Schematic diagram of hydrochars arranged in columns connected in series: 1) ES, 2) RH, 3) CP and 4) CS

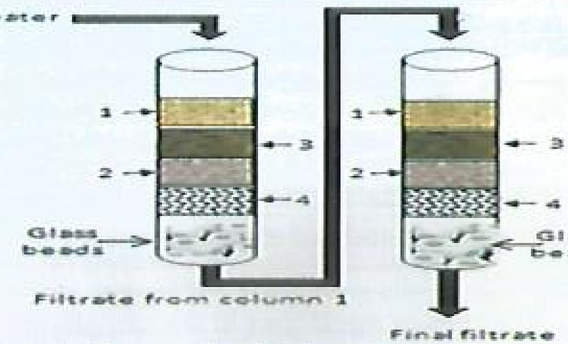

Figure 11: Schematic diagram of fixed-bed columns showing hydrochars arranged in layers

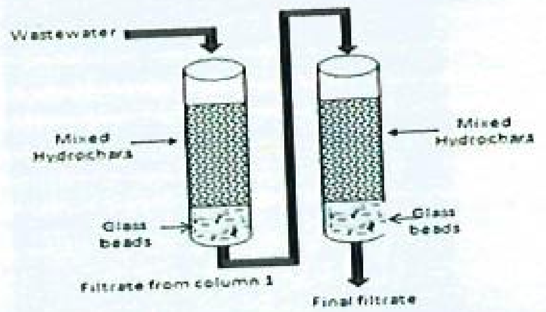

Figure 12: Schematic diagram of fixed-bed columns showing mixed hydrochar arrangement

Based on the three different column arrangements as illustrated above, the outcome of these experiments is expected to achieve the following: 1) the adsorption efficiency of each hydrochar will be determined 2) provide an opportunity to identify each hydrochar sorption affinity for contaminants in wastewater. 3) It would allow test results obtained from the series, layers and mixed arrangements to be compared in order to determine the best arrangement for removing multiple contaminants from a single sample of polluted wastewater.

Measurement of residual concentrations of heavy metals

In order to determine quantitatively the residual concentration of Cr, Cu, Fe and Pb ions in samples after adsorption, an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES-9000, Shimadzu Scientific Instruments, Japan) was used. In terms of reliability, the ICP-AES have a high part per billion (ppb) level of detection ability, thereby possessing broad concentration range of 5-6 digit analysis. The ICP-AES analysis is capable of achieving precision of < 0.1% relative standard deviation (RSD) with fast simultaneous determination of each elements of interest present, except mercury (Hg) . For precision and accuracy in the measurement of heavy metal ions in the sample filtrates, factors such as sample preparation technique, feeding of sample into the

plasma via nebuliser, calibration, detectors and peaks line selectors and internal standardisation were followed. It was ensured that the resulting linear calibration lines have R^2 values ranging between 0.996 - 1.00, which is the requirement for any sample measurement. Furthermore, a standard solution (10.0 mg/L) was sandwiched after every 10 measurements to check for accuracy.

Results and Discussion

The batch adsorption tests performed provided some basic information on equilibrium characteristics and adsorption kinetics. The batch experiments allow for the execution of numerous successive simulation runs and the data obtained can used to explore the parameter space of a model or to optimize a set of model parameters. However, in practice, its application to industries is un-economic. As such, fixed-bed column experiments have become essential for industrial design purpose. The fixed-bed column experiments provide a better understanding of the dynamics of contaminant flow through a porous media. Column study is distinct from the batch because it uses some parameters that would enable comparison with equilibrium saturation values obtained from the batch tests; with this, deviation can be determined. The results obtained from the column studies are summarised in Table 5

Table 5 Removal of metal ions through different hydrochar arrangements

Metal ion	Stand-alone Filtrate conc. (mg/L)	Layers Filtrate conc. (mg/L)	Mixed hydrochar Filtrate Conc. (mg/L)		FAO/WHO Limit (mg/L)
			Fresh hydrochar	Regenerated hydrochar	
Cr	0.285	0.210	0.184	0.180	0.10
Cu	0.280	0.657	0.136	0.205	0.20
Fe	0.513	0.708	0.224	0.220	5.0
Pb	1.150	0.626	0.540	0.434	5.0

Interestingly, this research discovered that all the known methods used single hydrochar with specific functional groups to adsorb heavy metal ions and dyes. In addition, the known methods did not consider hydrochars as sustainable adsorbents of contaminants in irrigation water. Furthermore, there is no reported single study that have considered arranging hydrochars as stand-alone, layers or even composite for the removal of heavy metals and dyes from polluted surface water used for agriculture. Hence, the innovation wherein reported will provide methods for reducing the concentration of heavy metals below the FAO/WHO recommended thresholds for irrigation water. This would safeguard human health from the dietary intake of crops irrigated with wastewater containing heavy metals and dyeing stuffs. However, one of the implications of poor agricultural practice is that the ill-irrigated crops cultivated are not only for local consumed, but also exported to international markets. This innovation herein will help in making an informed decision on to reduce the concentration

of micro-pollutants from industrial wastewater stream. A suggestion based on the findings of this research shall be sent to the policy-making bodies such as FAO/WHO at for consideration and possible adoption.

Table 5 shows the results obtained from different arrangements of hydrochars in columns. Therefore, as meant herein, the concentration of heavy metals (Cr(VI), Cu(II), Fe(II) and Pb(II)) in the final treated water falls within the FAO/WHO recommended threshold of trace metals in wastewater used for irrigation. The analysis filtrates from the series arrangement reveals Cr(VI) as 0.285 mg/L, Cu(II): 0.280 mg/L; Fe(II): 0.513 mg/L; and Pb(II): 1.150 mg/L. whereas, when the hydrochars are arranged in layers, the concentration of Cr(VI) ions was found to reduce to 0.210 mg/L. Furthermore, Cu(II) was measured as 0.0657 mg/L, Fe(II) 0.708 mg/L and Pb(II) of 0.626 mg/L in the final filtrate after the second column. In another method subject to step (a) when the hydrochars are mixed together, final filtrate from the second column containing Cr(VI) was measured as 0.182 mg/L, Cu(II) of 0.190 mg/L, Fe(II) of 0.224 mg/L and Pb(II) of 0.540 mg/L.

Of all the three column arrangements, the composite produced the best results. Filtrates analysis of the treated water obtained based on all hydrochar arrangement in columns were found to effectively decolourise the textile and tannery wastewater as well as significant reduction of the concentrations of the interacting metal ions. However, because Cr(VI) concentration is still slightly above the FAO/WHO limit of 0.10 mg/L; additional dosage of hydrochar or an extra column is required in order to further reduce the Cr(VI) concentration to a level below the recommended threshold.

On the other hand, all the different hydrochar arrangements in columns as described in Figures 10 to 12 were able decolourise the dye in the wastewater, thereby rendering the final filtrate colourless as shown in Figure 12.. Although, the stand-alone arrangement of hydrochar in columns as displayed in Figure 8(e) significantly reduced the concentration of the heavy metals as presented in Table 5, it failed to produce a desirable filtrate discolouration. This arrangement has shown that some functional groups in the individual hydrochar do not have the sufficient capacity to achieve a complete discolouration. On the other hand, Figure 11 (c) and (d) are the layer and mixed arrangements. This other sets of arrangement were able to remove colour completely. This shows a combined effect of the individual functionality groups in the hydrochars.

Considering the three different hydrochar arrangements, the layer and mixed produced the desired effect on the removal of dye colouration from the simulated textile and tannery wastewater. Therefore, a further analysis on hydrochars packed in layers have shown the remaining dye concentration in the filtrate after the first column is 0.4050 mg Pt/L and 0.3635 mg Pt/L was recorded after the second column. However, when the hydrochars were mixed, the dye concentration in the filtrate from the first column is 1.3657 mg Pt/L and 0.7373 mg Pt/L after the second column compared to 7.0 mg Pt/L Lovibond limit issued by .

The present invention found that the hydrochars arranged in layers produced better results in terms of colour removal compared to the composite. However, the generally completely remove the dye in textiles and tannery wastewater, rendering the water colourless and suitable for irrigation as shown in Figure 13(f).

The results obtained from batch and coloum experiments are summarised in Fig. 13 - 17 (for Cr), Cu, Fe and Pb adsorptions.

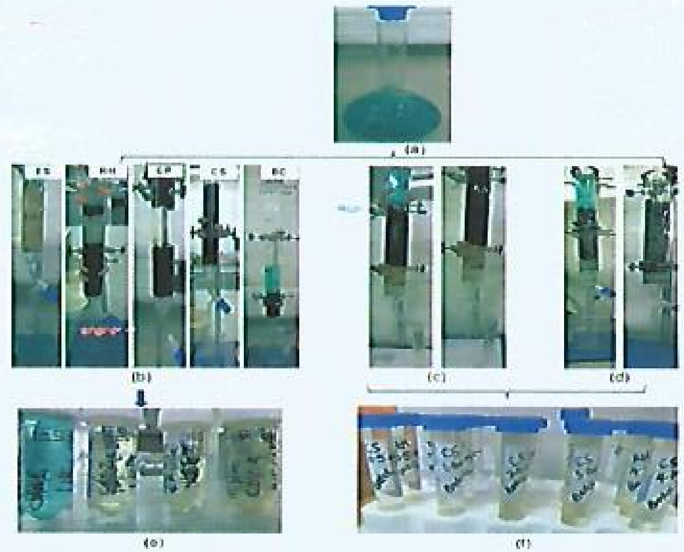

Figure* 1 *(a) Wastewater, (b) stand-alone (c) Layer (d) mixed/ composite (e) filtrates from b, (f) colourless treated water

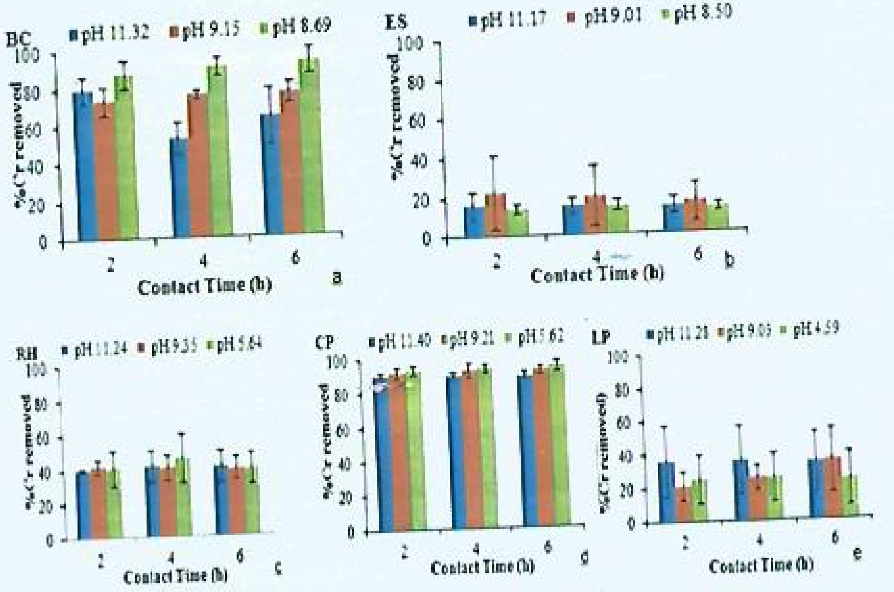

Figure 14: Shows the effect of contact time on % adsorption of Cr by (a) BC compared (b) ES (c) RH (d) CP and (e) LP

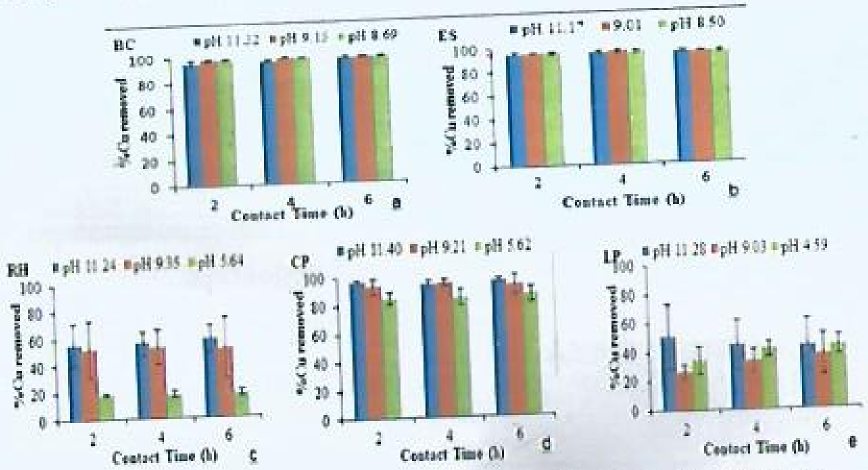

Figure 15:. shows the effect of contact time on % adsorption of Cu by (a) BC compared (b) ES (c) RH (d) CP and (e) LP

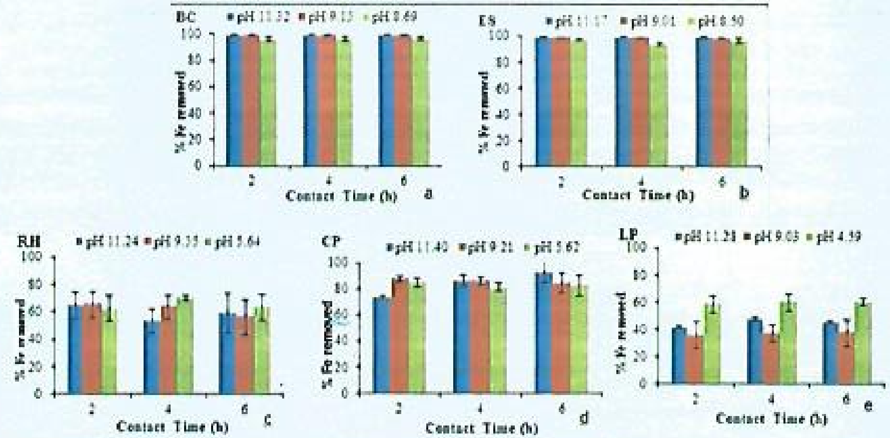

Figure 16: Shows the effect of contact time on % adsorption of Fe by (a) BC compared (b) ES (c) RH (d) CP and (e) LP

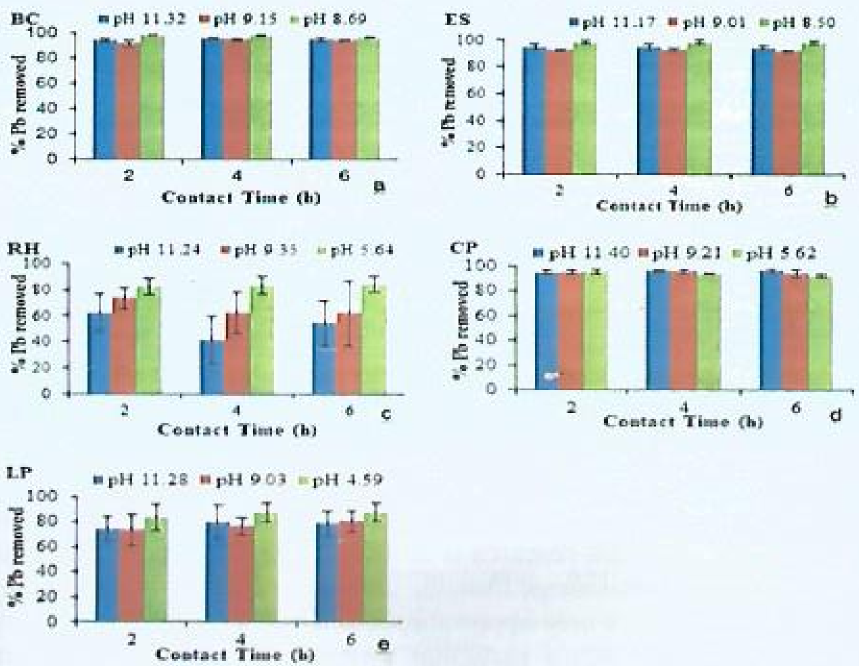

Figure 17: Shows the effect of contact time on % adsorption of Pb by (a) BC compared (b) ES (c) RH (d) CP and (e) LP

Conclusion

Identification, characterization, classification and risk assessment of carcinogenic substances by international organisations and national agencies of health and safety in the working environment, have been advanced in recent years. Information and data obtained on carcinogenic substances are collected, analysed and implementation in developed societies; regrettably, Nigeria and few other developing countries, lacks focus and peculiarity in information and data gathering and archiving; hence, making futuristic plans difficult.

Analysis of batch I sorption data as shown in Appendix A indicates that after 2 hr of contact time at pH9, the coco-peat was able to remove 92.6% of Cr(VI) ions against 87.0% using an activated bone char. This suggests that coco-peat has a higher affinity for Cr(VI) adsorption than activated bonechar. As such it provides a cost effective means of treating wastewater laden with Cr(VI) ions. Optimisation of batch I sorption data revealed 2-h (contact time) and pH8.5 as the conditions whereby adsorptions of most heavy metal ions were optimal.

Recommendations to Stakeholders

The work presented by this research has set a roadmap for the development of a simple, affordable and effective wastewater purification process. This research has successfully explored the potentials of using hydrochars produced from various biomass wastes to adsorb heavy metal ions and decolourise textile and tannery wastewater. It has also set a pace for the treatment of industrial wastewater used for crop irrigation not only in Nigeria but in many other developing countries around the world. If this technique is adopted, implemented and efficiently utilised; it can significantly reduce humans' exposure to high concentrations of heavy metals and other organics tenable through food chain. Since this research is in its early stage, the additional work needed to build upon range from the problems observed in the course of this study. There are now opportunities to fabricate a low cost cartridge of media beds to suit a particular wastewater treatment and reduce dependency on granular activated carbon (GAC) or reserve osmosis (RO).

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Note

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