



WATER POLLUTION AND THE QUEST FOR ITS REMEDIAATION: The Natural Resource Option

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SUMMARY OF PRESENTER'S BIODATA

Professor Muhammad Bashir Ibrahim was born on 15th May, 1968 at Indabawa Quarters, Kano. He attended Kwalli Special Primary School (1975-1981) where he obtained his Primary School Leaving Certificate. For his secondary education, he attended Government Secondary School, Karaye (1981-1982), Government Secondary School, Kafin Maiyaki (1982-1984) and Government Secondary School, Bichi (1984-1986) where he obtained his WAEC O'Level Certificate. He proceeded to the prestigious Bayero University, Kano in the 1986 and later obtained a B.Sc degree in Chemistry (with a Second Class Upper) in 1991. For his national service, he had his NYSC programme as a classroom teacher at Unwana Comprehensive Secondary School, Afikpo Local Government, Abia State (1991 – 1992).

On completion of the NYSC programme, he went back to Bayero University to enrol into an M.Sc (Physical Chemistry) programme which he completed in 1996. During his M.Sc programme, the University, recognising his academic potentials, employed him as a Graduate Assistant attached to the Department of Chemistry in 1993 from where he later rose through the ranks to become a professor of Physical Chemistry in October, 2015. As a staff of the University, he enrolled into a PhD (Physical Chemistry) programme within the University in 2004. He was supervised by Prof W. L. O. Jimoh and graduated in 2012.

Professor Muhammad Bashir IBRAHIM have taught numerous courses in physical chemistry and related areas across all levels; undergraduate, post graduate diploma, masters and doctoral till date across his 25 years of service to the University. Throughout this period he has also supervised 137 BSc undergraduate projects, 18 MSc dissertations in physical chemistry, 4 MSc dissertations in physical chemistry awaiting Viva voce, 5 MSc students undergoing research work and 5 PhD students either as the main supervisor or as a co-supervisor undergoing their research work.

Professor Muhammad Bashir Ibrahim has served as External Examiner for Masters and Doctoral degrees for many candidates at different universities within the country. He is presently serving as B.Sc External Moderator at Kano University of Science and Technology, Wudil since 2016.

Muhammad Bashir Ibrahim has also served as an External Assessor for the promotion to professorial cadre in Physical Chemistry for many Associate Professors and full-fledged Professors across various universities in the country.

Professor Muhammad Bashir IBRAHIM has discharged or is discharging various responsibilities within the University. These include: Departmental Examinations Officer (1995 – 2001), Member, Departmental Appointments and Promotions Committee (1998 - 2005), Pioneer Coordinator, B.Sc. Industrial Chemistry programme (2007 – 2012), Member, Departmental DTLC Committee (2011 – 2014), Member, Departmental Purchasing Committee (2012 – 2014), Member, Departmental Dress Code Committee (2012 – 2014), Head, Physical Chemistry Unit (2013 - 2015), Chairman, Departmental Seminar Committee (2013 – Date), Faculty of Science, Common Room Officer (2004 – 2006), Member, Faculty of Science Research Grant Committee (2008 – 2012), Member, Faculty Appointments and Promotions Committee (2012 – 2014; 2016 - 2018), Member, Faculty Seminar Committee (2012 – 2014), Assistant Faculty PG Coordinator (2014), Chairman, Faculty Webpage Development and Maintenance Committee (2017), Member, University Honorary Degree Committee (2017), Deputy Dean (GSP) School of General and Entrepreneurship Studies (2016 – Date).

As a community service, he has also served or is serving the following capacities: Resource Person, National Teachers' Institute Workshop for the Re-training of Primary School Teachers (April, 2006), Supervisor, JAMB Examination, G.G.S.S. Sha'iskawa, Kazaure Examination Centre (March, 2008), and FCE(TECH) Bichi (April, 2009), Member, Accreditation Sub-committee on Departmental Curriculum, Dept. of Chemistry, Umaru Musa Yar'Adua University, Katsina (April, 2012), Member, Electoral Committee for PTA of Caliphate Group of Schools (2013), Chairman, Accreditation Committee, Northwest University, Kano (2014), Member, Departmental Course Code Harmonisation Committee, NWU (2014), Chairman, Faculty Course Code Harmonisation Committee, NWU (2014), Member, University Ethics Committee, Northwest University, Kano (2014).

His experience and commitment to academic publications made him to serve many journals both within and outside the country in different capacities. The journals include: Bayero Journal of Pure and Applied Sciences (BAJOPAS), Nigerian Journal of Basic and Applied Sciences (NJBAS) from Usmanu Danfodiyo University Sokoto, International Journal of Biological and Chemical Sciences (IJBCS) from University of Dschang, Cameroon, ChemSearch Journal, BUK, Journal of Natural Sciences, Engineering and Technology (JNSET), Federal University of Agriculture, Abeokuta,

International Journal of Physical Sciences from Academic Journals, and Advances in Research (SCIENCEDOMAIN International).

Professor Muhammad Bashir Ibrahim has attended and presented papers in over 20 local and international conferences from 1993 to date. This experience has made him to serve in different capacities in various conference committees both within and outside Nigeria which include: Chairman, Faculty of Science 1st Annual International Conference Committee, Northwest University, Kano (2014 – 2015); Session Chair, 3rd Biological, Chemical and Environmental Conference (BCES), Kuala Lumpur, Malaysia (2015); Chairman, Faculty of Science 2nd Annual International Conference Committee, Northwest University, Kano (2016); Chairman, Faculty of Science International Conference Committee, Bayero University, Kano (BUKISC 2017); Chairman, Faculty of Science 3rd Annual International Conference Committee, Yusuf Maitama Sule University, Kano (YUMSCI 2017) and Chairman, Faculty of Science International Conference Committee, Bayero University, Kano (BUKISC 2018).

He is a member of professional bodies like the Chemical Society of Nigeria (CSN) and Institute of Chartered Chemist of Nigeria (ICCON).

Professor Muhammad Bashir Ibrahim has a total of fifty four (54) articles published from 1998 to 2017 in twenty eight (28) peer reviewed local/international journals and has over 200 citations (Google Scholar Citations). His book titled: *Selected Experiments in Physical Chemistry* was published in 2007.

His research interest comes from good theoretical and practical background knowledge of: Atomic Adsorption Spectrophotometry, Chromatographic Techniques, Electrochemical Techniques, UV-Visible Spectrophotometry, Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy and Energy Dispersive X – Ray Spectroscopy as applied to the thermodynamics and kinetics of bioremediation studies using different types of natural adsorbents and synthetic nanoparticles for the remediation of different environmental pollutants with efforts geared towards reclamation of waste water generated by various industries. Also, he has given distinct attention to researches in the area of corrosion control using various plant materials (extracts and latexes). Furthermore, biophysical researches of bio-macromolecules have also received special consideration.

Prof. Muhammad Bashir IBRAHIM loves reading, travelling and photographing. He is happily married and blessed with seven children.

WATER POLLUTION AND THE QUEST FOR ITS REMEDICATION: The Natural Resource Option

Introduction

What is Water?

Water is a transparent, tasteless, odourless, and nearly colourless chemical substance, which is the main constituent of Earth's streams, lakes, and oceans, and the fluids of most living organisms (Plate 1). It is vital for all known forms of life, even though it provides no calories or organic nutrients (Wikipedia, 2018). It is a liquid without colour, smell or taste that falls as rain, is in lakes, rivers and seas, and is used for drinking (Plate 1), washing etc. (*Oxford Advanced Learners' Dictionary*, 2010). The *Oxford Dictionary of Chemistry* also defined water as a colourless liquid, H_2O ; r.d.1.000 (4°C); m.p. 0.000°C ; b.p. 100.000°C . In the gas phase, water consists of single H_2O molecules in which the H–O–H angle is 104.5° (Plate 2) (*Oxford Dictionary of Chemistry*, 2008).



Plate 1: *Liquid Water*

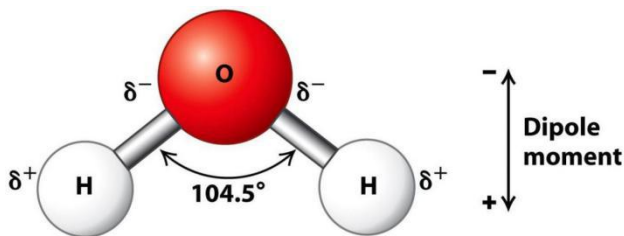


Plate 2: *Structure of Water Molecule*

Other properties that shows the unique nature of water are as shown in Table 1:

Table 1: Properties of Water

Property	Value
Molar mass	18.01528 g mol ⁻¹
Boiling Point	100°C
Melting(Freezing) Point	0°C
Density	999 kg m ⁻³
Viscosity	8.9 x 10 ⁻⁴ kgm ⁻¹ s ⁻¹
Conductivity	76 mS m ⁻¹
Surface Tension	72.0 (at 25°C), 58.0 mN m ⁻¹ (at 100°C)

On the average, a human being consumes about 2 litres of water every day and it accounts for about 70% of the weight of a human body, while about 80% of the Earth's surface is covered by water. Out of the estimated 1,011 million km³ of the total water present on Earth, only 33,400m³ of it is available for drinking, agriculture, domestic and industrial consumption (Dara, 2006). The rest is locked up in oceans as salt water, polar ice-caps and glaciers and ground water. Owing to increasing industrialisation on the one hand and exploding population on the other, the demands of water supply have been increasing tremendously.

Pollutants and Pollution

A pollutant is any substance, produced and released into the environment as a result of human activities, which at an unacceptable level, has damaging effects on the environment of living organisms. Pollutants may be toxic substances (e.g. pesticides) or natural constituents of the atmosphere (e.g. carbon dioxide) that are present in excessive amounts.

Classes of Pollutants:

- **Biodegradable** (e.g. sewage), i.e. can be rendered harmless by natural processes and need therefore cause no permanent harm if adequately dispersed or treated.
- **Non - biodegradable** (e.g. heavy metals (such as lead) in industrial effluents and other chlorinated hydrocarbons), which eventually accumulate in the environment and may be concentrated in food chains.
- **Other forms of pollution** in the environment include **noise** (e.g. from jet aircraft, traffic, and industrial processes) and **thermal** pollution (e.g. the

release of excessive waste heat commonly from heat-exchangers into lakes or rivers causing harm to wildlife).

Pollution is an undesirable change in the physical, chemical, or biological characteristics of the natural environment, brought about by man's activities. It may be harmful to human or non-human life. Pollution may affect the soil, rivers, seas, or the atmosphere.

Pollution can result from the disposal of radioactive waste; acid rain; photochemical smog; human waste; carbon dioxide and other greenhouse gases in the atmosphere; damage to the ozone layer by nitrogen oxides, chlorofluorocarbons (CFCs), and halons; and pollution of inland waters by agricultural fertilisers, sewage and industrial effluents.

Attempts to prevent pollution include strict regulations concerning factory emissions, the use of smokeless fuels, the banning of certain pesticides, the increasing use of lead-free petrol, and restrictions on the use of chlorofluorocarbons and persistent organic pollutants (UNTC, 2001), and the introduction, in some countries, of catalytic converters to cut pollutants in car exhausts (*Oxford Dictionary of Chemistry*, 2008).

Water Pollution

Water pollution is the contamination of water bodies, usually as a result of human activities (making it unfit for human use and aquatic lives) with cumulative effect over time. Water bodies include for example lakes, rivers, oceans, aquifers and groundwater. Water pollution results when contaminants are introduced into the natural environment. For example, releasing inadequately treated wastewater into natural water bodies can lead to degradation of aquatic ecosystems (Plate 3). In turn, this can lead to public health problems for people living downstream. Water pollution is measured by physical, chemical and biological analyses of water samples.



Plate 3: *A Polluted River*

Sources and Types of Water Pollution

Sources of water pollution: are point sources and non-point sources. Point sources have one identifiable cause of the pollution, such as the disposal of faecal sludge into water bodies (Plate 4), a storm drain, wastewater treatment plant or stream. Non-point sources are more diffuse having a large number of possible causes, such as agricultural run-offs. All plants and organisms living in or being exposed to polluted water bodies can be impacted. The effects can damage individual species and impact the natural biological communities they are part of.

The causes of water pollution include a wide range of chemicals and pathogens as well as physical parameters. Water pollutants can be divided in some general classifications into organic, inorganic, suspended solids, sediments, radioactive materials and, lastly, heat or elevated temperatures which lead to thermal pollution (Dara, 2006; Goel, 2006). A common cause of thermal pollution of waters is the use of water as a coolant by power plants and industrial manufacturers. Elevated water temperatures decrease oxygen levels, which can kill fish and alter food chain composition, reduce species biodiversity, and foster invasion by new thermophilic species (Laws, 2018).



Plate 4: *Disposal of Faecal Sludge into Water Body*

A United Nations report stated that: "There is enough water for everyone", but that access to it is hampered by **mismanagement** and **corruption** (UNESCO, 2006). In addition, global initiatives to improve the efficiency of aid delivery, such as the Paris Declaration on Aid Effectiveness, have not been taken up by water sector donors as effectively as they have in education and health, potentially leaving multiple donors working on overlapping projects and recipient governments without empowerment to act (Welle *et al.*, 2008). Observers have estimated that by 2025 more than half of the world population will be facing water-based vulnerability (Kulshreshtha, 1998).

MDG (2008) reported that access to safe drinking water has improved over the last decades in almost every part of the world, but approximately one billion people still lack access to safe water and over 2.5 billion lack access to adequate sanitation. It was reported that by 2030, in some developing regions of the world, water demand will exceed supply by 50% (2030 WRG, 2009).

Treatment of Polluted Waters

According to the U.N. (2018), control of water pollution requires appropriate infrastructure and management plans. The infrastructure may include wastewater, sewage and industrial wastewater treatment plants, and these would be required to protect water bodies from untreated wastewater. Agricultural wastewater treatment from farms, and erosion control from construction sites can also help prevent water

pollution. Nature-based solutions are another approach to prevent water pollution, such as effective control of urban run-offs targeting reducing speed and quantity of flow.

Municipal and Industrial Wastewater are typically treated at wastewater treatment plants. Mitigation of polluted surface run-off is addressed through a variety of prevention and treatment techniques.

Wastewater Treatment Techniques

Several methods such as *solvent extraction*, *reverse osmosis*, *precipitation*, *ion exchange*, etc. have been employed for the treatment of wastewaters (Bansal, *et al.*, 2009 and Gupta, *et al.*, 2003). However, these techniques have certain disadvantages, such as high capital and operational costs or treatment and disposal of the residual metal sludge. Therefore, the aforementioned methods are not economically feasible for small and medium scale industries. Hence, adsorption chromatography, an efficient and competitively economical means for the treatment of wastewaters, which if compared with other methods appears to be an attractive process due to its efficiency and ease with which it can be applied in the treatment of wastewater (Volesky and Holan, 1995).

Adsorption Chromatography

In 1906, Tswett devised a method for the separation of chlorophylls and other plant pigments using a tube (column) packed with dry, solid adsorbent with extraction performed by eluting the tube with selected organic solvents. He termed this technique as **Chromatography**. However, Martins, (1950) redefined **chromatography** as “the uniform percolation of a fluid through a column of finely divided substance, which selectively retards, by whatever means, certain components of the fluid”. Chromatography has been defined as a process in which a chemical mixture carried by a liquid or gas is separated into components as a result of differential distribution of the solutes as they flow around or over a stationary liquid or solid phase (Merriam-Webster, 2018).

Types of Adsorption Techniques

1. Dynamic (Column) Adsorption

In dynamic (column) adsorption chromatography (Plate 5), solution continuously enters and leaves the column so that the adsorbent in the column meets a fresh solution each time. Depending on the fluid velocity and bed height, the contact time for adsorption will vary. However, complete equilibrium is never established at any stage between the solute in solution and the amount adsorbed. There is, at the most,

an approach to equilibrium, which is termed as dynamic equilibrium, as it has to be continuously re-established each time the element meets fresh adsorbent (Kapoor and Rajagopal, 2001).

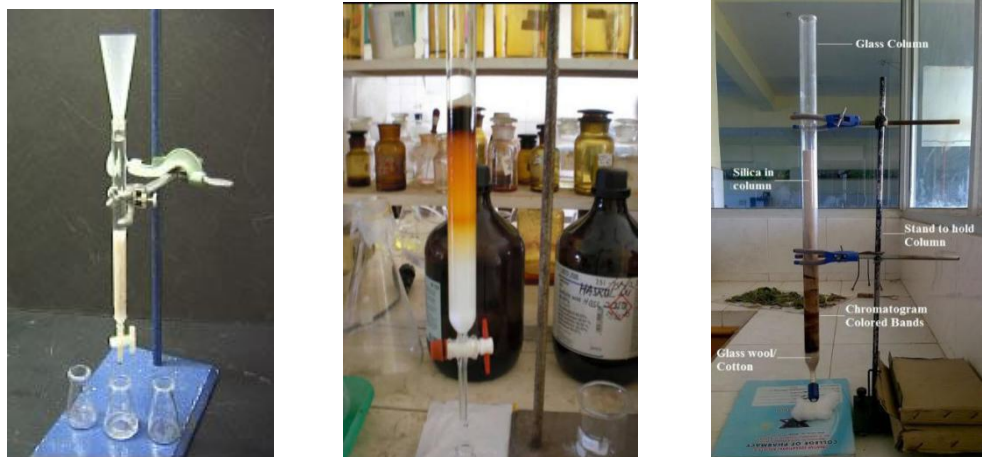


Plate 5: Column Chromatographic Set - up

Parameters to be Monitored

The operational parameters monitored in a dynamic adsorption studies include those that are related to the column, the adsorbent and the mechanism of the pollutant removal (Ibrahim and Mohammed, 2017; Yahuza *et al.*, 2017).

➤ **Exchange Capacity (EC)**

This is measured by determining the number of mill equivalents of sodium ion or chloride ion adsorbed by 1.0 g of the adsorbent such that;

$$\text{Exchange Capacity} = \frac{M_{\text{NaOH}} \times V_{\text{NaOH}}}{\text{Weight of Adsorbent (g)}} \quad (1)$$

Where M_{NaOH} = Molarity of NaOH
 V_{NaOH} = Volume of NaOH (cm³)

➤ **Active Site Density (ASD)**

This is the “product of exchange capacity of the adsorbent and the number of ions in one milliequivalent of the test solution (= 10⁻³ N_A), i.e.

$$ASD = EC \times \frac{6.022 \times 10^{23}}{1 \times 10^3} \quad (2)$$

➤ **Retention Time (t_R)**

This is the time required to elute a sample of adsorbate from the stationary phase; i.e. the time required for a mobile phase to sweep – off a component of the adsorbate from the adsorbent.

➤ **Retention Volume (V_R)**

This represents the volume of mobile phase required to elute an adsorbate component off the stationary phase.

$$V_R = F_0 t_R \quad (3)$$

Where F_0 is the flow rate of the mobile phase.

➤ **Void (Dead) Volume (V_m)**

Defined according to equation (4) as the product of the time (t_a) for average mobile phase molecule to flow from one end of the stationary phase to the other with the corresponding flow rate of the mobile phase.

$$V_m = F_0 t_a \quad (4)$$

➤ **Bulk Density**

Bulk density (g cm^{-3}) is an important characteristic of adsorbents as it is a measure of the amount of adsorbate the adsorbent can hold per unit volume (equation 5). It gives an idea of the volume activity of the adsorbents, and it depends on the adsorbent material.

$$\text{Bulk Density} = \frac{W_{\text{adsorbent}}}{V_{\text{adsorbent}}} \quad (5)$$

➤ **Breakthrough Capacity**

This is a plot of the ratio of concentration of the adsorbate in the eluate (C) to that of the adsorbate molecule initially presented to the stationary phase (C_0) against time of elution or concentration of the eluate (Fig. 1). It is useful in the design of adsorption columns for industrial purposes.

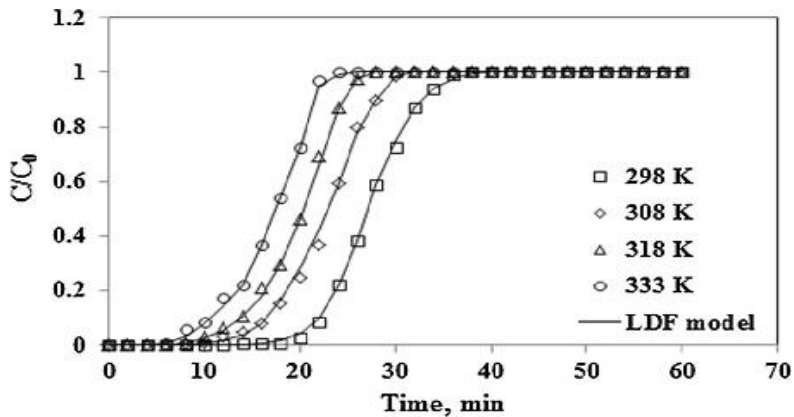


Fig. 1: *Breakthrough Curves*

2. Batch (Static) Adsorption

In static equilibrium adsorption, the same solution of adsorbate remains in constant agitation (Plate 6) with a given quantity of adsorbent. As the amount of solute adsorbed on the adsorbent increases and the solute concentration in solution reduces, the driving force for adsorption decreases with time accompanied by a reduction in the adsorption capacity. The adsorption process continues, however, till an equilibrium between the solute concentration in solution and the solute adsorbed per unit weight of adsorbent, is reached. The equilibrium established is static in nature, as it does not change further with time. The behaviour is characteristic of the nature of the adsorbent, the adsorbate, the solvent and the temperature (Kapoor and Rajagopal, 2001).



Plate 6: *Orbital Shakers*

Parameters Optimised

- Equilibrium Contact Time
- Agitation Speed
- Adsorbent Dose
- Adsorbent Particle Size
- Adsorbate Concentration
- Adsorbate pH
- Adsorption Temperature
- Adsorbent Activation, and
- Adsorbent Surface Modification

Analytical Techniques and Equipments Employed

Some analytical techniques employed to monitor the changes in both concentration of the pollutant and physical or chemical changes taking place on the adsorbent surface during the treatment process are as given in Plates 7 – 11.

1. Spectroscopic Techniques

- Atomic Absorption Spectrophotometry (AAS)



Plate 7: *Buck-Scientific 205 Atomic Absorption Spectrophotometre*

- UV – Visible Spectrophotometry



Plate 8: *Agilent Cary 60 UV Visible Spectrophotometre*

- Fourier Transform Infrared Spectroscopy (FTIR)



Plate 9: *Agilent Cary 630 FT-IR*

2. Scanning Electron Microscopy (SEM)



Plate 10: *Scanning Electron Microscope*

3. X – Ray Diffraction Analysis (XRD)

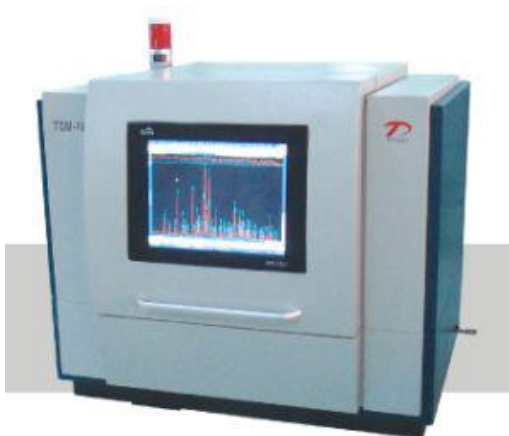


Plate 11: *Desktop X-Ray Diffractometre*

Wastewater Treatment Using Natural Materials

My experience in wastewater treatment began in the 1994 through my M.Sc. research entitled: “Investigation of Certain Local Materials as Matrices for Separation and Textile Wastewater Treatment” under the supervision of Late Prof. E. J. Ekanem. In this work, Dynamic Adsorption Technique was employed using three natural materials namely: maize cob peat, hardwood charcoal, cow dung and synthetic ion-exchange resins for the treatment of textile wastewater samples from Gaskiya Textile Limited, Bompai, Kano; Zaria Industries Limited and United Nigeria Textile Limited (UNTL), Kakuri, Kaduna.

The matrices were applied singly and combined in various mixtures to select an optimum treatment mixture for the effluents. The decolouration efficiency was found to depend on the format in which the component of the mixture were presented in addition to the source of the carbon and the particle size of all the components (Isuaikoh *et al.*, 2008; Bakalyil *et al.*, 2009; Ibrahim and Ekanem, 2009). In another work, the separation of anions ($\text{CO}_3^{2-}/\text{HCO}_3^-$, Cl^- and SO_4^{2-}) as sodium or potassium salts was achieved using synthetic and natural exchangers with extent of separation increasing from natural to the synthetic exchangers (Ibrahim, 2004).

During my PhD research, with the help of available current literature from colleagues, I engaged in a research entitled: “Adsorption and Thermodynamic Properties of Some Natural Adsorbents in Relation to Wastewater Treatment” using Batch Adsorption Technique.

Three adsorbents namely; maize cob, hardwood sawdust and coal were explored for the removal of heavy metals (*Ni, Fe, Cr* and *Cd*) from a single component modelled effluent and from five tanneries situated at Sharada and Challawa Industrial areas of Kano (Table 2).

Table 2: *Physical Characterisation of the Tannery Effluents*

Sample	pH	Cond. (mS)	Density(ρ) (g/cm ³)	Viscosity (η) (x10 ⁻⁴ kgm ⁻¹ s ⁻¹)	Cr(VI)Conc (x 10 ² mg/L)
Gods-Little Tannery	8.98	24.0	0.9961	11.102	2.1667
InterTan	10.01	23.8	0.9873	9.641	2.3333
Ayafa	9.59	24.5	0.9882	8.733	2.5000
Unique	8.83	38.4	0.9902	9.802	2.1667
Fata	8.96	36.2	0.9902	8.775	1.6667

Extent of Adsorption

The extent of adsorption of the various adsorbents was judged based on equations 6 & 7;

1. % Adsorptions

$$\% \text{ Adsorption} = \frac{C_o - C_e}{C_o} \times 100 \quad (6)$$

Where C_o and C_e are the concentrations (mg/L) of adsorbate initially and at equilibrium time.

2. Adsorption density q_e (mg/g)

$$q_e = \frac{(C_o - C_e) \times V}{w} \quad (7)$$

Where w is the weight (g) of the adsorbent while V is the volume of the adsorbate in litre.

The affinity of the adsorbent to the adsorbates as observed from Fig. 2 increases with increase in the amount of the adsorbent at the same initial adsorbates concentration of 20mg/L. With %removal varying according to the order $Cd (II) > Fe (II) > Ni (II) > Cr (VI)$, in which the least adsorbed ($Cr (VI)$) shows 94% removal (Ibrahim and Jimoh, 2008; Ibrahim, 2008; Ibrahim and Jimoh, 2010; Ibrahim and Jimoh 2011; Ibrahim, 2012).

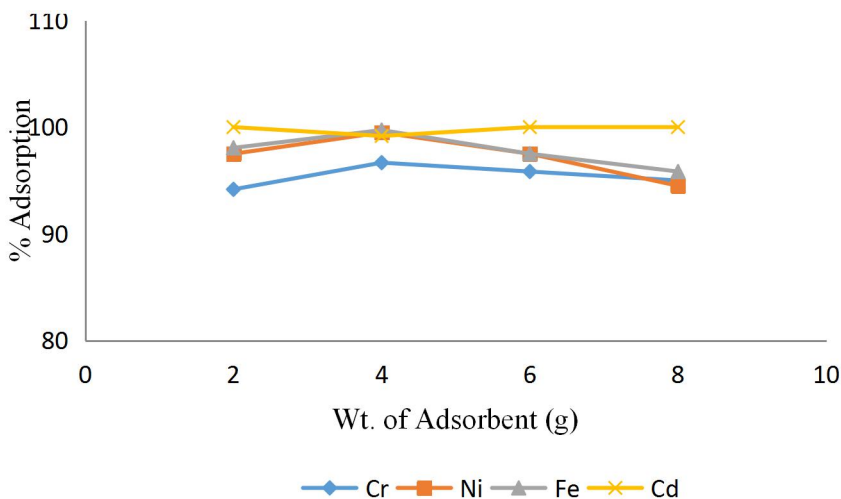


Fig. 2: Variation of % Adsorption with Weight of Maize Cob

Thermodynamic Parameters for the Adsorption Process

In order to fully understand the nature of the adsorption process, the thermodynamic studies play an important role to determine the spontaneity and the heat change for the adsorption process. The adsorption of the metallic ions (M^{n+}) onto a given adsorbent is a typical example of a heterogeneous equilibrium (Ibrahim, 2011a) which can be represented simply by equation (8)



The equilibrium constant for the distribution of the metal ions between the liquid and solid phases K_a , can be calculated from equation (9):

$$K_a = \frac{[M_{ad}]}{[M^{n+}_{(aq)}]} = \frac{q_e}{C_e} \quad (9)$$

Where $[M_{ad}]$ is the equilibrium concentration of the metal adsorbed onto the adsorbent which is equal to q_e (mg/g). $[M^{n+}_{(aq)}]$ is the equilibrium concentration of the metal ion left in the solution which is similar to C_e (mg/L).

Other thermodynamic parameters (Table 3) such as change in enthalpy (ΔH) and change in entropy (ΔS) can respectively be calculated from the slope and intercept of the Van't Hoff plots (equation (10));

$$\ln K_a = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10)$$

and change in Gibbs free energy (ΔG) was calculated from equation (11),

$$\Delta G_{ad} = \Delta H_{ad} - T\Delta S_{ad} \quad (11)$$

Where R (8.314Jmol⁻¹K⁻¹) is the gas constant and T (K) is the absolute temperature (Chen and Wang, 2006; Omar and Al-Itawi 2007; Zawani *et al.*, 2009; Muhammad and Wahab, 2011; Muhammad, 2011).

Table 3: *Thermodynamic Parameters for the Adsorption of the Various Metal ions onto Maize Cob*

Ions	Ka	$\Delta G = \Delta H - T\Delta S$ (Jmol ⁻¹)				ΔH (Jmol ⁻¹)	ΔS (Jmol ⁻¹ K ⁻¹)
		303K	313K	323K	333K		
Cr	0.3156	-581.91	-610.76	-639.60	-668.45	292.2371	2.8850
Ni	0.1125	-2288.96	-2389.39	-2489.83	-2590.26	754.1629	10.0433
Fe	0.4696	-71.7498	-80.0638	-88.3778	-96.6918	180.1644	0.8314
Cd	0.0250	-8936.44	-9293.03	-9649.62	-10006.2	1868.1558	35.6587

Adsorption Isotherms

This is a curve relating the concentration of an adsorbate on the surface of an adsorbent, to the concentration of the adsorbate in the liquid with which it is in contact.

Freundlich Adsorption Isotherm

The Freundlich model (equation 12) assumes that the uptake of metal ions occurs on a heterogeneous surface by monolayer adsorption (Bulut and Baysal, 2006). The model gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The constant, K_F , is indicative of the relative adsorption capacity of the adsorbent related to the bonding energy and can be defined as the adsorption or distribution coefficient. It represents the quantity of the metal ion adsorbed onto the adsorbent for unit equilibrium concentration. The constant $a = 1/n_F$ where n_F is the heterogeneity factor, represents the deviation from

linearity of adsorption as follows: if the value of $n_F = 1$, the adsorption is linear; if $n_F < 1$, the adsorption process is chemical, and if $n_F > 1$, the adsorption is a favourable physical process (Crini *et al.*, 2007; Ibrahim, 2011b). Also for all values of $1/n_F$ less than unity, adsorption is the predominant process taking place otherwise desorption becomes predominant.

$$\ln q_e = \ln K_F + \ln C_e \quad (12)$$

Langmuir Adsorption Isotherm

The Langmuir model (equation 13) represents one of the first theoretical treatments of non-linear sorption and suggests that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between the adsorbed molecules.

$$\frac{C_e}{q_e} = \frac{1}{kq_m} + \frac{C_e}{q_m} \quad (13)$$

Where the constants k and q_m are the adsorption equilibrium constant (dm^3/mg) and monolayer adsorption capacity of the adsorbent (mg/g) respectively (Bansal *et al.*, 2009).

The essential characteristics of the Langmuir isotherm may be expressed in terms of the dimensionless separation parameter R_L , which is indicative of the isotherm shape that predicts whether an adsorption system is favourable or unfavourable. R_L according to Malik (2004), Ibrahim *et al.* (2006), Nwabanne and Igbokwe, (2008), is calculated using equation 14:

$$R_L = \frac{1}{1 + kC_o} \quad (14)$$

Where C_o is the initial metal ion concentration (mg/L) and k is adsorption equilibrium constant which is obtained from the intercept of the Langmuir plot. The value of R_L indicates the type of the isotherm to be either (i) unfavourable if $R_L > 1$, (ii) linear if $R_L = 1$, (iii) favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$.

Dubinin – Radushkevich (D – R) Adsorption Isotherm

Like Freundlich model, Dubinin – Radushkevich model also assumes the uptake of the metal ions to take place on a heterogeneous surface by monolayer adsorption. The isotherm is generally expressed by equation (15);

$$\ln q_e = \ln q_m - K\varepsilon^2 \quad (15)$$

Where the constant K is related to adsorption energy having units of mol²kJ⁻² and it gives an idea about the mean free energy E (kJmol⁻¹) of adsorption per molecule of the adsorbate when it is transferred to the surface of the adsorbent from infinite distance in the solution which can be calculated from equation 16;

$$E = \frac{1}{\sqrt{2K}} \quad (16)$$

The parameter ε is the Polanyi potential (El-Nemr *et al.*, 2008) which is calculated from equation 17;

$$\varepsilon = RT \ln \left(1 + \frac{1}{c_e} \right) \quad (17)$$

In the D – R isotherm, the sorption energy is independent of the working temperature but varies with the nature of the adsorbent and adsorbate (Bansal *et al.*, 2009). The magnitude of E provides information on the nature of the sorption process, i.e., whether it is chemisorption or physisorption. If the values of E are in the range of less than 8kJmol⁻¹ the sorption process is physical in nature, otherwise it is a chemical adsorption process (Mataka *et al.*, 2010).

Tables 4 - 6 provides the values of the adsorption isotherm parameters for the adsorption of the tested metal ions on the respective adsorbents. It shows that the adsorption of Cr, Ni and Cd ions onto MC and for Cd ion onto SD (for which n < 1) is a chemisorption process, in other words, a localised monolayer adsorption. However, those of Cr and Ni onto SD (having n > 1) are favourable physisorption (multilayer) adsorption processes. Also it can be understood that the adsorption of Cd onto SD is linear indicating both chemisorption and physisorption are taking place at the same rate (Muhammad, 2011; Ibrahim, 2013).

Table 4: Numeric Constants for the Adsorption of the Metal ions onto the Adsorbents

Adsorbent	Ion	Freundlich		Langmuir		D – R	
		n_F	K_F	q_m (mg/g)	k (L/mg)	K (mol ² kJ ⁻²)	q_m (mg/g)
Maize Cob	Cr	0.2967	2.67×10^{-5}	500	-0.0769	12560	4.45×10^{38}
	Ni	0.2319	1.05×10^{-6}	500	-0.0541	8116	2.71×10^{35}
	Fe	2.0000	0.1233	-1000	-0.0175	22209	1×10^{-58}
	Cd	0.1872	4.60×10^{-7}	100	-0.1020	12988	6.08×10^{10}
Sawdust	Cr	1.4514	0.4325	-12.1951	-0.1595	4×10^6	2.93×10^{-19}
	Ni	1.6556	0.2254	-71.4286	-0.0718	1×10^6	1.75×10^{-20}
	Fe	1.0627	0.5105	-27.0270	-0.0673	4×10^6	1.02×10^{22}
	Cd	0.5627	0.0015	0.0000	0.0000	250.9	2.60×10^{69}
Coal	Cr	0.8424	0.3342	28.5714	0.1144	2×10^6	7.36×10^{19}
	Ni	-4.9261	0.6095	-9.7087	-0.2081	-21196	-----
	Fe	1.4728	0.8128	-1.7953	-0.4220	10×10^6	8.78×10^{19}
	Cd	0.2235	5.12×10^{-6}	125	-0.1067	14123	2.52×10^{11}

Table 5: Variation of the Sorption Energy (E) of the Adsorbates onto the Various Adsorbents

Ion	Dubinin – Radushkevich Sorption Energy ($E = 1/\sqrt{2K}$)					
	Maize Cob		Sawdust		Coal	
	K	E	K	E	K	E
Cr	12560	0.0063	4×10^6	0.0004	2×10^6	0.0005
Ni	8116	0.0079	1×10^6	0.0007	-21196	-----
Fe	22209	0.0047	4×10^6	0.0004	1×10^7	0.0002
Cd	12988	0.0062	250.9	0.0446	14123	0.0060

Table 6: Variation of R_L for the Various Adsorbents with Increase in Initial Metal Ion Concentration

Langmuir Separation Parameter (R_L) Co(mg/L)	Maize Cob				Sawdust				Coal			
	Cr	Ni	Fe	Cd	Cr	Ni	Fe	Cd	Cr	Ni	Fe	Cd
20	-1.8571	-12.333	1.5405	-0.9608	-0.4565	-2.2941	-2.8947	1.0000	0.3042	-0.3163	-0.1344	-0.8824
30	-0.7647	-1.6087	2.1111	-0.4852	-0.2641	-0.8667	-0.9821	1.0000	0.2257	-0.1908	-0.0858	-0.4546
40	-0.4815	-0.8605	3.3529	-0.3245	-0.1858	-0.5343	-0.5914	1.0000	0.1794	-0.1366	-0.0630	-0.3061
50	-0.3514	-0.5873	8.1429	-0.2438	-0.1433	-0.3861	-0.4231	1.0000	0.1488	-0.1063	-0.0498	-0.2308
60	-0.2766	-0.4458	-19.000	-0.1952	-0.1167	-0.3023	-0.3293	1.0000	0.1272	-0.0871	-0.0411	-0.1852

Supervised Research Outputs

In our research group series of natural materials employed for the removal of various pollutants alongside published articles are outlined in Table 7.

Table 7: *List of Adsorbents and Pollutants Remedied*

S/N	ADSORBENT	POLLUTANTS	REFERENCE
1	Groundnut Shell and Orange Peel	Crystal Violet	Muhammad <i>et al.</i> , (2012)
2	Sugarcane Bagasse and Bambara Groundnut Shell	Congo red	Muhammad <i>et al.</i> , (2013)
3	Neem Leaves and Watermelon Rinds	Congo red and Methyl Orange	Ibrahim and Sani, (2014); Ibrahim and Sani, (2015); Muhammad <i>et al.</i> , (2015)
4	Sugarcane Bagasse	Methylene Blue, Alizarin Red, Methyl Red	Muhammad and Yahaya, (2015); Muhammad and Yahaya, (2016)
5	Groundnut Shell and Banana Peels	Methylene Blue, Malachite Green	Samaila <i>et al.</i> , (2016)
6	<i>Albizia lebbek</i> Shell	Auramine Yellow, Malachite Green and Basic Violet	Ibrahim and Umar (2016)
7	Orange Peel	Ni(II), Cu(II) and Pb(II)	Salisu and Ibrahim, (2017)
8	Mahogany Leaves and Neem Leaves	Ni(II) and Cd(II)	Ibrahim and Mohammed, (2017)
9	Axle-Wood	Methyl Blue, Basic Magenta and Reactive Red	Yahuza <i>et al.</i> , (2017)
10	Modified Watermelon Rind	Congo Red, Methyl Orange and Rhodamine B	Muhammad and Ali, (2017)
11	Modified Neem Leaves Carbon	Eriochrome Black T and Methyl Orange	Jimoh and Ibrahim, (2017); Jimoh and Ibrahim, (2018)

Conclusion

The quest for availability and access to safe water for drinking and other domestic and agricultural purposes is a continuous process that our research group will continue to pursue as many others are doing. Many local/natural materials which

appeared to be waste may, if properly utilised, turn to wealth and save lives. Research collaborations and expanded partnership with donor agencies will greatly improve the water sector in a similar manner as such partnerships have improved the health and education sectors.

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