

Characterization and Adsorptive Performance of Hen Feather and Eggshell as Non-Convective Low-Cost Sorbents

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Abstract

The characterization and adsorptive performance of hen feather and eggshell as non-convective low-cost sorbents have been investigated. The analysis carried out for both samples were: fourier transform infra-red analysis (FTIR), moisture content, ash content, volatile matter content, fixed carbon content, pH, iodine adsorption number (IAN), bulk density, specific surface area, and heavy metal analysis. The results obtained for p^H , Moisture content, ash content, volatile matter content, fixed carbon content, bulk density, iodine number and surface area as follows: Eggshell - 8.5, 7.68%, 2.24%, 8.50%, 81.58%, 2.51g/ml, 981.117% and 1000.3m²/g; Hen feather - 8.0, 6.70%, 1.13%, 9.0%, 83.17%, 0.79g/ml, 755.33% and 1170m²/g. Hen Feather was found to contain 3.44 ppm of iron, 0.0 ppm of mercury, 0.11 ppm of cadmium, 0.33 ppm of lead and 6.1 ppm of zinc; while Eggshell has 18.7 ppm of iron, 0.0 ppm of mercury, 0.73 ppm of cadmium, 2.81 ppm of lead and 13.6 ppm of zinc for the heavy metal analysis. The Hen Feather was found to have a better adsorptive performance as an adsorbent over Eggshell.

Keywords: Hen Feather, Eggshell, physico-chemical properties, heavy metals, adsorption.

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I. INTRODUCTION

Adsorption is a process, whereby gas, liquid or dissolved solid (called adsorbate) adheres to a solid's surface or liquid (called adsorbent), thereby, creating a molecular film. The specie that is adsorbed is termed adsorbate while the material on whose surface the adsorption happens is called the adsorbent. Many methods including coagulation, hydrogen peroxide, membrane separation and reverse osmosis are used in adsorbing dye from wastewater, but adsorption is more efficient, cost effective and effluent quality is high [1], in dye adsorption. Adsorption is applied extensively in laboratories and industries, in softening water using ion exchange, removal of dye and pigments from wastewater, removal of impurities from sugar, the activity of cleaning in soaps and detergents, removing organic materials from water and humidity control [2]. Hen Feather and Eggshell are products from the fowl. Hen Feather serves as a covering for both male and female fowl while Eggshell is got from the egg of the female fowl, hen.

Eggs are generally used as food in homes, eateries and restaurants, food processing manufacturing companies. The shells of the eggs are usually thrown away as waste [3]. Previous studies have examined the useful application of eggshell. In such works, eggshell was used as livestock feed additive, fertilizer and was efficient for dye and heavy metals removal from aqueous solution [4]; [5]; [6]; [7]. Besides the use of the regular man-made fertilizers, waste from agriculture (like the eggshells) and their by products can be employed as fertilizers [8]. Eggshell is discarded to fill lands without any pretreatment because it had no useful application. Eggshell waste is biodegradable, and so may give odour to the environment, as such, the practice of such management of waste above is not appropriate [9]; [10]. It is vital to avert this menace, so as to breathe in fresh air in our surrounding environment. There have been various researches to discover how egg shell is beneficial. These works reveal that egg shell is applied to plants as fertilizer, utilized as additives to the feed of livestock, and as adsorbent for treating polluted water. [4]; [5]; [6]; [7].

[1] successfully showed that egg shell is a good cost-effective adsorbent for removing Crystal Violet from aqueous solutions. The works of [11] also established that eggshell is a promising adsorbent for removing Reactive Yellow 205 from wastewater. Eggshell possesses a high content of calcium trioxocarbonate (IV) – CaCO₃, and it is porous in nature. From assessment, it has around 7000-17000 pores [12]; [13]. Hence, it is a

good adsorbent material. Current studies show that egg shell can efficiently remove dye and toxic substances in industrial wastewater [14]; [15].

Hen Feather (HF) is a covering for birds like hens and is plucked out, when the hen is killed (and dressed as a meal – meat, or used for some other purpose) and in most cases, thrown away. They magnify the beauty of the hen and also help to protect the hen and keep it warm. It is a waste product from the livestock poultry. They are mainly composed of keratin (about 91%), 1% lipids and 8% water. Feathers, generally, are well organized, hierarchical structures, being ranked among the most complex keratin structures in vertebrates (Bansal and Singh, 2016). Hen feathers are generated and discarded yearly into lands and rivers and creating significant waste. They are dumped without prior treatment, creating bad odour problems due to attached remnant flesh. Also, the dumped site becomes a breeding spot for flies, which can further cause other diseases that are contagious [16].

Feathers contain keratin, a self-organized protein with high mechanical firmness [17]. Functional groups like carboxyl, hydroxyl and amino-groups are also present on backbone and side chain of polypeptide molecules. Thus, giving it a very interesting physicochemical property for adsorption [18]; [1]. This study aims to characterize and determine the adsorptive performance of hen feather and egg shell as non-convectioal low-cost bio-sorbent.

II. MATERIALS AND METHODS

Collection and preparation of samples

About 500g of Eggshells were obtained from the poultry farm of Delta State University Abraka, Delta State, Nigeria and the Hen Feather was also collected from the same source.

Eggshell

The collected Eggshells were washed with detergent, and then carefully rinsed with distilled water to remove dust and dirt. They were washed with 0.5 mol/dm³ of dilute HCl, to remove other remaining forms of impurities, and washed several times with water so as to attain a neutral pH. The Eggshells were then dried under sunlight for a few days and then oven-dried at 80°C until they become crispy. The dried samples were pulverized by grinding in a mortar to increase surface area. They were then sieved with a 500 µm mesh and stored in air-tight containers for further analyses.

Hen Feather

The Hen Feather were first washed using detergent several times, and rinsed with distilled water repeatedly to remove adhered dirt, chicken dung and blood and were then air-dried for one week. They were cut into lengths of 3cm, using scissors and oven-dried for 2 hours at 40°C. They were then dried further in an oven at 80°C for 2 hours, so as to achieve a better dryness that will improve feather adsorption capacity. Then, it was blended in an electric blender and stored in air-tight container for subsequent use.

Preparation of Activated Carbon

Activated Carbons were prepared from the Hen Feathers and Eggshells using chemical activation method described by [19]. 100g of the powdered each sample were treated with 5M solution of 85% Phosphoric acid, respectively. They were then activated for 40 minutes at a carbonization temperature of 800°C using Fisher Scientific Isotemp Muffle Furnace. The activated carbons produced were washed with 0.5 M acetic acid solution, rinsed thoroughly with distilled water until the pH were within the range of 6-7. The samples were sun-dried and sieved with 500 µm mesh. Portions of the activated carbons retained on the mesh were oven dried for 1 hour and stored in air-tight containers

Characterization of raw activated carbon

Proximate Analysis

American Society for Testing and materials, ASTM defines proximate analysis as determination using prescribed methods of moisture, volatile matter, ash and fixed carbon. The proximate analysis of activated carbon samples was done following the procedure below:

Determination of Moisture Content

The Association of Official Analytical Chemists' method [20] was used in determining the moisture content. 5g of each sample were weighed in clean, dried and pre-weighed crucibles. The crucibles plus their contents were dried in the moisture extraction oven at 105°C for 1 hour using Thermo Scientific Vacuum Oven. They were then removed, cooled and reweighed. The samples were again put back into the oven and dried until constant weight was obtained. This analysis was carried out in triplicate and the average value was recorded as moisture content.

Calculation

Weight of petri dish = w_1

Weight of petri dish and sample before drying = w_2

Weight of petri dish and sample after drying = w_3

% moisture content =

$$\frac{(w_2 - w_1) - (w_3 - w_1)}{\text{weight of sample}} \times \frac{100}{1}$$

Determination of Ash Content

The [20] method was used for ash content determination. Clean dried crucibles were weighed using electronic balance and 10g of each sample was weighed into the crucibles. They were dried using moisture extraction oven until constant weights were obtained. Then, the samples were transferred into muffle furnace using pair of tongs and ashed at 550⁰C for 4 hours until a white ash was obtained. The samples were removed and cooled in a desiccator, and reweighed. The percentage ash was obtained and an average taken:

Calculation

Weight of empty platinum crucible = w_1

Weight of empty platinum crucible and sample after burning and cooling = w_2

Ash content = $w_2 - w_1$

$$\% \text{ ash} = \frac{w_2 - w_1}{\text{weight of sample}} \times \frac{100}{1}$$

Determination of Volatile Matter Content

10g of each sample (Eggshell and Hen Feather) of moisture-free activated carbon was heated in a furnace at 600⁰C for 10 minutes without air. Ratio of change in weight to original weight in percentage gives the volatile matter content and is given by:

$$\frac{w_1}{w_0} \times 100$$

Where:

W_1 = Weight loss (Original weight – final weight)

W_0 = Original weight

Determination of Fixed Carbon Content

This is the residue left after the moisture, volatile and ash is given up. It is deduced by subtracting from 100, the percentage of moisture, volatile matter and ash content. The fixed carbon content (FC) is given as:

FC = 100 – (%moisture + %volatile matter + %ash)

Determination of pH

Exactly 10ml of each sample was poured in a clean dry 25ml beaker and 13ml of hot distilled water was added and stirred slowly to cool. The PH electrode of pH-meter (Hanna Instruments HI 98107) is standardized and the electrode immersed in the sample and the pH value is read and recorded.

Determination of Iodine Adsorption Number (IAN)

The iodine number is determined according to American Society for Testing and Materials [21] method. 1g of each (Eggshell and Hen Feather) sample was weighed in a beaker and 25 ml of standard iodine solution (0.023 M) added. The mixture was swirled vigorously for 10 minutes and filtered using a funnel impregnated with clean ash less glass wool. 20 ml of filtrate was titrated with 0.1095 M thiosulphate solution to a persistent pale yellow colour. 5 ml of freshly prepared starch indicator was added and titration resumed slowly until a colorless solution appeared, the procedure was done two more times. The titrations were also repeated with 20 ml portions of standard iodine solution not treated with sample to serve as the blank titration. The iodine number (IAN) was got from:

$$\text{IAN} = \frac{12.69 \times N (V_2 - V_1)}{w} (\text{mole iodine/g sample})$$

Where:

N is Normality of thiosulphate solution.

12.69 is the amount of grams of iodine contained in the Normality of iodine (in one litre of 0.1 N iodine).

V_1 (ml) is volume of thiosulphate used for titration of sample –treated aliquot (part or fraction).

V_2 (ml) is volume of thiosulphate used for blank titration.

W is sample mass (g)

Determination of Bulk density

Bulk density was got with method of [22]. 20 g of each sample of Eggshell and Hen Feather was put in a 100 ml-graduated cylinder. All analysis were in triplicate. Bulk density was derived using:

Bulk Density (g/ml) =

$$\frac{\text{Weight of Sample}}{\text{Volume of Sample after tapping}}$$

Determination of Specific Surface Area

Activated carbon samples' specific surface areas were got using Brunauer-Emmett-Teller (BET) method. The BET instrument (Micrometrics Gemini 2375 and Gemini V) gives sample specific surface area. Samples were dried using vacuum nitrogen purging at high temperatures. P/P_0 of 0, 1, 0, 2 and 0, 3 were utilized as measurement points. Gas volumes adsorbed were measured at -196°C (nitrogen's boiling point nitrogen). They were correlated with particle total surface area including pores based on BET theory.

BET equation is:

$$\frac{1}{[V_a (\frac{P}{P_0} - 1)]} = \frac{C-1}{V_m C} \times \frac{P}{P_0} + \frac{1}{V_m C}$$

Where:

P_0 (Pascal) = adsorbate saturation pressure

P (Pascal) = adsorbate equilibrium pressure

V_a (ml) = volume of gas adsorbed.

V_m (ml) = volume of gas adsorbed in the monolayer

C = Dimensionless BET constant.

$$C = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

E_1 = first layer adsorption heat

E_L = higher layers adsorption heat

A plot of $\frac{1}{[V_a (\frac{P}{P_0} - 1)]}$ versus $\frac{P}{P_0}$ is a straight line, from which V_m and C are calculated from slope and intercept respectively. Slope is A, while the y-intercept is I.

$$V_m = \frac{1}{A+I}$$

$$C = 1 + \frac{A}{I}$$

BET sample surface area is:

$$S = \frac{V_m N s}{V X}$$

Where:

N = Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$)

S (m^2) = adsorption cross-section of specie being adsorbed

V (ml) = adsorbate molar volume

X (g) = adsorbent mass

Heavy Metal Analysis

Sample digestions and analysis were done as described [23] with slight modification. Analysis was made for five selected heavy metals (iron, mercury, cadmium, zinc and lead). All reagents that were used were of analytical grade and doubled-distilled water was also utilized for preparing them. All glass materials were

thoroughly washed, soaked overnight in dilute nitric acid, HNO₃ (10%), rinsed using distilled water and oven-dried before usage. 2 g of each sample was accurately weighed and treated with 10 ml aliquots of high purity concentrated trioxonitrate (V) solution, HNO₃. The mixture was heated on a hot plate until sample was almost dry and then cooled. This was repeated using another 10ml of concentrated HNO₃ followed by 10 ml of 2M hydrochloric acid, HCl to re-dissolve the residue. The extracts were filtered using Whatman filter paper (No. 42) into 50ml capacity bottle and brought up to volume with doubled-distilled water.

Heavy metal concentrations were determined with Atomic Absorption Spectrophotometer (Buck 210 AAS, 2005, USA).

III. RESULTS AND DISCUSSION

Characterization of Sorbents

Fourier Transform Infra-red Analysis (FTIR)

Fourier Transform Infra-Red (FTIR) identifies organic, inorganic compounds, functional group found in a material. FTIR spectroscopy was utilized in determining adsorbent carbons within 400-4000 cm⁻¹ wave number. FTIR analysis for Eggshell is depicted in Plate1 and that for Hen Feather is shown in Plate2. Different peaks were observed for both adsorbents.

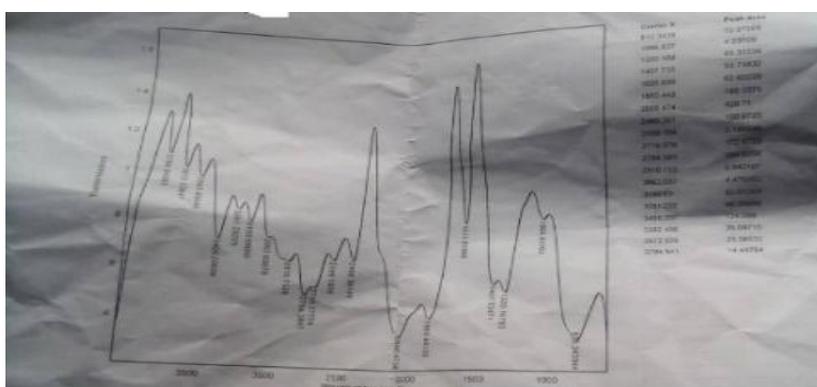


Plate1: FTIR Spectra of Eggshell

FTIR analysis results for Eggshell gave a proof of carboxyl and hydroxyl functional groups, calcium trioxocarbonate (IV) in Eggshell. FTIR spectra for Eggshell activated carbon had peaks at 1635 cm⁻¹ (N-H bonds or C-O asymmetric stretching), 2919 cm⁻¹ (C-H bonds in = C-H and = CH₂ groups), 1760 cm⁻¹ (C=O stretching vibration in carboxylic groups), 1650 cm⁻¹ (amide C=O stretching), 1431 cm⁻¹ (CaO, C=C) and 712 cm⁻¹ (2 CO₃ - of calcite). It had features traceable to amines, amides, CaCO₃, = C-H and =CH₂, present in Eggshell activated carbon after preparation at 400°C. Peaks at 3794 and 1066 cm⁻¹ of C-O asymmetric stretching and out of plane bending vibration modes. The peaks indicating amines and amides are also located at 3367 cm⁻¹ with an additional peak at 1650 cm⁻¹, showing that organic components of Eggshell activated carbon were not totally decomposed after carbonization. Identical results were recorded by [9] in the characterization and adsorption properties of eggshells and eggshell membrane.

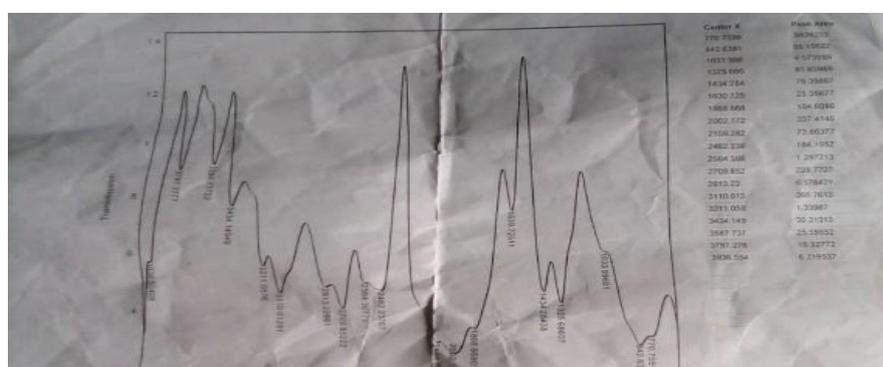


Plate 2: FTIR Spectra of Hen Feather

The FTIR spectrum of Hen Feather activated carbon shows that highest peaks were from alkane H-CH asymmetric and symmetric stretching vibrations (1630 to 2462.23 cm^{-1}). At (1635.69 cm^{-1}) is a stretching mode of carbonyls mainly ketones of C=O. Intense peaks in region (1512.24 to 1411.94 cm^{-1}) originate from the secondary amines N-H, while stretching at (1157.33 cm^{-1}) for C-O come from ethers. Peaks at (2360.95 cm^{-1}) originated from C \equiv C or C \equiv N. This is identical with the report of [24] in mechanical and morphology properties of feather fiber composite for dental post application.

Physiochemical Characterization of Eggshell and Hen Feather

The parameter and values of physiochemical characterization of Eggshell and Hen Feather are depicted in Table 1.

Table 1: Physiochemical Properties of Eggshell and Hen Feather

Property	Value	
	Eggshell	Hen Feather
Sorbent		
pH	8.5	8.0
Moisture Content (%)	7.68	6.70
Ash Content (%)	2.24	1.13
Volatile Matter Content (%)	8.50	9.00
Fixed Carbon Content (%)	81.58	83.17
Bulk Density (g/ml)	2.51	0.79
Iodine Number (%)	981.17	755.33
Surface Area (m^2/g)	1000.30	1170.0

The pH value of activated carbon is a measure of whether it is acidic or basic. A lower value of pH gives an adsorbent a better adsorptive property. In table 1, it was observed that eggshell and hen feather were both slightly basic. The bulk density of adsorbent determines the amount of adsorbent that can be contained in a filter of a given solid capacity and the quantity of the treated liquid that is retained by the filter cake. Bulk density is effected by the raw material used and the degree of activation. The bulk densities for both samples were 2.51 and 0.79 gm/l for eggshell and hen feather respectively. It was observed that both samples have high surface area and used within the range of commercial grade. Most widely used commercial activated carbon has specific surface area of the order of 800 – 1500 m^2/g . Studies have shown that increase in surface area of sorbents increases the rate of adsorption of the adsorbate due to the creation of more pores and micro-capillaries as sites for adsorption.

Table 2: Heavy Metal Content of Eggshell and Hen Feather

SAMPLE	Eggshell	Hen Feather
Iron (ppm)	18.70	3.44
Mercury (ppm)	0.00	0.00
Cadmium (ppm)	0.73	0.11
Lead (ppm)	2.81	0.33
Zinc (ppm)	13.60	6.10

The permissible limit of cadmium is 0.05 ppm [25] and both eggshell and hen feather are above the permissible limit. The concentrations of iron, mercury, lead and zinc in the samples were very high. There was no trace of mercury in the samples tested.

IV. CONCLUSION

This investigation concludes that Eggshell and Hen Feather both possess good adsorbents qualities, but Hen Feather proved to have higher adsorbent qualities than Eggshell. The reason is that keratin is highly available in Hen Feather (about 90% by weight). Functional groups like the carboxyl, hydroxyl and amine-groups are available in Hen Feather which gives it a suitable ability for adsorption purposes [18]; [1]. The concentrations of the metals were very high in both samples except mercury without any trace. This study also give a means to accomplish one of the seventeen sustainable goals of the United Nations by the year 2030 - (number 3: to enable the accessibility of Good Health and Well-being) Also, with the use of Hen Feather and Eggshell for this study, the environment is rid of excess Hen Feather and Eggshell that may have constituted bad odour and litter the environment.

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