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Chapter

Adsorption of Heavy Metals from Industrial Wastewater Using Nanoparticles from Agro Wastes

Lekan Taofeek Popoola and Alhaji Shehu Grema

Abstract

Effluents from essential industries have been characterized with heavy metals which are non-biodegradable in nature and also detrimental to health when accumulated in body tissues over long exposure. Adsorption was proved as the best efficient process amongst others to remove these heavy metals from industrial wastewater due to its excellent features. Activated carbons from nanoparticles of agricultural wastes such as pods, shells, husks, peels, shafts and many prepared via calcination process at high temperature can be used as active adsorbent for the industrial wastewater treatment involving heavy metals removal. This chapter discusses heavy metals in industrial wastewater effluents and potential agro wastes from which nanoparticles of activated carbon for industrial wastewater purification could be generated. The transformation of agro wastes nanoparticles into activated carbons via calcination and their applications for heavy metals removal from industrial wastewater via adsorption were examined. Various characterization techniques to study the effects of calcination on structural, morphological and textural properties of activated carbon prepared from agro waste nanoparticles were also discussed. Various isotherm, kinetics, mechanistic and thermodynamics models to investigate the adsorptive nature of the process were presented. Error functions and algorithms for both the linear and non-linear isotherm models regression to affirm their fitness for prediction were presented. Lastly, proposed adsorption mechanisms of heavy metals removal from industrial wastewater using activated carbons from nanoparticles of agro wastes were presented.

Keywords: Adsorption, Industrial wastewater, Nanoparticles, Agro wastes, Heavy metals, Calcination

1. Introduction

Water has been identified as the most essential element needed by man for existence on Earth. However, the natural nature of water is altered when contaminated by waste substances generated from human activities. Water, whose biological, chemical or physical properties have been altered due to the introduction of certain substances, is called wastewater. This renders it useless and makes it unsuitable for industrial and domestic purposes. Some of these contaminants are heavy metals which exist in aqueous waste streams of several industries such as mining operations, dye industries, metal plating, tanneries, alloy industries,

smelting, textile industry, radiator manufacturing, and many more. Heavy metals associated with these essential industries include chromium, lead, nickel, cadmium, mercury and iron. They are known with non-biodegradable attribute and their accumulation in body tissues may lead to disruption of functioning cells, kidney congestion, liver damage, nausea, chronic asthma, diarrhea, dermatitis and many more [1, 2]. In order to keep our environment safe from these carcinogenic substances, wastewater treatment techniques are required. Various means of removing heavy metals from wastewater such as coagulation, flocculation, flotation, ion exchange, membrane filtration, electrochemical treatment and chemical precipitation have been presented [3]. However, adsorption was proved to be the most efficient unit operation for the removal of hazardous heavy metals from wastewater solution [4]. Amongst its outstanding features are design and operation simplicity, toxic pollutants insensitiveness, cost effectiveness, high heavy metals sorption efficiency and negligible sludge formation [5]. Nonetheless, nanoparticles synthesized from agro wastes via calcination at higher temperatures have proved to be effectively used as activated carbon for heavy metals removal from industrial wastewater. This chapter general discusses generation of activated carbons from nanoparticles of agro waste as adsorbents for the removal of heavy metals that are usually found in industrial wastewater.

2. Heavy metals in industrial wastewater

The high rate of global industrialization has contributed adversely to the industrial wastewater generated annually. Industrial wastewater contributed to tens of millions of cubic meters per day of the total wastewater discharged globally. In developing countries, record shows that almost 80–90% of all the wastewater is directly discharged untreated into surface water bodies [6]. This causes pollution of water bodies and rivers which consequently endangers the living species around this area and also makes the water unsuitable for usage. Many industrial activities such as petrochemical, electronic, chemical, electrochemical and food processing industries require the use of water for production and cleaning activities. During this process, the water is contaminated by dissolved substances which are needed to be removed before the water is discarded. Industrial wastewater characteristics, quality and volume vary from industry to industry based on the materials they are handling. Industrial wastewater effluent can contain metals, toxic organic compounds, biodegradable organic matter, suspended solids, phosphorus, nitrogen and pathogenic organisms [4]. However, industrial wastewater pollutants of major concern in this context are the heavy metals because of their high toxicity to human beings and plants. They pose risks to human health and the environment at certain concentrations and exposure period. Examples include lead, cadmium, iron, mercury, nickel, zinc, chromium, arsenic, aluminum and barium. **Figure 1** shows the distribution of most widely studied heavy metal ions.

3. Potential agro wastes for industrial wastewater purification

During agricultural practices, some fractions of agricultural biomass which are non-edible in nature are discarded as wastes. These are termed agro wastes and constitute environmental pollution after being discarded. Studies have shown that approximately one-third of 1.6 to 6 billion tons of crops produced globally per year constitutes environmental pollution [8]. However, these agro wastes have exhibited excellent adsorption attributes in removing different pollutants (such as heavy
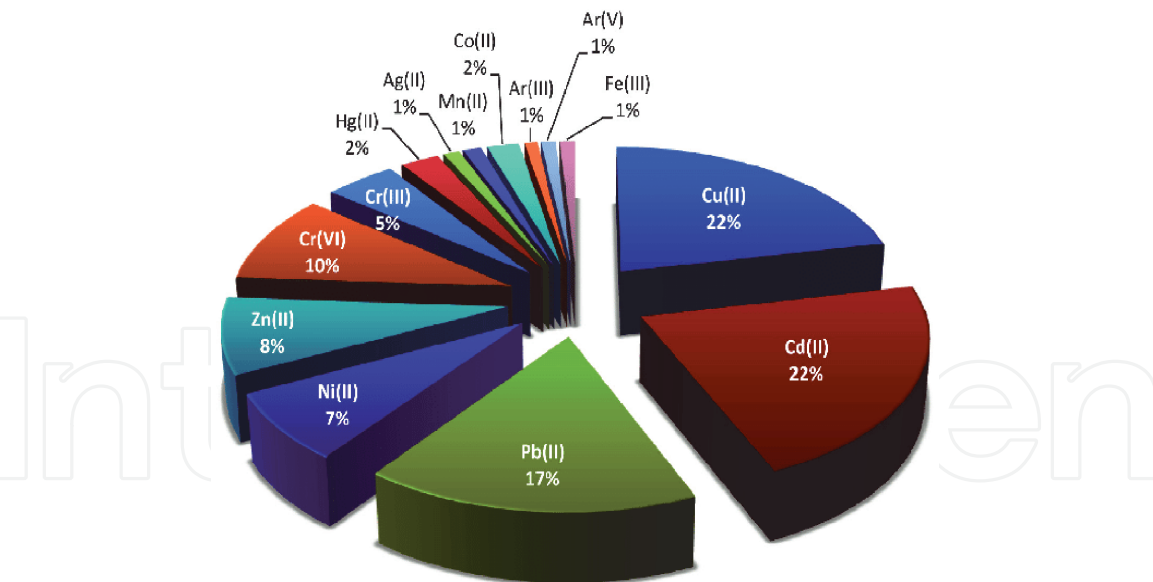
Figure 1.
Distribution of most widely studied heavy metal ions [7].

Figure 2.
Agro wastes for nanoparticles preparation [13].

metals) from wastewater either after chemical or physical modifications; or in their natural state [9]. This could be attributed to active functional groups such as carbonyl, acetamido, phenolic, alcoholic, amino and sulfhydryl which are present in them [10]. Nevertheless, the structural composition of agro wastes to include hemicellulose, lignin, lipids, simple sugars, starch and proteins helps in their adsorption capacity of heavy metals removal from industrial wastewater [11]. Nanoparticles for heavy metals removal from different forms of contaminated water had been prepared from different agro waste such as cotton seed hulls, snail shell, fruit peels, cotton plant wastes, hen feathers, peanut hull, jatropa deoiled cakes, soybean hulls, coconut shells, walnut shells, maize bran, mangosteen shell, wheat shell, *Ceiba pentandra* hulls and many more [12]. **Figure 2** shows different agro wastes that can be transformed into nanoparticles for heavy metals removal from industrial wastewater.

4. Transformation of agro wastes into activated carbon nanoparticles

Nanoparticles (NPs) are broad group of materials that include particulate substances, with dimensions ranging between 1 and 100 nm [14]. They found wide industrial applications when researchers realized the significance of size on the physiochemical properties of a substance [15]. NPs are made up of three layers namely: surface layer (functionalized with a mixture of small metal ions, molecules, polymers and surfactants), shell layer (chemically different material from the core in all aspects), and lastly the core layer (essentially the NP central portion of the NP) [16]. Consequently, studies have shown nanoparticles prepared from agro wastes via physicochemical transformation (such as calcination) as good adsorbents for heavy metals removal from solution [17]. Calcination involves subjecting solids into heating under controlled temperature and environment, purposely to remove volatile substances in order to improve their purity level [18]. In most cases, it is carried out in furnaces which are purposely designed to exclude air such that an inert gas may be replaced. The influence of this method on particle shape, size and crystalline nature of the prepared nanoparticles from agro wastes supports its' suitability for application in industrial wastewater treatment [19]. Factors that determine the physical and chemical properties of activated carbon nanoparticles prepared via calcination of solids (such as agro wastes) include temperature, heating rate, calcination time, particle size and material nature [20].

5. Characterization of nanoparticles from agro wastes

The characterization of nanoparticles prepared from agro wastes for heavy metals removal from industrial wastewater can be categorized into structural; morphological; optical; and particle size and surface area characterizations.

5.1 Structural characterization

The structural characterization gives information about bulk properties, composition and bonding nature of the nanoparticles. These include X-ray diffraction (XRD), energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS). However, the first-two are the most prominent. XRD gives detailed information about nanoparticles phase and crystallinity [21]. Information about the crystal lattice is obtained by X-rays, high-energy electrons and neutrons of absorbed or scattered radiation striking the nanoparticles. The diffraction pattern is obtained via elastic interaction between incident radiation of smaller wavelengths and regular arrays of atoms in a crystal lattice. Nanoparticles crystalline structure depends on diffraction angles and intensities in diffracted beams [22]. The atomic numbers of the constituent atoms and their geometrical relationship with respect to the lattice points determine the diffracted angle. The mean crystal size of the nanoparticles can be determined from line widths which could be calculated using Eq. (1) [23].

$$\beta = \frac{K\lambda}{D\cos\theta} \tag{1}$$

where β = line width at half the maximum peak intensity, K = correction factor for nanoparticle shape (taken as 0.9 for spheres), D = crystallite size, and θ is the angle of incidence for the selected diffraction peak.

Another structural characterization usually used in obtaining information about the composition of nanoparticles from agro wastes for treatment of industrial wastewater via X-ray spectrum analysis is the energy dispersive X-ray (EDX) [24]. This is often used in conjunction with scanning electron microscopy (SEM) to obtain nanoparticles elemental composition measured in wt %. The mechanism involves emission of an electron from an inner electron shell of a sample resulting from an incident electron or photon (such as γ –ray or X-ray) hitting an atom at a ground state which leaves a vacancy site in the shell. This electron vacancy site is filled by a more energetic valence electron from the outer shell causing the release of excess energy in the form of an X-ray emission. The intensity of the X-ray emitted by electron beam irradiation is a function of the constituent elements in the nanoparticle. A directly proportional relation exists between the intensity of specific X-ray and the concentration of the explicit element present in the agro waste nanoparticle. **Figure 3** is a typical EDX result obtained for activated carbon prepared from nanoparticles of composite snail shell and rice husk.

The X-ray photoelectron spectroscopy (XPS) is used to know the elements bonding nature and their respective ratio in agro waste nanoparticles. Under this, X-ray photons between 200 and 2000 eV interact with a sample under vacuum via exchange of enough energy with core-level electrons close to the material surface to cause electron ejection. The atomic electron binding energy (E_b) is determined using Eq. (2). A typical XPS spectrum indicating a plot of number of electrons against the electrons binding energy (eV) is obtained for interpretation. Specific set of XPS peaks for each element at its own fingerprint binding energy value can be generated [26]. This characterization technique is highly sensitive and can be used to obtain overall composition and compositional variation of nanoparticles with depth.

$$E_k = hv - E_b - \Phi \tag{2}$$

where E_k = kinetic energy of ejected core electrons, hv = exciting photon energy and Φ = material characteristic work function.

5.2 Morphological characterization

This characterization category is imperative as it gives information about nanoparticles morphology which is an influential factor in determining most of their properties. The most important techniques under this are scanning electron microscopy (SEM) and transmission electron microscope (TEM).

In recent times, morphology of nanoparticles from agro wastes has been analyzed using SEM. It utilizes electrons with small wavelengths which are thermally
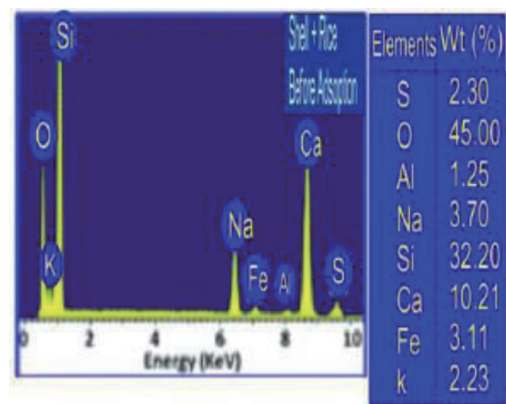

Figure 3.
EDX result of activated carbon from nanoparticles of composite snail shell and rice husk [25].

excited to obtain high resolution of an electron microscope. The electron beam is focused on the nanoparticle sample surface with the aid of electromagnetic lenses to obtain a three-dimensional image of varying magnification and field depth. **Figure 4** is a typical SEM result of activated carbon from nanoparticles of composite snail shell and rice husk.

In a similar manner, TEM is also based on the principle of electron transmittance. However, carbon coated copper grid is used to support the nanoparticle sample during its interaction with the electron beam. The three major parts of TEM include the illumination system where emitted electron beam is allowed to pass through the nanoparticle sample; objective lens and stage; and the imaging system. The image is produced with the aid of connecting devices, intermediate lenses and a projector lens. The image can be taken as either diffraction pattern mode or image mode based on the selection of either the image plane or backfocal plane as the objective plane of the intermediate lens and projector lens.

5.3 Particle size and surface area characterization

The previously discussed XRD, SEM and TEM can be used to determine nanoparticles size and surface area [27]. However, the most common technique for measuring nanoparticles surface area and size is the Brunauer–Emmett–Teller (BET) method [28]. The technique of adsorption and desorption principle is adopted using nitrogen gas. The specific surface area of agro waste nanoparticle is calculated using a monolayer adsorbate weight (W_m) obtained from the slope and intercept of a linear plot of $\frac{1}{W[(P_o/P)-1]}$ against $\left(\frac{P}{P_o}\right)$ in Eq. (3).

$$\frac{1}{W[(P_o/P)-1]} = \frac{1}{W_mC} + \frac{C-1}{W_mC}\left(\frac{P}{P_o}\right)$$

(3)

where W = weight of the gas adsorbed at a relative pressure P/P_o, P/P_o = true equilibrium pressure/equilibrium pressure if no gas were adsorbed and C = BET constant which is a function of adsorption energy of the first adsorbed layer. **Table 1** gives information about surface area, total pore volume and average pore diameter of activated carbon prepared from nanoparticles of agro wastes for heavy metals removal from solution.
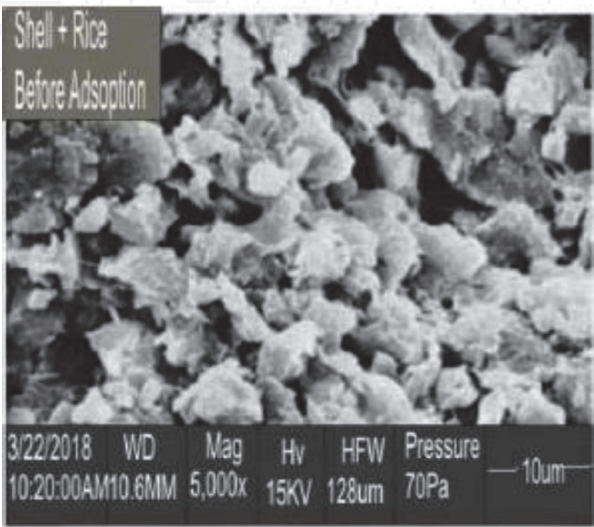

Figure 4.
SEM image of activated carbon from nanoparticles of composite snail shell and rice husk [25].

Agro waste sources for activated carbon	Surface area (m^2/g)	Total pore volume (cm^2/g)	Average pore diameter (Å)	Reference
oil palm frond	700.00	0.3200	5.85	[29]
kenaf core fiber	4.00	0.1128	28.39	[30]
wood	101.51	0.0567	22.35	[31]
walnut shell-rice husk	126.72	0.0811	4.18	[32]

Table 1.
Textural properties of activated carbons from nanoparticles of agro wastes used as adsorbent.

Another prevailing quantitative characterization of nanoparticle from agrowaste is the Fourier transform infrared spectroscopy (FTIR). The principle involves passage of infrared (IR) radiations through the nanoparticle sample. Some of these IR radiations are absorbed by the material and the remaining transmitted. Absorption peaks at corresponding vibrations frequency between the atomic bonds are obtained in the resulting IR spectrum for interpretation. The peaks size in the spectrum gives information about the amount of material and chemical bonds present.

6. Adsorption of heavy metals from industrial wastewater using agro wastes nanoparticles

Adsorption process as industrial wastewater treatment had also proved to be superior to other conventional treatment techniques such as coagulation, flocculation, flotation, ion exchange, membrane filtration, electrochemical treatment, chemical precipitation and so on [33]. Adsorption involves binding of particles or molecules in a solution onto adsorbent surface (e.g. activated carbon from nanoparticles of agro wastes) and thus, it is usually a surface phenomenon. Heavy metals present in industrial wastewater can be removed from solution by adsorption process using activated carbon prepared from nanoparticles of agro wastes through calcination process. Advantages include adsorbent regeneration and reuse attribute, high adsorption efficiency, low cost of operation, heavy metals recovery possibility and low sludge formation [34, 35]. A temperature-controlled equipment with a stirring feature is usually used to study the batch adsorption process while concentration of heavy metals in solution is measured via atomic absorption spectrometer. Major factors that affect adsorption process of heavy metals from industrial wastewater using activated carbon (AC) prepared from nanoparticles of agro wastes include temperature, reaction time, AC dosage, stirring rate, solution pH and heavy metal concentration in solution [36]. The adsorption capacity of the AC from nanoparticles of agro wastes, q_e (mg/g) at equilibrium could be measured using Eq. (4).

$$q_e = (C_o - C_e)\frac{V}{W} \qquad (4)$$

where C_o and C_e are initial and final concentrations of heavy metals in solution (mg/L), V is the volume of solution (L) and W is the weight of adsorbent (g).

Adsorption mechanisms of heavy metals over agro wastes nanoparticles from industrial wastewater include chemisorption, physisorption, complexation, ion exchange and pores diffusion through pores. Chemisorption is an irreversible process which involves chemical bonding of molecules in solution onto adsorbent surface while physisorption is a reversible process in which transfer or sharing of electrons does not occur.

7. Isotherm, kinetics and thermodynamics studies of heavy metals removal from industrial wastewater using activated carbon (AC) prepared from nanoparticles of agro wastes

Various isotherm, kinetics, mechanistic and thermodynamics models that can be used to study the adsorptive nature of activated carbon from nanoparticles of agro wastes on heavy metals in industrial wastewater are summarized in **Table 2**. The

Models	Equations	Applicability	Assumption
Isotherm Models			
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	1. Heterogeneous surface energy systems. 2. Multilayer description adsorption with interaction between adsorbed molecules.	1. Adsorption of pollutant onto heterogeneous adsorbent
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$ $R_L = \frac{1}{1 + K_L C_o}$	1. Monolayer coverage relationship formation of adsorbate molecules.	1. Existence of homogeneous active sites at adsorbent surface for monomolecular adsorbed layer formation. 2. Negligible interactions between adsorbed species.
Temkin	$q_e = b_T In A_T + b_T In C_e$	1. Covers adsorbate-adsorbent interaction.	1. Molecules heat adsorption decreases with adsorbent surface coverage increase. 2. Binding energies uniform distribution at the adsorbent surface.
Dubinin-Radushkevich	$In(q_e) = In(q_m) - B_D \varepsilon^2$ $\varepsilon = RT In\left(1 + \frac{1}{C_e}\right)$ $E = \frac{1}{\sqrt{(-2B_D)}}$	1. Adsorbate-adsorbent equilibrium relation can be expressed independently of temperature.	1. Adsorbent size is comparable to micropore size. 2. Characteristic curve Gaussian-type distribution
Harkin-Jura	$\frac{1}{q_e^2} = \frac{B_{HJ}}{A_{HJ}} - \left(\frac{1}{A_{HJ}}\right) \log C_e$		1. Multilayer adsorption on adsorbent surface with heterogeneous pore distribution.
Halsey	$In q_e = \frac{1}{n_H} In K_H - \frac{1}{n_H} In C_e$	1. Multilayer adsorption	1. Heterogeneous adsorbent if equilibrium data are well fitted using Halsey isotherm.

Models	Equations	Applicability	Assumption
Redlich-Peterson	$In\left(K_{RP}\frac{C_e}{q_e}-1\right)=\beta_{RP}InC_e+Ina_{RP}$	1. Prediction of homogenous and heterogeneous adsorption systems.	
Sips	$In\left(\frac{q_e}{q_m-q_e}\right)=\frac{1}{n}In(C_e)+In(b_s)^{\frac{1}{n}}$	1. Merged Langmuir and Freundlich models. 2. Effectively reduced to Freundlich isotherm and disobey Henry's law at low adsorbate concentration. 3. Prediction of monolayer sorption capacity based on Langmuir isotherm at high concentrations of adsorbate.	
Toth	$In\left(\frac{q_e^{n_t}}{q_m^{n_t}-q_e^{n_t}}\right)=n_tInC_e+n_tInK_t$		
Adsorption Kinetics			
Pseudofirst-Order	$In\left(q_e-q_t\right)=Inq_e-k_1t$		
Pseudosecond-Order	$\frac{t}{q_t}=\frac{1}{k_2q_e^2}+\frac{t}{q_e}$		
Adsorption Mechanistic Modeling			
Intraparticle Diffusion	$q_t=K_{id}t^{0.5}+C$	1. Studies rate controlling step of biosorption process	
Adsorption Thermodynamics			
Thermodynamics	$\Delta G^o=-RTInK_L$ $\Delta G^o=\Delta H^o-T\Delta S^o$ $InK_L=\frac{\Delta S^o}{R}-\frac{\Delta H^o}{RT}$		

q_e (mg g^{-1}): Experimental adsorption capacity at equilibrium, K_F (mg g^{-1}) (L mg^{-1})$^{1/?}$: Freundlich isotherm constant describing sorption capacity, C_e (mg L^{-1}): Adsorbate equilibrium concentration, n: a constant which gives information on heterogeneity grade, K_L (L mg^{-1}): Langmuir constant describing binding sites affinity and energy of adsorption, C_o (mg L^{-1}): highest initial adsorbate concentration, R_L: dimensionless Langmuir equilibrium parameter, q_m (mg g^{-1}): adsorbent maximum monolayer adsorption capacity, R (8.314 J mol^{-1}): universal gas constant, T (°K): absolute temperature, b_T (J mol^{-1}): Temkin constant indicating heat of adsorption, A_T (L mg^{-1}): equilibrium binding constant related to maximum binding energy, B_D (mol^2 kJ^{-2}): Dubinin-Radushkevich isotherm constant of adsorption energy, ?: Polanyi potential related to the equilibrium concentration, E (kJ mol^{-1}): mean free energy of adsorption, A_{HJ} and B_{HJ}: Harkin-Jurah adsorption constants; K_H and n_H: Halsey isotherm constants; K_{RP} (L/g): Redlich–Peterson isotherm constant, a_{RP} (L/mg): Redlich–Peterson isotherm constant, β: Redlich–Peterson exponent with values between 0 and 1, b_s: Sips isotherm constant related to energy of adsorption, K_t: Toth model adsorption isotherm constant, n_t: Toth model exponent, b_K: Khan model constant, a_K: Khan model exponent, q_t (mg g^{-1}): equilibrium adsorption uptake at time, t, k_1 (min^{-1}): pseudo-first-order rate constant of adsorption, k_2 (g mg^{-1} min^{-1}): pseudo-second-order rate constant of adsorption, K_{id} (mg g^{-1} min$^{-0.5}$): Intraparticle diffusion rate constant, C (mg g^{-1}): boundary layer diffusion effect, $\Delta G°$ (kJ mol^{-1}): change in Gibbs free energy, $\Delta H°$ (kJ mol^{-1}): change in enthalpy, $\Delta S°$ (kJ mol^{-1} K^{-1}): change in entropy, andK_{eq}: thermodynamic equilibrium constant.

Table 2.
Isotherm, kinetics, mechanistic and thermodynamics models for heavy metals [35].

adsorption isotherms explain the distribution of adsorbed molecules between industrial wastewater and activated carbon when equilibrium is attained during adsorption process. The isotherm models for fitting experimental data by linear regression method include two-parameters (Freundlich, Langmuir, Temkin, Dubinin-Radushkevich, Harkin-Jura and Halsey) and three-parameters (Redlich-Peterson, Sips and Toth) isotherm models. Adsorption kinetic studies predict the degree of heavy metals removal from industrial wastewater which governs adsorption reaction or residence time. The adsorption efficiency is a function of adsorbent adsorption potential. Adsorption mechanistic model gives information about the intraparticle diffusion of heavy metal molecules from bulk solution of industrial wastewater into pores of AC adsorbent. The correlation coefficient (R^2 value) then determines the isotherm, kinetics and mechanistic equations fitness for the adsorption process. Values of R^2 close to unity signify excellent fitness of models.

For thermodynamic analysis, the Gibbs free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) give information about inherent energetic changes during adsorption and show whether the reaction can happen spontaneously or not. Positive value of ΔG^o implies adsorption cannot happen spontaneously at examined temperatures. Also, values of ΔG^o between 0.0–20 kJ/mol and 80–400 kJ/mol respectively imply physical and chemical adsorption respectively. A positive value of enthalpy change (ΔH^o) suggests endothermic behavior of the

Error Function	Abbreviation	Model
Nonlinear chi-square test	χ^2	$\chi^2 = \sum_{i=1}^{n} \frac{\left(q_{e,\exp} - q_{e,calc}\right)^2}{q_{e,\exp}}$
Sum of squares of the errors	SSE	$SSE = \sum_{i=1}^{n} \left(q_{e,\exp} - q_{e,calc}\right)^2$
Average relative error	ARE	$ARE = \frac{100}{n} \sum_{i=1}^{n} \left\| \frac{q_{e,\exp} - q_{e,calc}}{q_{e,\exp}} \right\|$
Residual root mean square error	RMSE	$RMSE = \sqrt{\frac{1}{n-2} \sum_{i=1}^{n} \left(q_{e,\exp} - q_{e,calc}\right)^2}$
Coefficient of determination	R^2	$R^2 = \frac{\sum \left(q_{e,\exp} - \bar{q}_{e,calc}\right)^2}{\sum \left(q_{e,\exp} - \bar{q}_{e,calc}\right)^2 + \sum \left(q_{e,\exp} - q_{e,cal}\right)^2}$
Standard deviation of relative errors	S_{RE}	$S_{RE} = \sqrt{\frac{\sum_{i=1}^{n} \left[\left(q_{e,\exp} - q_{e,calc}\right) - ARE\right]^2}{n-1}}$
Marquardt's percent standard deviation	MPSD	$MPSD = 100 \sqrt{\frac{1}{n-p} \sum_{i=1}^{n} \left(\frac{q_{e,\exp} - q_{e,calc}}{q_{e,\exp}}\right)^2}$
Normalized standard deviation	NSD	$NSD = \Delta q(\%) = 100 \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left(\frac{q_{e,\exp} - q_{e,calc}}{q_{e,\exp}}\right)^2}$
Hybrid functional error	HYBRID	$HYBRID = \frac{100}{(n-p)} \sum_{i=1}^{n} \frac{\left(q_{e,\exp} - q_{e,calc}\right)}{q_{e,\exp}}$
Sum of absolute error	EABS	$EABS = \sum_{i=1}^{n} \left\| q_{e,\exp} - q_{e,calc} \right\|$

$q_{e,\exp}$ (mg g^{-1}): value obtained from the batch experiment, $q_{e,calc}$ (mg g^{-1}): calculated value from the isotherm for corresponding $q_{e,\exp}$, $\bar{q}_{e,calc}$ (mg g^{-1}): mean of $q_{e,\exp}$, n: number of experimental data points, and p: number of parameters in the respective model.

Table 3.
List of error functions for isotherm and kinetics models fitness.
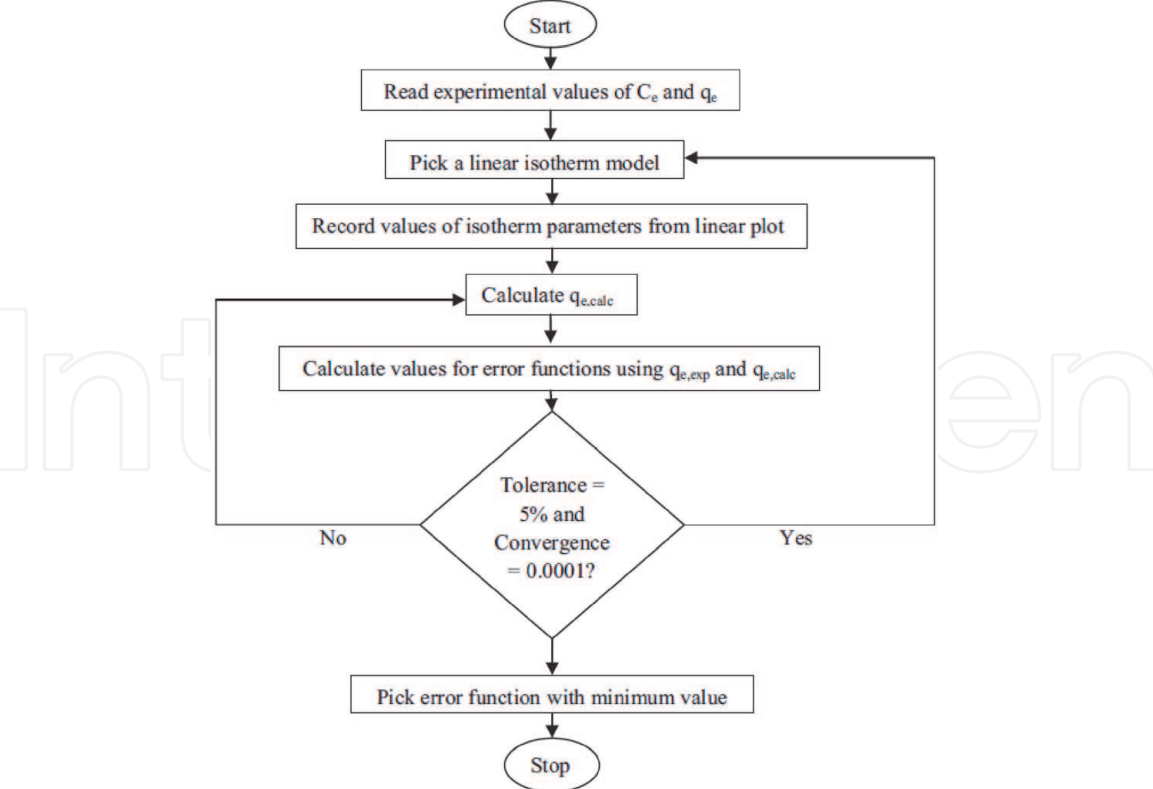
Figure 5.
Algorithm for linear isotherm models regression using error functions [38].

heavy metals adsorption process onto AC nanoparticles of agro wastes. Neverthe-less, enthalpy change within 2.1–20.9, 20.9–80.0 and 80.0–418.4 kJ mol^{-1} implies physisorption, physisorption coupled with chemisorptions, and chemisorptions, respectively [37]. Positive value of entropy change (ΔS^o) indicates increase in the degree of freedom and disorderliness at solid–liquid interface during removal of heavy metals molecules on AC active sites.

The list of error functions that can be used to predict the degree of fitness of isotherm and kinetic models for heavy metals removal from industrial wastewater using AC from nanoparticles of agro wastes is presented in **Table 3**. The algorithms that can be used for both the linear and non-linear isotherm models regression are presented as **Figures 5** and **6** respectively [38].

8. Adsorption mechanism

The proposed mechanism of heavy metals (HMs) removal from industrial wastewater using activated carbon from nanoparticles of agro wastes (ACNAWs) involves binding electrostatic forces existence between positively charged HMs and existing negatively charged ions (-OH, -NH and COO$^-$) on ACNAWs. The ioniza-tion depends on the solution pH of the HMs which involves gaining or losing of a proton to solution. At low pH, ACNAWs become positively charged via gaining of a proton as written in Eqs. (5)–(7).
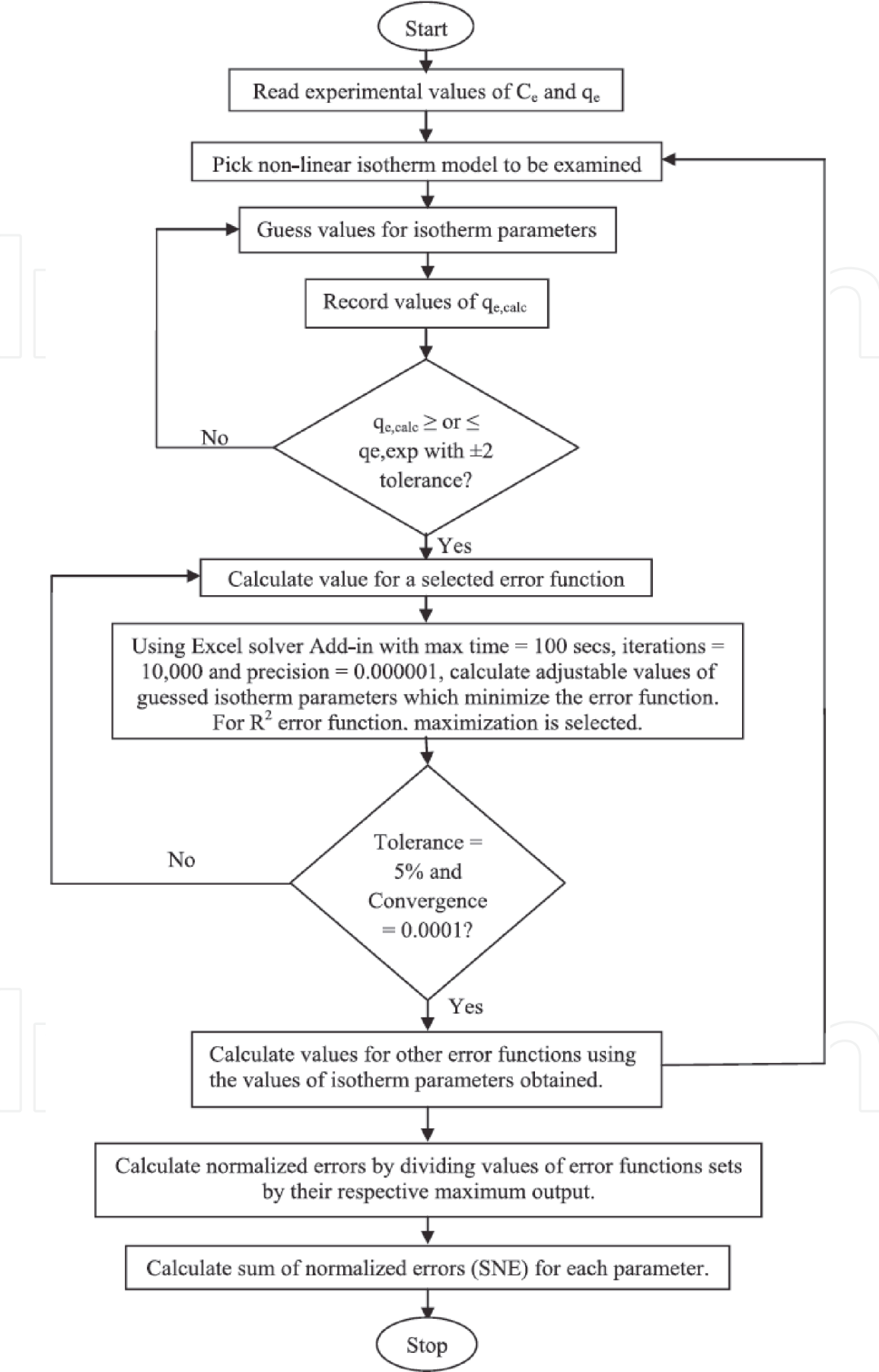
$$\text{ACNAW–OH} + \text{H}^+ \rightarrow \text{ACNAW–OH}_2{}^+ \tag{5}$$

$$\text{ACNAW–NH} + \text{H}^+ \rightarrow \text{ACNAW–NH}_2{}^+ \tag{6}$$

$$\text{ACNAW–COOH} + \text{H}^+ \rightarrow \text{ACNAW–COOH}_2{}^+ \tag{7}$$

Figure 6.
Algorithm for non-linear isotherm models regression using error functions [38].

At very high pH, the surface of ACNAW becomes negatively charged via losing a proton as written in Eqs. (8)–(10).

$$\text{ACNAW–OH} + \text{OH}^- \rightarrow \text{ACNAW–O}^- + \text{H}_2\text{O} \qquad (8)$$

$$\text{ACNAW–NH} + \text{OH}^- \rightarrow \text{ACNAW–N}^- + \text{H}_2\text{O} \qquad (9)$$

$$\text{ACNAW–COOH} + \text{OH}^- \rightarrow \text{ACNAW–COO}^- + \text{H}_2\text{O} \qquad (10)$$

The removal of HMs from industrial wastewater via adsorption onto ACNAW is then influenced by electrostatic attractive forces at high solution pH as written in Eqs. (11)–(13).

$$\text{ACNAW–O}^- + \text{HM} \rightarrow \text{ACNAW–O}^{-\cdots}\text{HM} \qquad (11)$$

$$\text{ACNAW–N}^- + \text{HM} \rightarrow \text{ACNAW–N}^{-\cdots}\text{HM} \qquad (12)$$

$$\text{ACNAW–COO}^- + \text{HM} \rightarrow \text{ACNAW–COO}^{-\cdots}\text{HM} \qquad (13)$$

9. Conclusions

Heavy metals are hazardous substances which could be found in industrial wastewater effluents of industries. They cause havoc when absorbed into the body system. Also, wastes usually generated from agricultural practices pollute the environment and constitute nuisance. However, these agro wastes can be transformed into nanoparticles via mechanical technique and then to activated carbon via calcination process. These activated carbons can be used to remove heavy metals from industrial wastewater effluents via adsorption process. They have proved to be effective. Characterization techniques also revealed significant effects of calcination on structural, morphological and textural properties of activated carbon prepared from agro waste nanoparticles. Also, information obtained from isotherm, kinetics, mechanistic and thermodynamics studies give information about the adsorptive nature of the process. Conclusively, proposed adsorption mechanism is a key factor to know to how heavy metals are removed from industrial wastewater using activated carbons from nanoparticles of agro wastes.

Conflict of interest

No conflict of interest.

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References

[1] Ernhart CB. A critical review of low-level prenatal lead exposure in the human: 1. Effects on the fetus and newborn. Reprod. Toxicol. 1992; 6(1): 9-19.

[2] Khlifi R., Hamza-Chaffai A. Head and neck cancer due to heavy metal exposure via tobacco smoking and professional exposure: a review. Toxicol. Appl. Pharmacol. 2010; 248(2):71–88.

[3] Azimi A, Azari A, Rezakazemi M, Ansarpour M. Removal of heavy metals from industrial wastewaters: A review. Chemical and Biochemical Engineering Reviews. 2016; 4:37-59

[4] Gunatilake S. Methods of removing heavy metals from industrial wastewater. Journal of Multidisciplinary Engineering Science Studies. 2015; 1: 12-18

[5] Lasheen MR, El-Sherif IY, El-Wakee ST, Sabry DY, El-Shahat MF. Heavy metals removal from aqueous solution using magnetite Dowex 50WX4 resin nanocomposite. JMES. 2017; 8(2): 503-511.

[6] Shannon MA, Bohn PW, Elimelech M, Georgiadis JG, Marinas BJ, Mayes AM. Science and technology for water purification in the coming decades. Nature. 2008, 452, 301–310.

[7] Reddy DHK, Lee S, Seshaiah K. Removal of Cd(II) and Cu(II) from Aqueous Solution by Agro Biomass: Equilibrium, Kinetic and Thermodynamic Studies, Environ. Eng. Res., 2012; 17(3):125-132.

[8] FAO. Food wastage footprint impacts on natural resources: summary report. 2013. Food and Agriculture Organization of the United Nations, Rome.

[9] Kadirvelu K, Thamaraiselvi K, Namasivayam C. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Bioresource Technology. 2001; 76(1): 63–65.

[10] Renu MA, Singh K, Upadhyaya S, Dohare R. Removal of heavy metals from wastewater using modified agricultural adsorbents. Mater. Today Proc. 2017; 4(10):534–538

[11] Huang J, Cao Y, Liu Z, Deng Z, Tang F. Efficient removal of heavy metal ions from water system by titanate nanoflowers. Chem. Eng. J. 2012; 180:75–80.

[12] Bailey SE, Olin TJ, Bricka M, Adrian DD. A review of potentially low-cost sorbents for heavy metals. Water Res. 1999; 33:2469–2479.

[13] Adelere IA, Lateef A. A novel approach to the green synthesis of metallic nanoparticles: the use of agro-wastes, enzymes and pigments, Nanotechnol Rev. 2016; 5(6):567–587

[14] Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L, Muller RN. Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. Chem. Rev. 2010; 110.

[15] Tiwari JN, Tiwari RN, Kim KS. Zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructured materials for advanced electrochemical energy devices. Prog. Mater Sci. 2012; 57: 724-803.

[16] Shin,W.-K, Cho J, Kannan AG, Lee Y.-S, Kim D.-W. Cross-linked composite gel polymer electrolyte using mesoporous methacrylate-functionalized SiO$_2$ nanoparticles for lithium-ion polymer batteries. Sci. Rep. 2016; 6, 26332.

[17] Bhatnagar A, Sillanpaa M. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment: a review. Chem. Eng. J. 2010; 157:277–296.

[18] Pokhrel M, Wahid K, Mao Y. Systematic studies on RE_2-Hf_2O_7:5%Eu^{3+} (RE = Y, La, Pr, Gd, Er, and Lu) nanoparticles: effects of the A-site RE^{3+} cation and calcination on structure and photoluminescence. J. Phys. Chem. C 2016; 120:14828-14839.

[19] Dash S, Kamruddin M, Ajikumar P, Tyagi A, Raj B. Nanocrystalline and metastable phase formation in vacuum thermal decomposition of calcium carbonate. Thermochimica Acta, 2000; 363(1):129–135.

[20] Chandrasekhar S, Pramada PN, Majeed J. Efect of calcination temperature and heating rate on the optical properties and reactivity of rice husk ash. J Mater Sci. 2006; 41(23): 7926–7933

[21] Ullah H, Khan I, Yamani ZH, Qurashi A. Sonochemicaldriven ultrafast facile synthesis of SnO_2 nanoparticles: growth mechanism structural electrical and hydrogen gas sensing properties. Ultrason. Sonochem. 2017; 34:484-490.

[22] Jenkins R, Snyder R. Introduction to X-ray Powder Diffractometry, 2012; Vol. 267, Wiley, Interscience.

[23] Hammond C, Hammond C. The Basics of Crystallography and Diffraction, 2009; 3rd edition, Oxford, United States, Oxford University Press Inc., New York.

[24] Iqbal N, Khan I, Yamani ZH, Qurashi A. Sonochemical assisted solvothermal synthesis of gallium oxynitride nanosheets and their solar-driven photoelectrochemical water-splitting applications. Sci. Rep. 2016; 6, 32319.

[25] Popoola LT, Aderibigbe TA, Yusuff AS. Synthesis of composite snail shell-rice husk adsorbent for brilliant green dye uptake from aqueous solution: Optimization and Characterization. Environmental Quality Management (Published online). 2019; DOI: https://doi.org/10.1002/tqem.21602.

[26] Lykhach Y, Kozlov SM, Skála T, Tovt A, Stetsovych V, Tsud N, Dvořák F, Johanek V, Neitzel A, Myslivecek J, Fabris S, Matolín V, Neyman KM, Libuda J. Counting electrons on supported nanoparticles. Nat. Mater. 2015; http://dx.doi.org/10.1038/nmat4500.

[27] Kestens V, Roebben G, Herrmann J, Jämting A, Coleman V, Minelli C, Clifford C, De Temmerman P.-J, Mast J, Junjie L, Babick F, Colfen H, Emons H. Challenges in the size analysis of a silica nanoparticle mixture as candidate certified reference material. J. Nanopart. Res. 2016; 18, 171.

[28] Brunauer S, Emmett P, Teller E. Adsorption of gases in multimolecular layers. Journal of the American Chemical Society, 1938; 60(2):309–319.

[29] Zainol MM, Asmadi M, Amin NAS. Preparation and Characterization of Impregnated Magnetic Particles on Oil Palm Frond Activated Carbon for Metal Ions Removal. Sains Malaysiana, 2017; 46(5):773-782.

[30] Idan IJ, Luqman CA, Thomas SYC, Siti NABMJ. Equilibrium, kinetics and thermodynamic adsorption studies of acid dyes on adsorbent developed from kenaf core fiber. Adsorption Science and Technology, 2018; 36(1–2):694-712.

[31] Sahu JN, Acharya J, Meikap BC. Response surface modeling and optimization of chromium(VI) removal from aqueous solution using tamarind wood activated carbon in batch process. Journal of Hazardous Materials, 2009; 172(2-3):818-825.

[32] Popoola LT. Nano-magnetic walnut shell-rice husk for Cd(II) sorption: design and optimization using artificial intelligence and design expert. Heliyon. 2019; 5:e02381.

[33] Feng L, Cao M, Ma X, Zhu Y, Hu C. Superparamagnetic high-surface-area Fe_3O_4 nanoparticles as adsorbents for arsenic removal. Journal of Hazardous Materials. 2012; 217, 439–446.

[34] Burakov AE, Galunin EV, Burakova IV, Kucherova AE, Agarwal S, Tkachev AG, Gupta VK. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: a review. Ecotoxicol. Environ. Saf. 2018; 148:702–712.

[35] Popoola LT, Aderibigbe TA, Yusuff AS, Munir MM. Brilliant green dye adsorption onto composite snail shell –rice husk: Adsorption isotherm, kinetic, mechanistic and thermodynamic analysis. Environmental Quality management. 2018. (published online)DOI: https://doi.org/10.1002/tqem.21597.

[36] Popoola LT Tetracycline and sulfamethoxazole adsorption onto nanomagnetic walnut shell-rice husk: isotherm, kinetic, mechanistic and thermodynamic studies. International Journal of Environmental Analytical Chemistry. 2019a; Article in Press. DOI: 10.1080/03067319.2019.1646739

[37] Yalcin S. The mechanism of heavy metal biosorption on green marine macroalga Enteromorpha linza. CLEAN-Soil, Air,Water. 2014; 42(3): 251-259.

[38] Popoola LT. Characterization and adsorptive behaviour of snail shell-rice husk (SS-RH) calcined particles (CPs) towards cationic dye. Heliyon. 2019b; 5: e01153.doi:10.1016/j.heliyon.2019. e01153.