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Treatment of Poultry Wastewater Using Shells from African Cherry Seeds, Egg and Crab

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Authors' contributions

This work was carried out in collaboration among all authors. Author AOA designed the study, wrote the protocol and managed the literature searches. Author FBA supervised the work and provided technical support. All authors contributed to the analyses of samples, collection of data and development of the final manuscript. All authors read and approved the final manuscript.

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ABSTRACT

This study investigated the potential of some agricultural wastes viz; African Star apple seed shell (ASS, plant source), crab shell (CS, animal source) and chicken egg shell (ES, animal source) as eco-friendly and low-cost biological materials for the removal of heavy metals from poultry wastewater. TS, TSS and TDS of the wastewater sample were assayed by filtration methods, chloride content by previously reported method and heavy metal contents (Zn, V, Cd, Fe, Ni, Cu, Co, Pb, Cr and Mn); were analyzed using Microwave Plasma Atomic Emission Spectrometer. The results of the solids and chloride contents of the poultry wastewater were TDS (3100 mg/L), TS (3700 mg/L), TSS (6000 mg/L) and chloride (4.7 g/L); all above the EPA permissible limits. Results of the FTIR analysis showed that ASS is an amide polymer while the CS and ES shells are mixtures of amide and carbonate polymers. Also, results of heavy metal analysis before and after adsorption showed that ASS caused removal of Zn, V, Fe, Cu, Co/ Pb and Mn by 48.27, 32.22, 49.64, 91.44, 100 and 82.39% respectively while Cd, Ni and Cr contents increased by 31, 61 and 48.3% respectively. CS showed removal of Fe, Ni/ Co/ Cr, Pb and Mn by 89.64, 100, 3.51 and 95.96% respectively while Zn, V, Cd and Cu contents increased by 1.7, 61.2, 76.1 and 68.1%

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respectively. Meanwhile, with ES, the contents of Zn, Fe, Ni, Cu, Cr and Mn increased by 31.56, 86.36, 100, 55.5, 45.80 and 90.33% respectively while the contents of V, Cd, Co and Pb decreased by 78.9, 86.7, 42.5 and 46.2% respectively. This study demonstrated the use of ASS, CS and ES as low- cost and eco-friendly agricultural wastes with significant potential for removal of heavy metals from wastewaters.

Keywords: Adsorption; African star seed shell; crab shell; egg shell; FTIR; low-cost adsorbents; heavy metals; wastewater treatment.

1. INTRODUCTION

Environmental pollution is currently one of the most important issues facing humanity. It has increased exponentially in the past few years and has reached alarming levels in terms of its effects on the echo system. Toxic heavy metals are considered one of the pollutants that have direct effect on man and animals. For instance, industrial and farm wastewaters containing lead, copper, cadmium and chromium etc. can contaminate groundwater resources and thus lead to a serious groundwater pollution problem [1,2].

Water is a vital natural resource used for sustenance of life, household and industrial purposes. Clean water is a necessity to keep human healthy at all times [3]. Due to the fact that it is a universal solvent, diseases are easily contacted through it. Pollution and health issues are intertwined. Water pollution occurs when substances have built up in water to a point that they cause problems for living organisms like plants, animals and humans. World health organization (WHO) found that 80% of diseases are water borne [4]. Expulsion of domestic and industrial effluent wastes, escape from water tanks, marine dumping, pesticides and fertilizers and atmospheric deposition are major causes of water pollution. Heavy metals discharged from industrial wastes can build up in lakes and river, resulting to harm to living organisms. Human health is strongly influenced by the direct damage of plants and animal nutrition which is caused by polluted water. Diseases like immune suppression, reproductive failure, acute poisoning, cholera, typhoid fever, gastroenteritis, diarrhea, vomiting, and problem and so on are results of toxins taken in through the consumption polluted plants and animals nutrients [5-7].

Today, the quality of water becomes a major problem that needs serious attention. Good quality or portable water has become an expensive item due to the problem of water pollution. According to a survey conducted by United Nation Environmental Program, 20% of world's population lacks access to safe water and 50% of the world's population lacks access to safe sanitation [8].

Adsorption is a renowned and powerful technique for treatment of contaminated wastewater due to its effectiveness, flexibility, simplicity of design, availability of materials and ease of operation for eliminating trace levels of heavy metal ions [3,9,10]. Researchers have done a lot in developing operational, low cost and easily adopted adsorption processes. Before now, different treatment technologies such as photodegradation [11], electrocoagulation [12], photochemical oxidation, membrane filtration, reverse osmosis, precipitation, coagulation & flocculation, membrane separation, and ion exchange have been used for the removal of pollutants such as organic and inorganic substances from wastewater. These conventional approaches have some setbacks when it comes to low cost, simple modification, reusability, low energy consumption, good performance, and their use for different types of pollutants [9,13-15].

Different adsorbents have being in use and in most cases, waste materials. The use of plant materials as natural coagulants to clarify turbidity of wastewaters is of common practice since ancient times. Powdered roasted grains of *Zea maize* were used by soldiers in Peru as a means of settling impurities in the 16th and 17th century. In India, ancient writings refer to the use of the seeds of the Nirmali tree (*Strychnos potatorum*) as a clarifier. The sap of tuna cactus (*Opuntia fiscus indica*) is widely used in Chile as water purifying agent [16,17].

As a result of the chemical composition of a shell, it can be used in waste water treatment either as a coagulant or adsorbent. As a coagulant, it helps to neutralize fine particles of suspended and dissolve matter in a water supply or sample to form flocs that settles and can be filtered out. The choice and dose rate of the coagulant will depend on the characteristics of the waste water to be treated.

Biological sorbents generated from food, sea and agricultural industry waste, such as waste egg shell, crab shell, snail shell etc., can be used to treat polluted waters. If low-cost biological sorbents can be used in the wastewater pre-treatment process, the overall management cost will be reduced significantly [18]. Moreover, it is a green approach as these sorbents are generally biodegradable and hence, more environmentally friendly.

Natural organic polymers have been used for more than 2000 years in India, Africa, and China as effective coagulants and coagulant aids at high water turbidities. They may be obtained from plant seeds, leaves, and roots as wells as some crustaceans shells e.g. crab, snails, periwinkles etc. [19]. These natural organic polymers are interesting because, comparative to the use of synthetic organic polymers containing acrylamide monomers, there is no human health danger and the cost of these natural coagulants would be less expensive than the conventional chemicals since it is locally available in most rural communities. Natural adsorbents have bright future and are of interest to many researchers because of their abundant source, low price, environment friendly, multifunction, and biodegradable nature in water purification.

In general, an adsorbent can be assumed as “low-cost” if it requires a little bit of processing, it is abundant in nature, or is a by-product or a waste from an industry. Natural material or certain waste from industrial or agricultural operation is one of the resources for low cost adsorbents. Generally, these materials are locally and easily available in large quantities. Therefore, they are inexpensive and are perceived to have little economic value [20].

The low cost adsorbents used for this work are those from waste materials such as African star apple seed shell (plant source), crab shells and egg shells (animal source).

African star apple (*Chrysophylum albidum*) is a plant which belongs to the family of trees known as *Sapotaceae*. Though, it is available in the Northern part of Nigeria, and it is more common in the Southern part. It is commonly known as *Agbalumo* and *Udara* in Yoruba and Igbo languages respectively. When fully ripe fruits the color is pale yellow with pink endocarp. It is available from January through April. The pink-colored pulp and the whitish cover of the brown-colored seeds of the fruit are consumed, while the empty pale yellow pericarp and the brown-colored seeds are discarded [21]. It has high micronutrient content and vitamin, low in gross energy, antinutrients, carbohydrate content, calorie, and sugar. It is a good source of antioxidant [22]. Culturally, African star apple (Agbalumo) seeds are threaded as anklets in dancing in Nigeria. Also, young people, especially boys, use the seed to play a peculiar out-door game. African star apple has low calorie and can make you full because of the high content of fiber.

The leaves, fruit and the seeds are excellent herbal medicine often used by the south western part of the country to cure malaria [23,24], skin infections [25], stomach ache, diarrhea and vaginal infections [26] also prevent heart disease [27].

Among various bio-sorbents, chitin is the second most abundant natural biopolymers after cellulose. However, more important than chitin is chitosan, which has a molecular structure similar to cellulose. Presently, chitosan is attracting an increasing amount of research interest, as it is an effective scavenger for heavy metals. Chitosan is produced by alkaline N-deacetylation of chitin, which is widely found in the exoskeleton of shellfish, crabs and other crustaceans. The growing need for new sources of low-cost adsorbent, the increased problems of waste disposal, the increasing cost of synthetic resins undoubtedly make chitosan one of the most attractive materials for wastewater treatment. Treatment of water with chitosan would be a cost effective and safer method over the traditional methods of removal of toxic metal species using chemicals [28].

Tumova [29] researched that egg shell by-product represents about 10% of the total weight (~average weight of an egg is 60 g) of egg. Eggs are used in enormous amounts by food manufacturers and restaurants and the shells are discarded as waste. It was reported that about 28% of all eggs produced are sent to commercial breaking operations for manufacturing of egg products [30]. The egg shell byproduct which results from these breaking operations represents a significant waste from the processing industries as they are traditionally useless after the production of their products, especially from bakeries and restaurants. Most of this waste is commonly disposed in landfills without any pretreatment. Occasionally, a few percentages of these byproducts are reused and applied as a fertilizer or feed additive because of their high nutrition contents such as calcium, magnesium and phosphorus [31,32]. On behalf of the bio-resource recovery and reuse, many investigations have been conducted to explore useful applications for egg shells.

Borhade and Mignardi [33,34] reported the chemical composition of the eggshell as 94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate and approximately 4% of organic matter. The egg shell by-product is, thus, inevitably composed of calcium carbonate (egg shell) and egg shell membrane (ESM). Considering the intrinsic pore structure of the eggshell, the available amounts and the bio resource recycling, the proposal of reusing eggshell and ESM as adsorbents has increased in recent years.

This study was undertaken to investigate the ability of locally available adsorbents such as African star apple seed shell, crab shell and egg shell to treat wastewater sample from the poultry farm.

2. MATERIALS AND METHODS

2.1 Sample Collection and Preparation

Wastewater samples were collected from the drainage facility of Babcock University poultry farm Ilishan-Remo Ogun State Nigeria and stored in a refrigerator until further use. African star Apples were obtained from Ilishan market in Ogun State Nigeria. The seed of the star apple was cracked and the seed was removed. The shell was washed thoroughly with copious amount of water and dried in an oven (Model NO.DHG-9101.SA GALLENKOMP) at 50-60°C for 48 hours. Similarly the eggs were cracked, the inner membrane was removed and the shell was thoroughly washed with water and dried in an oven at 50-60°C for 48 hours. Crabs were obtained from Mushin market in market in Lagos, Nigeria. The crabs were boiled and the shell obtained, washed thoroughly with water and dried at 50-60°C for 4 hours. The shells were pulverized with a laboratory blender (Lexus Model No.25520) and were sieved with a 0.2 mm wire mesh to obtain a fine powder of the shells. The Africa star apple seed shell, egg shell and crab shell powder were kept in a desiccator until further use. Aldrich chemicals were used in this study and are of analytical grade with percentage purity of 99.9%.

2.2 Physical Parameters

2.2.1 Ph

The pH of water sample was determined with pH meter model 320 serial No Mu150. The pH meter was tested with distilled water and calibrated with pH 4 and 7. The electrode of pH meter was washed with distilled water after each measurement. 25 mL of sample water and distilled water were used in the analysis. Three data points were obtained.

2.2.2 Total Suspended Solids (TSS) and Total Dissolved Solid (TDS)

The measurements of TSS and TDS in water samples were carried out according to the standard methods [35-37] which are filtration processes.

2.2.3 Chloride ion determination

The concentration of chloride ion was determined by Mohr method [38].

Table 1 shows the specification of the unfiltered (raw) poultry farm wastewater.

Table 1. Specification of the poultry farm wastewater (unfiltered)

Parameter (unit)	Average ± Std. Dev.
pH	7.4 ± 0.12
TDS (mg/L)	3100 ± 0.27
TS (mg/L)	3700 ± 0.33
TSS (mg/L)	6000 ± 0.61
Chloride ion (g/L)	4.7 ± 0.086

TDS=Total Dissolved Solid; TS = Total solid; TSS= Total Suspended Solid

2.2.4 Column adsorption process

20 g of each adsorbent were packed into three chromatographic columns and the wastewater sample (50 mL) was channeled into the column for a contact time of twenty minutes before allowing it to pass through the packed column into a conical flask. The eluent from the column was then analyzed for heavy metal content to determine the removal efficiency of the selected heavy metals by each adsorbent.

2.2.5 Digestion of water sample

This approach was partly modified from that of Zheljazkov and Nielson [39]. The conical flask was rinsed, three 100 mL of sample waters were poured into three different conical flasks. 5 mL of conc. nitric acid was poured into each conical flask containing the sample water, and placed on the hot plate and allowed to digest till 10-15 mL of sample water remained. Thereafter, the conical flask was brought out and allowed to cool down to room temperature. The remaining sample was filtered with a filter paper into a measuring tube. The filtrate was then made up to 50 mL with distilled water and used for analysis of metal content.

2.2.6 Heavy metal analysis

The instrument used was Agilent MP-AES (Microwave Plasma Atomic Emission Spectrometer). The analysis of ten heavy metals Cd, Pb, Co, Cu, Zn, Fe, Ni, V, Cr and Mn were carried out. The results were recorded automatically on a computer connected with the AES system. Three data were obtained for all the metals.

2.3 FTIR Analysis

Two 0.5 g each of the three adsorbents were dried in the oven at 60°C and kept in a desiccator to cool for analysis. One set of the adsorbent were packed into a column and sample water were run through them. After adsorption, each of the three adsorbents were dried in an oven and kept in small sample cups in a desiccator for analysis. 10 mL of the wastewater sample before and after adsorption from each adsorbent were collected into a small tightly closed glass bottles and used for FTIR analysis. Also 0.5 g of each adsorbent (before and after adsorption) was used for functional group analysis on FTIR (Instrument model: SHIMADZU FTIR-8400S).

3 RESULTS AND DISCUSSION

3.1 pH

The pH of the poultry wastewater after adsorption with African star apple seed, crab, and chicken egg shells were 7.9, 8.1 and 6.8 respectively.

3.2 Chloride Ion Concentration

Moderate level of chlorides indicated pollution of sewage, harms metallic pipes and structures and poses the problem of taste and odor and a risk to species survival, growth, and/or reproduction when above 250 mg/L concentration [40,41]. The average Chloride ion concentration in this waste water is 4.70 g/L (Table 1) which is way too high above the permissible limit; hence the wastewater needs to be treated before releasing it into the environment.

3.3 Heavy Metals

Ten heavy metals (Zn, V, Cd, Fe, Ni, Cu, Co, Pb, Cr and Mn) were tested for in the wastewater before and after treatment and were found to be in appreciable concentrations in the waste water.

The plant shell used was African star apple seed shell (ASS) and the animal shells used were from crab shell (CS) and chicken eggshell (ES). The results are shown in Tables 2 - 4. Concentrations of most of the heavy metals in the wastewater were higher than the recommended limit by [42-44].

Zinc (Zn): Zinc is one of the important trace elements that play a vital role in the physiological and metabolic process of many organisms. It is hardly toxic and thereby regarded as nontoxic [45]. The permissible limit of zinc in drinking water is <3 mg/L concentration [44]. The zinc concentration of the waste water sample before adsorption was 0.694±0.0001 mg/L concentration which is below the permissible limit. After adsorption with African star apple seed shells (ASS), the concentration reduced to 0.359, 0.706 mg/L (crab shells) and 0.475 mg/L (egg shell) respectively. This implies that the absorbents remove zinc effectively except for crab shell which may be due to the interaction between the wastewater sample and the adsorbent having high concentration of zinc in its composition.

Vanadium (V): vanadium is used for treating prediabetes and diabetes, low blood sugar, high cholesterol, heart disease, tuberculosis, syphilis etc. [46]. The permissible limit of vanadium in water is 0.01 mg/L concentration [44]. The concentration of vanadium in the waste water sample before adsorption was 0.558 mg/L which has exceeded the permissible limit. After adsorption with in ASS, CS and ES, it was found to be 0.373, 1.428 and 2.640 mg/L respectively. From this result, the only efficient adsorbent for vanadium is ASS which could be due to its higher concentration of pores for effective adsorption compared to its counterpart [47]. It was found that there is an increase in the concentration of vanadium in case of CS and ES. This could have resulted from accumulation of this element (V) in CS and ES in their structural composition.

Cadmium (Cd): cadmium is a heavy metal with a high toxicity. It accumulates in the human body and especially in the kidneys [48]. The maximum permissible limit for Cd in waster is 0.003 mg/L concentration [44]. The concentration of cadmium in the waste water sample before adsorption was 0.390 mg/L which is higher than the permissible limit. The concentration in waste water sample after adsorption with ASS, CS and ES were 3.565, 1.619 and 0.935 mg/L respectively. This result showed an increase in Cd with the three adsorbents which proved that some level of concentration of Cd is present in all the adsorbents which is in accordance to the literature especially in ES. Birds eliminate heavy metals from their body through their discharges and eggs that they lay [49,50].

Iron (Fe): Iron in drinking water is present as Fe^{2+} or Fe^{3+} in suspended form. It comes into water from natural geological sources, industrial waste, and domestic discharge. Excess amount of iron (more than 10 mg/L) causes rapid increase in pulse rate and coagulation of blood in blood vessels, hypertension and drowsiness [51]. The maximum allowed concentration of iron in water is 1.0 mg/L [44]. Before adsorption Fe concentration in the waste water was 13.825 mg/L which is above the permissible limit. The concentration of waste water after adsorption with ASS, C and ES are 6.961, 1.433 and 1.886 mg/L respectively. The adsorbents had reduced the concentration of Fe to a reasonable extent, especially with CS.

Nickel (Ni): Nickel is used for increasing iron adsorption, promote production of red blood cells, and treating weak bones (osteoporosis), improves lactation. Exposure to high level of nickel promotes various pathological effects such as skin allergies, lung fibrosis etc. [52,53]. The maximum permissible limit for Ni in water is 0.2 mg/L [44]. The concentration of Ni in waste water sample before adsorption was 0.130 mg/L which is below the permissible limit. Ni was not detected in the waste water sample after adsorption with ASS, CS and ES. This means that the adsorbents of Ni are efficient with the three adsorbents.

Copper (Cu): Copper deficiency and copper excess affect human body. When accumulated in liver and brain, it causes toxicity which is the fundamental cause of Wilson's disease [54]. The maximum permissible limit for Cu in water is 2 mg/L [44]. In the waste water sample, its concentration before adsorption was 1.110 mg/L which is below the permissible limit. Cu concentration in the waste water sample after adsorption with ASS, CS and ES are 0.095, 3.484 and 0.494 mg/L respectively. There was increase in concentration of this metal in waste water after adsorption with CS. This could be that the crabs have accumulated Cu metal in the shell.

Cobalt (Co): Cobalt is used in the body to help adsorb and process vitamin B_{12}. In addition, cobalt helps treat illnesses such as anemia and certain infectious disease [55]. The concentration of Co in the waste water sample ranged from 0.32 to 2.79 ppb. The permissible limit of Co is not specified by WHO [43] for water. The concentration of waste water sample before adsorption was 0.28 mg/L. Their concentrations in the waste water sample after adsorption with ASS, CS were ND but in ES are ND, ND and 0.487 mg/L respectively. This implies that ASS and CS were able to remove Co but ES was not able to do so instead it increases due to the interaction between the shell and the waste water.

Lead (Pb): Lead is a useful metal, but it is also toxic to humans. The maximum permissible limit of lead in water is 0.05 mg/L concentration [44]. The lead concentration of waste water sample before adsorption was 0.498 mg/L which is higher than the permissible limit. The concentration of waste water sample after adsorption with ASS was ND, CS was 0.481 mg/L and ES was 0.7755 mg/L concentration. This indicates that ASS is a good adsorbent for removal of Pb in waste water while CS removed very little of the Pb and ES did not remove anything instead interacted with the waste water to release more Pb into the wastewater.

Chromium (Cr): Chromium helps the body regulate blood sugar levels by transporting glucose to the cells. It also works with trace elements in breaking down proteins, fats and carbohydrates [56]. The maximum permissible limit for Cr in water is 0.05 mg/L [44]. The concentration of Chromium in waste water sample before adsorption was 1.557 mg/L which is way higher than the permissible limit. The Chromium concentration of waste water sample after adsorption with ASS was 3.009 mg/L, CS

Table 2. Heavy metals in the poultry wastewater before and after treatment with African Star apple seed shell

Heavy metals (mg/L)	Zn (mg/L)	V (mg/L)	Cd (mg/L)	Fe (mg/L)	Ni (mg/L)	Cu (mg/L)	Co (mg/L)	Pb (mg/L)	Cr (mg/L)	Mn (mg/L)
Waste water before adsorption	0.694±0.0001	0.55±0.002	0.390 ±0.001	13.825 ±0.0003	0.130 ±0.001	1.110 ±0.001	0.280 ±0.002	0.498 ±0.0001	1.557 ±0.0002	8.395 ±0.0002
Waste water after adsorption	0.359 ±0.0001	0.373 ±0.0001	0.565 ±0.0001	6.961 ±0.0001	0.329 ±0.0003	0.095 ±0.0002	ND	ND	3.009 ±0.0002	1.478 ±0.0002
Removal effectiveness (%)	48.27	32.22	-31.0	49.64	-61.0	91.44	100	100	-48.3	82.39
Permissible limit (EPA/WHO)	<3 mg/L	0.01 mg/L	0.003 mg/L	1.0 mg/L	0.2 mg/L	2 mg/L	-	0.05 mg/L	0.05 mg/L	< 0.01 mg/L

Data are averages of three determinations

Table 3. Heavy metals in the poultry wastewater before and after treatment with Crab Shell

Heavy metals (mg/L)	Zn (mg/L)	V (mg/L)	Cd (mg/L)	Fe (mg/L)	Ni (mg/L)	Cu (mg/L)	Co (mg/L)	Pb (mg/L)	Cr (mg/L)	Mn (mg/L)
Waste water before adsorption	0. 694 ±0.0001	0.558 ±0.0002	0.390 ±0.001	13.80 ±0.03	0.130 ±0.001	1.11 ±0.001	0.28 ±0.001	0.498 ±0.0003	1.557 ±0.0001	8.395 ±0.0001
Waste water after adsorption	0.706 ±0.0001	1.428 ±0.0001	1.619 ±0.0001	1.43 ±0.001	ND	3.484 ±0.0002	ND	0.481 ±0.0001	ND	0.339 ±0.0002
Removal Effectiveness (%)	-1.70	-61.2	-76.1	89.64	100	-68.1	100	3.51	100	95.96
Permissible limit (EPA/WHO)	<3 mg/L	0.01 mg/L	0.003 mg/L	1.0 mg/L	0.2 mg/L	2 mg/L	-	0.05 mg/L	0.05 mg/L	< 0.01 mg/L

Data are averages of three determinations

Table 4. Heavy metals in the poultry wastewater before and after treatment with egg shell

Heavy metals (mg/L)	Zn (mg/L)	V (mg/L)	Cd (mg/L)	Fe (mg/L)	Ni (mg/L)	Cu (mg/L)	Co (mg/L)	Pb (mg/L)	Cr (mg/L)	Mn (mg/L)
Waste water before adsorption	0.694 ±0.0001	0.558 ±0.0001	0.390 ±0.001	13.825 ±0.001	0.130 ±0.001	1.110 ±0.001	0.280 ±0.001	0.498 ±0.0002	1.557 ±0.0003	8.395 ±0.0002
Waste water after adsorption	0.475 ±0.0001	2.640 ±0.001	2.935 ±0.0003	1.886 ±0.0001	ND	0.494 ±0.0001	0.487 ±0.0001	0.776 ±0.0001	0.844 ±0.0001	0.812 ±0.0001
Removal Effectiveness (%)	31.56	-78.9	-86.7	86.36	100	55.50	-42.5	-46.2	45.80	90.33
Permissible limit (EPA/WHO)	<3 mg/L	0.01 mg/L	0.003 mg/L	1.0 mg/L	0.2 mg/L	2 mg/L	-	0.05 mg/L	0.05 mg/L	< 0.01 mg/L

Data are averages of three determinations was ND and ES was 0.844 mg/L concentration. ASS adsorbent did not remove Cr but release more Cr into the waste water. CS was very efficient in removing Cr while ES mildly remove Chromium.

Manganese (Mn): Manganese is essential for bone health, including bone development and maintenance [57]. The standards permissible limit in water is < 0.01 mg/L [44]. The concentration Manganese in the waste water sample before adsorption was 8.395 mg/L. The concentration of waste water sample after adsorption with ASS was 1.478 mg/L, CS was 0.339 mg/L and ES was 0.812 mg/L concentration. The three adsorbents are efficient for the removal of Mn in waste water especially CS having the lowest value of concentration.

3.4 FT-IR Data Analysis

Fig. 1 and Table 5 show the Infrared (IR) data of African Star apple shell before and after adsorption of the poultry waste water. The IR data of the shell before adsorption shows that the shell contains carbonyl, amino and aliphatic and aromatic CH absorptions stretching's. After adsorption, the shell shows new frequencies that include cumulative carbonyl and alkene, conjugated alkene, aliphatic C-H and aromatic stretching's which may arise from deposits from the wastewater. The frequencies seen in the IR spectrum strongly suggest that the shell composition is a polyamide polymer.

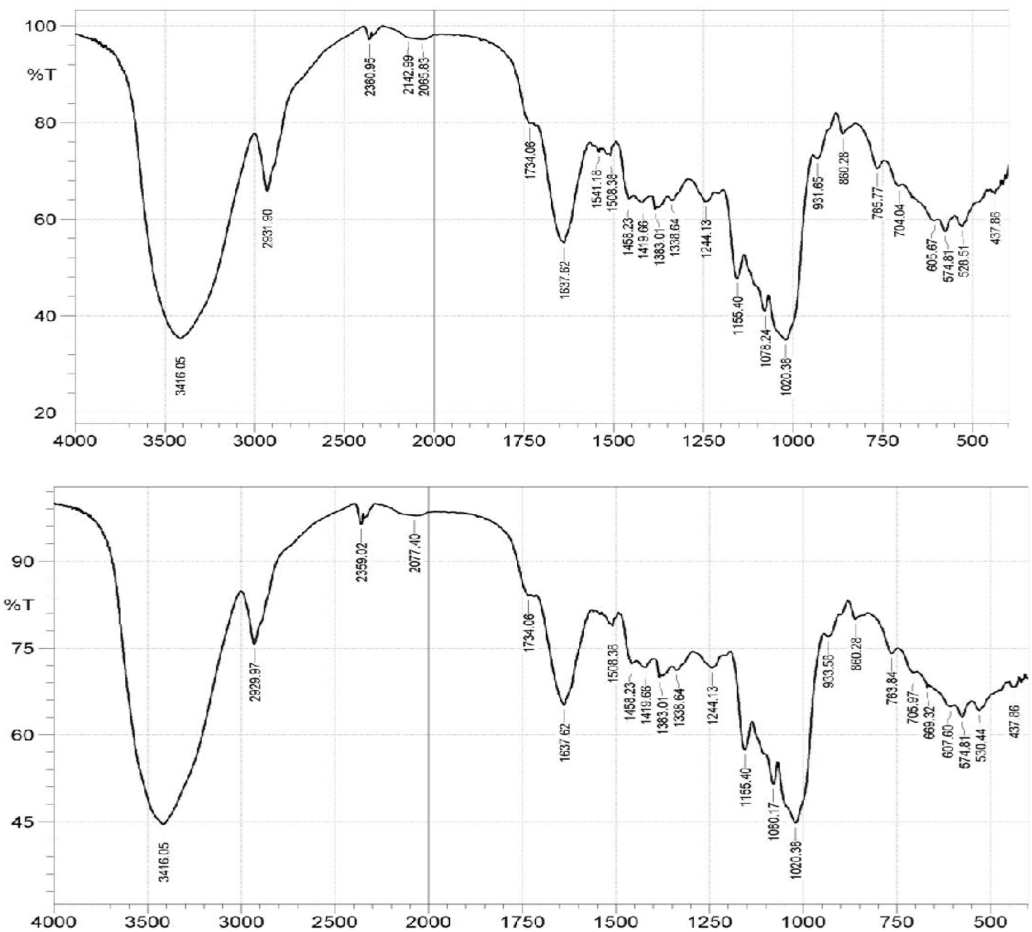
Fig. 2 and Table 6 show the IR data of the crab shell before and after adsorption treatment of the poultry wastewater. The IR data of the crab shell before adsorption shows that the shell contains amide, carbonate, cumulate and aliphatic alkene and aromatic stretching frequencies. The IR data of after adsorption shows new signals that include aliphatic alkane, cumulative carbonyl, tertiary amine and C-O of an anhydride which may be signals from deposits on the shell from the wastewater. The IR data show that the shell composition is a mixture of carbonate and amide polymer

Fig. 3 and Table 7 show the IR data of egg shell before and after adsorption treatment with the poultry wastewater. The IR data of the egg shell before adsorption shows that the shell contains amide, carbonate, cumulate carbonyl, conjugated alkene, and aromatic stretching signals. New signals that appears in the spectrum after adsorption with the waste water includes C-H stretching's and tertiary amine which might be deposits on shell after treatment with the wastewater. The IR data shows that the shell composition is a mixture of carbonate and amide polymer.

Table 5. IR absorption frequencies of African star apple seed shell before (ASS) and after (ASS-A) wastewater treatment

Item	Frequency before (cm^{-1})	Frequency after (cm^{-1})	Functional group
1	3416	3416.05	N-H stretching of a secondary amide
2	2931	2929.97	C-H alkane stretching
3	2360	2359.02	O= C=O stretching
4	2142, 2065	2077.40	Cumulative C=C
5	1734	1734.06	C=O aldehyde stretching
6	1637	1637.62	Conjugated C=C stretching
7	1541	-	C-N amide
8	1508	1508.38	N-O stretching of an amide
9	1458, 1419	1458.23, 1419.66	C=C alkene stretching
10	1383	1383.01	Nitro group aliphatic
11	1338	1338.64	bending N-H of an amide
12	1155.40	1155.40	C-=C conjugated stretching
13	1244	1244.13,	C-N aromatic stretching
14	1078	1080.17,	C-O stretching
15	1020	1020.36	C-N stretching
16	933-705	933.58, 860.28,	C-H aromatic bending

A



B

Fig. 1. FTIR spectrum African star apple seed shell (a) before (b) After adsorption

Table 6. IR absorption frequencies of crab shell before (CS) and after (CS-A) wastewater treatment

Item	Frequency before (cm^{-1})	Frequency after (cm^{-1})	Functional group
1	3444	3450.77	N-H stretching of a secondary amide
2	2962, 2895	2962.76, 2895.25	C-H alkane stretching
3	2519	2521.05	NH tertiary amine
4	-	2357.09	O= C=O stretching
5	2142	2131.41	C= C stretching
6	1799	1797.72	C=O stretching
7	1635	1637.62	C=C stretching
8	1417	1417.73	carbonate stretching
9	1384	-	N-O stretching
10	1155	1153.47	C=C conjugated stretching
	1030	1028	C-N stretching
11	952	952.87	C=C bending
12		873.78, 715.61	in and out plane mode for calcium carbonate (Carvalho et.al., 2011; Guunasekaran, et.al., 2006)
13	613-428	607.60 - 426.28	C-H aromatic bending

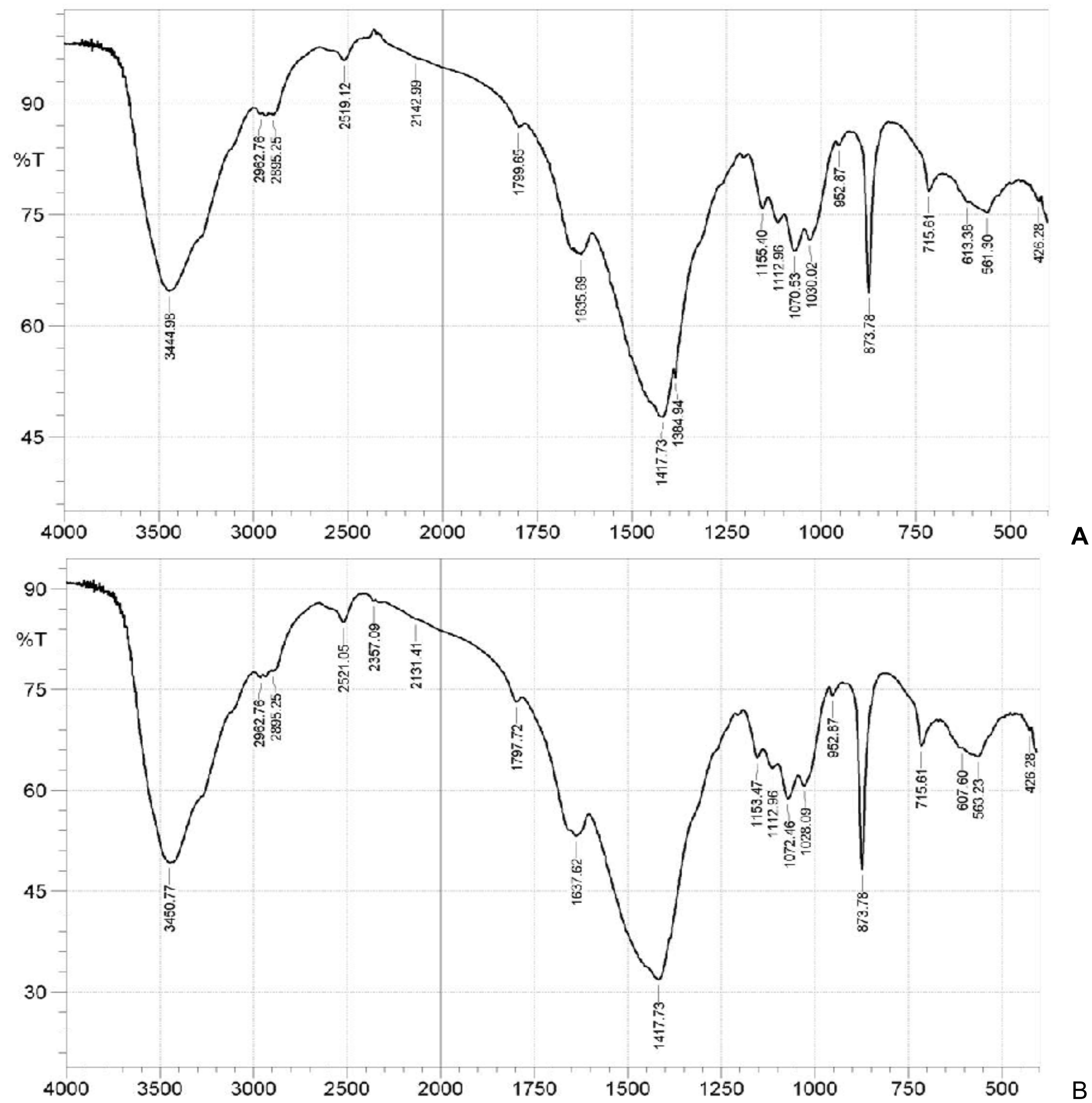


Fig. 2. FTIR spectrum crab shell (a) before (b) After adsorption

Table 7. IR Absorption frequencies of egg shell before (ES) and after (ES-A) wastewater treatment

Item	Frequency before (cm^{-1})	Frequency after (cm^{-1})	Functional group
1	3425	3450.77	N-H stretching of a secondary amide
3	2980, 2874	2978.19, 2874.03	C-H alkane stretching
5	2515	2515.26	NH tertiary amine
6	2359	2351.30	O= C=O stretching
7	1799	1799.65	C=O stretching
8	1635	1633.76	C=C stretching
9	1421	1421.58	Carbonate stretching
10	-	1384.94	C-H bending
11	1084	1084.03	C-O stretching
12	875, 711	875.71, 711.76	Carbonate bending
15	584-402	592.17	C-H aromatic stretching

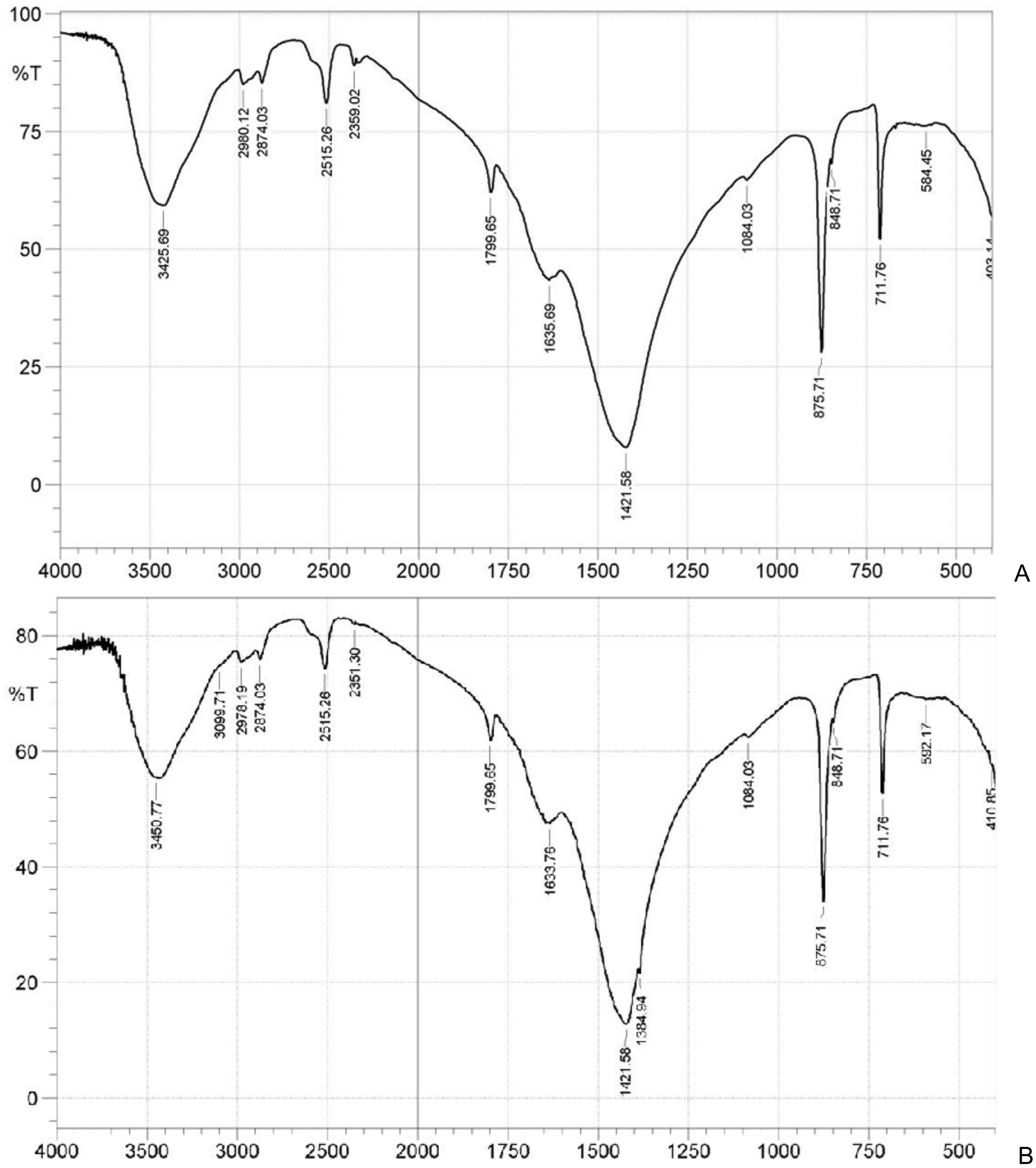


Fig. 3. FTIR spectrum egg shell (A) Before (B) After adsorption

4. CONCLUSION

From the results of this study, the three materials proved to be efficient metal adsorbents but were also metal selective. Co and Pb were completely adsorbed by ASS, Ni, Co and Cr were completely adsorbed by CS while only Ni was completely adsorbed by ES. This showed that each adsorbent was an excellent removal of the aforementioned heavy metals. It is also noteworthy that the three adsorbents caused increase in the concentration of Cd with ES causing the highest increase followed by CS and the least was caused by ASS. From the FT-IR analyses, the animal shell are made up of amide and carbonate polymers and the plant shell is made of amide polymers. The FTIR results indicated adsorbent- wastewater interaction and also showed that these adsorbent are not efficient for the removal organic components from the wastewater sample since no major significant differences were seen in the spectra between wastewater sample before and after adsorption with the adsorbents. Although there was no significant comparable advantage of plant shell over the animal shells, the three adsorbents proved to be good low-cost adsorbents for the removal of heavy metals from poultry farm wastewater.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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