Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

p-ISSN: 0972-6268
(Print copies up to 2016)
e-ISSN: 2395-3454

Vol. 21 | No. 3 | pp. 1003-1014 | 2022

Review Research Paper

https://doi.org/10.46488/NEPT.2022.v21i03.007

Open Access Journal

Use of Agricultural Waste-Based Biosorbents for the Removal of Heavy Metals from Aqueous Solution: A Review

K. Harshala*† and N. D. Wagh**
*School of Applied Sciences, Amity University, Mumbai-410206, India
**Department of Environment Science, School of Applied Sciences, Amity University, Mumbai-410206, India
†Corresponding author: K. Harshala; harshala26@rediffmail.com

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 05-06-2021
Revised: 10-10-2021
Accepted: 22-10-2021

Key Words:
Agricultural waste
Crop residue
Biosorption
Kinetics
Regeneration

ABSTRACT

Agriculture is the immemorial benefaction of man for the existence and welfare of the human race. Being an agricultural country, it is the prime source of livelihood in India. This review focused on the present scenario of Indian Agriculture with respect to crop production, factors affecting productivity, and agricultural waste-related issues in India. Agrowaste can be helpful to farmers but economic costs are less than the cost of collection, transportation, and processing for profitable use. In this consequence, the review has presented considerable information on the alternative use of agrowaste to control water pollution. The review focused the light on the replacement of conventional chemicals with agro-based waste to develop fully green and sustainable biosorbents. It also highlighted the potential of biosorbents and biosorption technology in terms of their adsorption capacities, cost-effectiveness, binding mechanisms, and interfering factors such as pH, temperature, initial concentration, dose, and pre-treatments. Biosorption isotherms and sorption kinetics models were used for the characterization of agrowaste and developed biosorbent, and recovery of sorbent was also reviewed. The review concluded that further research is required to investigate novel biosorbents that may be a good option for bioremediation for the removal of a large range of toxic heavy metals. The utilization of plant waste as biosorbent will also open a new window of agricultural waste management.

INTRODUCTION

Agricultural Sector in India

Agriculture is the backbone of the Indian economy; it will continue to be so for a long time. It supports about 17 percent of the world's population from 2.3 percent of the world's land area and 4.2 percent of the world's water resources (Pandey 2009). India has adopted modern methods of cultivation and contrived significant progress. Agricultural Science and engineering have altered its image from a "begging bowl" to a "breadbasket" by adapting effective infrastructure and sustainable use of natural resources. Over the last five decades, Indian agriculture has evolved into a mature and modern business. India is the world's second-largest producer of rice, wheat, spices, spice products, and vegetables and fruits (APEDA 2018-19).

Agricultural Waste-Related Issues in India

United Nations defines agricultural waste as waste produced as a result of various agricultural operations (UN, Glossary of Environment Statistics, 1997). Agricultural waste is a non-commodity product of agricultural product production and processing that may contain material that is beneficial to individuals but whose economic value is less than the cost of collection, transport, and processing for profitable use. Agricultural waste can take the form of liquid, slurry, or solids, depending on the system and type of agricultural activity (Obi et al.2016). Unsustainable agricultural development leads to huge adverse effects on the rural and global environment (Nguyen 2017, Pappu et al. 2006).

Crop residue waste: According to the Indian Ministry of New and Renewable Energy (MNRE), the annual generation of crop residues in India is an average of 500 million tons. After the utilization of these crop residues as fodder or fuel still, there is a leftover of 140 Mt of which 92 Mt is burned each year (Ministry of Agriculture, India 2014) The 'rice-wheat cropping system' (RWCS) is the best planting system in South Asia (Hobbs & Morris 1996) which is followed by many Indian states. Rice and wheat contribute about 70% of the crop residues. Based on Jain et al. (2013) and the Intergovernmental Panel on Climate Change (IPCC), more than 25% of crop residues have been burnt on the farm. It was also reported that across all states the fraction of burnt crop residue ranged from 8–80% for paddy waste (Jain et al. 2013) Among various crop residue, major contributors were 43% of rice, wheat 21%, sugarcane 19%, and oilseed 5%

(Sahai et al. 2010). During the post-harvest period, 80% of the crop is burned.

Emission of greenhouse and other gases: Burning crop residues is a major source of GHGs, as well as other chemically relevant trace gases, aerosols, and other hydrocarbons. Burning rice straw emits Carbon (C) as CO_2 (70%), CO (7%), and CH_4 (0.66%) whereas 2.09% of Nitrogen (N) is emitted as N_2O (Ministry of Agriculture, India 2014). Apart from that, large amounts of particulates containing a mixture of organic and inorganic species such as Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Dibenzo-p-dioxins (PCDDs), and Polychlorinated Dibenzofurans (PCDFs) are emitted (PCDFs). Greenhouse gases contribute to global warming and climate change (Gadde et al. 2009). A huge annual welfare loss (Rs. 76 million) in terms of health damage is caused by air pollutants created by agricultural residue open burning (Kumar et al. 2015, Lohan et al. 2017). Furthermore, one of the significant repercussions of stubble burning is the loss of soil flora and fauna, including microbes (Kaur & Rani 2016).

APPLICATION OF AGRICULTURAL WASTE FOR POLLUTION CONTROL

Using agricultural waste products to reduce pollution is a long-term strategy that can also provide additional revenue for producers (Manique et al. 2012). Agricultural waste with carboxyl, hydroxyl, and other active groups can be used as a biomass-based adsorbent to accomplish the "treatment waste by waste" effect (Dai et al. 2018). It was suitable for recovering ecological pollutants due to its loose surface, porosity, exceptional mechanical strength, and chemical stability. Several research papers showed how different forms of agricultural wastes can be used to adsorb metal ions from aqueous solutions (Hossain et al. 2012a, 2012b).

Removal of Inorganic Contaminants

Removal of inorganic contaminants could be carried out using waste biosorbents through modern and traditional treatment methods. The studies carried out by various workers for the application of agrowaste for the removal of inorganic contaminants are given in Table 1.

Removal of Organic Contaminants

The studies carried out by various workers for the application of agrowaste for the removal of organic contaminants are given in Table 2.

Getting Rid of Harmful Gases

The rapid increase of greenhouse gases like carbon dioxide (CO_2) and nitrous oxide (N_2O) is one of the reasons for global warming and climate change (Dai et al. 2018). Hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are common pollutants in the production/processing of oil and gas, wastewater treatment plants, combustion of fossil fuel, and landfill gases, which can cause corrosion and harmful gaseous emissions (Bamdad et al. 2018).

Application of biochar developed by carbonization of leaf waste at 400°C removed 84.2% H_2S successfully from raw biogas in a continuous adsorption tower for 25 min (Sahota et al. 2017). Sugarcane bagasse (SB) and Hickory wood (HW), which were used to make biochar at a higher temperature, had the maximum physisorption of CO_2 (73.55 $mg.g^{-1}$ at 25°C) (Creamer et al. 2014) The CO_2 adsorption efficiency on charcoal rice straw was found to be around 80 $mg.g^{-1}$ at 20 °C in a study (Huang et al. 2015). The highest performance conditions were obtained by treating soybean straw with CO_2 and NH_3 at high temperatures, with the absorptivity of 49.87 $mg.g^{-1}$ (Zhang et al. 2016). The surface chemistry, porous structure, and morphology of activated carbon were studied, and the absorptivity was found to be 78.10 $mg.g^{-1}$ (Shahkarami et al. 2015)

ADSORPTION

Adsorption is a surface phenomenon, in which the transfer of molecules from the bulk solution to the solid surface is done, depending on the concentration gradient (Qiu et al. 2009). This process is parameter-dependent such as molecular weight, shape, or polarity of the adsorbing material, which holds the molecule strongly and makes separation easier. The adsorption rate is equal to the square root of contact time with the adsorbent (Mathew et al. 2016).

Types of Adsorption Processes

The process of adsorption can be achieved by batch, semi-batch, and continuous processes. In batch, processes contact time of adsorbing material and adsorbent play's an important role (Mishra & Tripathi 2008). Adsorbate and adsorbent are attracted to one other by attractive forces such as weak Van der Waals forces or strong chemical bonds. At low temperatures, weak van Der Waals forces are active in physisorption (Fraissard 1997). While chemical forces or chemical bonds are active in chemisorption, its efficacy is determined by the adsorbent's surface area (Apple & Ma 2002).

Factors Affecting the Adsorption Process

Biosorption depends on many factors that are related to environmental conditions that can affect the process. Factors that interfere with the biosorption process are:

Temperature: Biosorption efficiency remains uninfluenced within the range 20-35°C ℃, at high temperatures, e.g.,

Table 1: Application of agrowaste for removal of heavy metals, nitrogen and phosphorus.

Sr. No.	Removal of pollutant	Argowaste as adsorbent	Adsorption capacity ($mg.g^{-1}$) or %	References
1.	Heavy metal			
	Lead (II)	Wheat bran	69-87 $mg.g^{-1}$	Bulut & Baysal 2006
		Coir fibers	263 $mg.g^{-1}$	Kadirvelu & Namasivayam 2000
		Pumpkin waste	14.286 $mg.g^{-1}$	Okoye et al. 2010
		Tea leaves	96%	Ahluwalia & Goyal 2005
		heartwood powder of Areca catechu		
		Acid-modified rice straw	97%	Chakravarty et al. 2010
		Rice straw		
		Plum stone	18.98 $mg.g^{-1}$	Guo et al. 2015
		Banana peels	42.55 $mg.g^{-1}$	Amer et al. 2017
			80.65 $mg.g^{-1}$	Parlayıcı & Pehlivan 2017
			>90%	Ibisi & Asoluka 2018
	Nickel (II)	Tobacco stem	97.32 $mg.g^{-1}$	Rao et al. 2014
		Cocoa shell	97.59 $mg.g^{-1}$	Kalaivani et al. 2014
		Peel orange fruit	96%	Ajmal et al. 2000
		pomegranate peel	52 $mg.g^{-1}$	Bhatnagar & Minocha 2009
	Copper (II)	Mango peel	46.09 $mg.g^{-1}$	Iqbal et al. 2009
		Sorghum bicolor	15.151 $mg.g^{-1}$	Salman et al. 2020
		Sugar beet pulp	28.5 $mg.g^{-1}$	Aksu & Isoglu 2005
		Watermelon shell	9.54 $mg.g^{-1}$	
		Potato peel	84.74 $mg.g^{-1}$	Mohammed & Ibrahim 2016 Guechi & Hamdaoui 2015
	Cadmium (II)	Sorghum bicolour	17.241 $mg.g^{-1}$	Salman et al. 2020
		Banana peels	>90%	Ibisi & Asoluka 2018
		Sawdust	94.02%	Naiya et al. 2008a
		Neem bark	86.24%	Naiya et al. 2008b
	Zinc (II)	Sawdust	87.23%	Naiya et al. 2008a
		Neem bark	84.75%	Naiya et al. 2008b
	Chromium (VI), (III)	Modified groundnut shell	131 $mg.g^{-1}$	Owalude & Tella 2016
		mango kernel	7.8 $mg.g^{-1}$	Rai et al. 2016
		Date palm leaves	98%	Fawzy et al. 2015
		Broad bean shoots	95%	Fawzy et al. 2015
		Banana peels	96%	Ali et al. 2016
	Arsenic (III), (V)	Java plum seeds	97%	Shakoor et al. 2018
		Rice polish	41.18 and 49 µg/ g, respectively	Hasan et al. 2009
		Chir pine leaves		Shafique et al. 2012
		Walnut shell	3.27 $mg.g^{-1}$	Saqib et al. 2013
		Rice husk	88%	Amin et al. 2006
			89% and 87%respectively	
2.	Nitrogen	Banana peels	-	Akpor et al. 2013
	Ammoniacal nitrogen	Sugarcane bagasse ash	60%	Mor et al. 2019
	Phosphate	Rice husk	89%	Mor et al. 2016
		Banana peels	-	Akpor et al. 2013

50°C, biosorption activity and kinetic energy of the adsorbate increases which may destruct the physical structure of the biosorbent. Adsorption reactions are generally exothermic and the degree of adsorption increases with falling temperature (White et al.1997, Abdi et al. 2015). There could be a modification in the equilibrium capacity of the adsorbent for a particular adsorbate due to a change in temperature. There is better adsorption acquired at higher temperatures (Park et al. 2010, Malkoc & Nuhoglu 2005, Goyal et al. 2003).

pH: pH affects the movement of the functional groups in the adsorbent, the solution chemistry of the metals, and the competition between metallic ions (Joo & Hassan 2010). It has been shown that the affinity of cations in the functional groups present on the cellular surface is strongly dependent on the solution pH (Alfarra et al. 2014). The biosorption capacity reduces with low pH values and increases with pH until it reaches optimum pH. Metal ions precipitated due to the high concentration of hydroxyl anions in the solution

Table 2: Application of agrowaste for removal of organic contaminants.

Sr. No.	Removal of pollutant	Argowaste as adsorbent	Adsorption capacity ($mg.g^{-1}$) or %	References
1.	Dyes			
	Methylene Blue Dye	Lemon leaf powder	19.19 $mg.g^{-1}$	Sarath Babu & Yamini 2020
		Cauliflower leaves Rice husk composite	149.22 $mg.g^{-1}$	Ansari et al. 2016
	Azodyes (Congo red, Crystal violet, Methyl orange)	Linseed oil cake	77-81%	Rafique & Zulfiqar 2014
	Synolon black HWF-FS	Fruit shell of Bengal gram *Cucumis sativus*	6.89 $mg.g^{-1}$	Safa 2015
	Acid blue 25		29.41 $mg.g^{-1}$	Krishna et al. 2016
	Crystal violet		40.82 $mg.g^{-1}$	Smitha et al. 2012
2.	Drugs			
	Fluoroquinolone	Rice husk	63.50 $mg.g^{-1}$	Ashrafi et al. 2015
3.	Pesticides 2,4-dichlorophenoxyacetic acid	Bagasse fly ash	7.14 $mg.g^{-1}$	Deokar et al. 2016
4.	Aromatic compounds			
	phenol	*Acacia tortilis* pod shell	95%	Malakootian et al. 2018
		Rice husk ash	95%	Mandal et al. 2019
5.	Oil substances	Banana peels	5-7 $mg.g^{-1}$	Alaa El-Din et al. 2017

when the pH was greater than 5.5. As a result, the trials were not carried out at pH levels higher than 5.5 (Witek-Krowiak et al. 2010)

Pre-treatment: Because of the nature of biosorbent application, physical treatments such as drying, boiling, autoclaving, and mechanical disruption will cause changes in binding properties. Chemical treatments, such as alkali treatment, improve biosorption capacity, which is especially visible in some fungal systems with higher metal affinities (Abdi & Kazemi 2015).

Acidity: Biosorption is comparable to the ion-exchange process, in which biomass is used as a natural ion-exchange medium with weakly acidic and basic groups (Ahalya et al. 2003). Metal biosorption has been shown to be strongly pH-dependent in almost every system studied. At low pH, cations and protons compete for binding sites, which explains why metal absorption of Cu, Cd, Ni, Co, and Zn is normally reduced (Obi et al 2016).

Biomass concentration: The concentration of biomass in solution influences the specified metal uptake (Modak & Natarajan 1995). The adsorption of metal by biomass is shown to be greater at low cell densities at a given equilibrium concentration (Gourdon et al. 1990). Because an increase in biosorbent concentration actively encourages interference between binding sites, the specific metal absorption increases at lower biomass concentrations (Zouboulis et al. 1997). Metal ions cannot get to the exact location of the binding site because of the high biomass concentration (Malkoc & Nuhoglu 2005).

Initial metal ion concentration: The initial metal ion concentration provides an important driving force for controlling all-metal mass transfer resistance between the fluid and adsorbed phases (Kutahyali et al. 2010). When the initial metal ion concentration is high, all-metal ions in the solution engage with binding sites, accelerating adsorption by roughly 99% until saturation is reached.

Agitation speed: Increasing the agitation speed accelerates the biosorption of adsorptive metal by lowering the mass transfer resistance, however, it may harm the biosorbent's physical structure (Park et al. 2010)

Contact time: Physical adsorption of metal at the cell surface is claimed to be fast and occurs in a short period. The active sites on the adsorbent become occupied as the contact time increases and gradually diminishes with time until it reaches equilibrium (Mishra & Tripathi 2008, Witek-Krowiak et al. 2010).

Biosorbent size: Decrease biosorbent size is favorable for batch process due to the higher surface area of the biosorbent, but due to its low mechanical strength and clogging of the column, it is not advantageous for column process (Park et al. 2010, Abdi et al. 2015).

Other pollutant concentration: Various metals and coexisting metals present in wastewater compete with a target

pollutant for binding sites and can form any complex with it. This can be reduced by the biosorptive removal of the target metal ions (Park et al. 2010)

MECHANISM OF HEAVY METAL CAPTURE

Weak forces, chemical reactions, and ionic strength interact in biosorption, resulting in stronger binding. (Achak et al. 2009) These interactions can occur inside or outside of the pores, as well as on the surface of agricultural wastes (Silva et al. 2013). The actual mechanism of biosorption is still a mystery. Although several mechanisms for heavy metal ion binding to sorbent surfaces have been suggested (Salman et al. 2015) Adsorption mechanisms such as chemisorption, ion exchange, surface adsorption, complexation reactions, electrostatic interactions, diffusion via pores, and others are predicated by ionic interactions that occur during adsorption. Fig. 1 shows the many pathways involved in the biosorption of heavy metals

It is possible that different mechanisms can operate concurrently to varying degrees. The study of mechanisms involved in the uptake of Cr (III) and Cr (VI) by *Cupressus lusitanica* bark revealed that the principal mechanisms for Cr (III) biosorption is found to be Ion exchange and electrostatic interaction (Netzahuatl-Munoz et al. 2012). In the adsorption of Cu (II), Zn (II), and Pb (II) ions using orange peels, the process was governed by ion-exchange predominantly (Feng & Guo 2012). The study of removal of Pb (II) from aqueous solution using *Triticum aestivum* followed adsorption as well as ion-exchange mechanism (Farooq et al. 2007). Similar results were found using potato peel for Pb (II), Zn (II), and Cd (II) adsorption (Taha et al. 2011).

The dominant mechanisms involved in the biosorption of Cr (III) and Cu (II) onto soybean meal waste are ion exchange, precipitation, and chelation by hydroxyl and carboxyl groups. (Witek-Krowiak et al. 2016). The study stated that in the removal of Pb (II) from an aqueous solution, the prime responsible groups were the carboxyl and hydroxyl groups that existed on the surface of sorghum biomass (Salman et al. 2014). The study of Ni (II) sorption onto *Caesalpinia bonducella* seed powder described that the functional groups hydroxyl, amine, carboxyl, and carbonyl were responsible for the adsorption mechanism. (Gutha et al. 2011) While the involvement of carboxyl and hydroxyl groups in the uptake of the metal ions by grafted polymerization-modified orange peel was also explored (Feng et al. 2011) Adsorption of low concentrations of lead, zinc, and cobalt (less than 100 $mg.L^{-1}$) from an aqueous solution utilizing a mangosteen shell explained the involvement of amino and carboxyl groups (Zein et al. 2010) Various other studies affirmed the effective interaction of carboxyl and hydroxyl groups towards heavy metal ions (Vieira et al. 2012, Araújo et al. 2010, Martín-Lara et al. 2013). As biosorption process may be influenced by conditions such as the chemical state of binding sites, the number of binding sites, their availability, and attraction between the sites and metal ions (Volesky 1994)

ADSORPTION ISOTHERMS

Adsorption isotherm represents the equilibrium relationship between the concentration of sorbate in the solution and the adsorbate concentration in the adsorbent at a constant temperature (Vijayaraghavan & Yun 2008). It is a plot of the amount of sorbate per unit weight of adsorbent q_e versus the equilibrium solute concentration in the solution C_e. Adsorp-

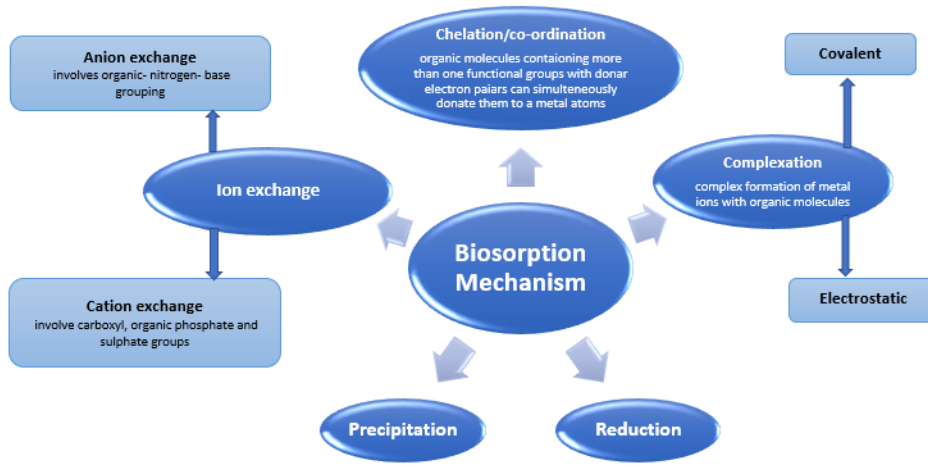

Fig.1: Mechanism of biosorbents.

tion isotherm is used to calculate the capacity of a biosorbent to attract the adsorbate. Some typical isotherm shapes are represented as arithmetic graphs in Fig. 2 (Abbas et al. 2014)

From the above curves, it will be noticed that the adsorption is a specific property that depends on the type of the adsorbate-adsorbent system (Vijayaraghavan & Yun 2008). Various isotherm equations exist to analyze the equilibrium behavior of an adsorption system, but the well-known adsorption isotherm models used for single solute systems are Langmuir (1918) and Freundlich's (1906) isotherms. Both adsorption isotherm models appear to be more appropriate for explaining the relationship between q (quantity adsorbed at equilibrium, $mg.g^{-1}$) and C (concentration of adsorbates remained in the bulky solution at the equilibrium, $mg.L^{-1}$). Description and nomenclature of different adsorption equilibrium models are given in Table 3.

Literature shows that most of the studied biosorption systems followed the Langmuir equilibrium model which indicated that monolayer adsorption was the possible mechanism of metal ions retention on the biomass surface (Khairia & Al-Qahtani 2016, Fawzy et al. 2015, Rai et al. 2016, Salman et al. 2020) Freundlich isotherm model elucidated the adsorption on heterogeneous surfaces with interactivity occurring between the adsorbed molecules and is not restricted to a monolayer formation (Febrianto et al. 2009) Some studies revealed that the metal ion adsorption follows the Freundlich model more as compared to others (Guiza 2017, Sadeek et al. 2015, Pino et al. 2006, Naiya et al.2008b, Giwa et al. 2013)

ADSORPTION KINETICS

Adsorption kinetics is the measurement of the adsorption uptake over time at constant pressure or concentration and is applied to measure the adsorbate diffusion in the pores. Numerous studies have been evaluated using the pseudo-first-order kinetic model and pseudo-second-order kinetic model.

Pseudo-First-Order Model

Pseudo-first-order is derived from the fact that the rate of reaction is proportional to the number of free accessible binding sites present on the biosorbent material (Ho et al.2000)

The linear form of the Lagergren pseudo-first-order rate statement is:

$$\text{In } (q_e - q_t) = \text{In } q_e - k_1 t$$

Where, q_e and q_t are the amounts of metal ion absorbed ($mg.g^{-1}$) on absorbent at equilibrium at time t respectively. k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). Taking ln (q_e - q_t) on the y-axis and 't' on the y-axis, a linear plot is generated having the slope '$-k_1$' and intercept 'ln q_e'. From value of intercept 'q_e' can be calculated and compared to the experimental value. The precision between the calculated and experimental 'q_e' values gives an idea about the possible order of the biosorption process.

Pseudo-Second-Order Model

The pseudo-second-order model is derived from the fact that the rate of biosorption is proportional to the square of several active binding sites on the surface of the biosorbent.

The linear form of pseudo-second-order model expression is:

$$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \frac{t}{q_e}$$

Where, k_2 ($g.mg^{-1}.min^{-1}$) is the rate constant of the pseudo-second-order kinetic equation, q_e and q_t is the amount of metal ion absorbed ($mg.g^{-1}$) on absorbent at equilibrium at time t respectively. A plot between $(t.q_t)^{-1}$ and (t) should generate a straight-line having slope of $(1.q_e^{-1})$ and intercept $(1.k_2q_e^{-2})$. The calculated q_e value compared with that of the experimental value. Another important factor that determines the applicability of a specific model to the experimental ki-

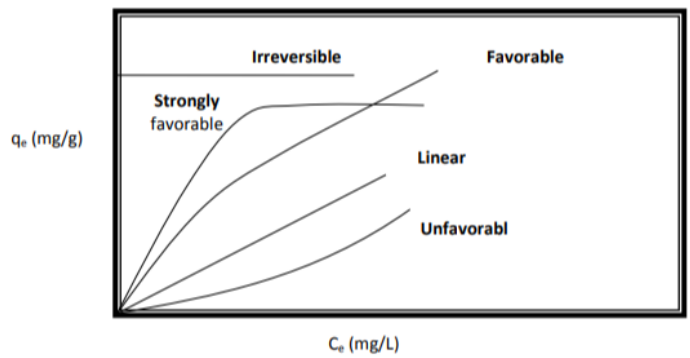

Fig. 2: Types of adsorption equilibrium isotherm relations (Abbas et al. 2014).

Table 3: Adsorption equilibrium models: description and nomenclature.

Isotherm Model	Model equation	nomenclature	Reference
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	q_e (mg/g) = adsorption capacity at equilibrium; C_e (mntg.L^{-1}) = metal concentration at equilibrium; q_m (mg.g^{-1}) = monolayer adsorption capacity of adsorbent; KL= Langmuir constant representing energy constant in relation to the heat of adsorption.	Langmuir 1918
Freundlich	$q_e = K_F C_e^{1/n}$	q_e (mg.g^{-1}) = adsorption capacity at equilibrium; C_e (mg.L^{-1}) = metal concentration at equilibrium; K_F (L.g^{-1}) and n are indicative of the extent of adsorption and the degree of non-linearity, respectively	Freundlich 1906
Redlich-Peterson	$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^{\beta}}$	K_{RP} = Redlich-Peterson constant (L.g^{-1}); αR = constant having unit (L.mg^{-1}); C_e (mg.L^{-1}) = metal concentration at equilibrium; β = exponent that lies between 0–1	Redlich and Peterson 1959
Koble -Corrigan	$q_e = \frac{A_{KC} C_e^{p}}{1 + B_{KC} C_e^{p}}$	A_{KC}, $B_{KC,}$ and p are the Koble -Corrigan parameters. This model is valid when p > 1	Koble and Corrigan 1952
Sips	$q_e = \frac{K_s C_e^{\beta_s}}{1 + \alpha_s C_e^{\beta_s}}$	Ks (l.g^{-1}) and αs (l.mg^{-1}) are the Sips isotherm constants and β is the exponent which lies between 1 and 0.	Sips 1948
Tempkin	$q_e = 1n(K_T C_e)$ $B_1 = \frac{RT}{K_T}$	B_1 (kJ.mol^{-1}) = heat of adsorption; K_T (L mol.kJ.g^{-1}) = adsorption potential; qe (mg.g^{-1}) = adsorption capacity at equilibrium; Ce (mg.L^{-1}) = metal concentration at equilibrium	Tempkin and Pyzhev 1940
Dubinin– Radushkevich	$q_e = q_m e^{-B_{DR} \varepsilon^2}$	q_e (mg.g^{-1}) = adsorption capacity at equilibrium; q_m (mg.g^{-1}) = Dubinin– Radushkevich monolayer capacity; BDR= constant related to sorption energy; ε= Polanyi potential	Dubinin and Radushkevich 1947
Flory-Huggins	$\frac{\theta}{C_0} = K_{FH}(1 - \theta)^{n}$	θ =degree of surface coverage; K_{FH} and n are the indications of its equilibrium constant and model exponent.	Horsfall and Ayebaemi, 2005
Hill	$q_e = \frac{q_m C_e^{n}}{K_D + C_e^{n}}$	-	Hill 1910
Unilan	$q_e = \frac{q_m}{S} 1n\left[\frac{1 + d\exp(S) C_e}{1 + d\exp(-S) C_e}\right]$	S and d = temperature-dependent model constants.	Ismadji and Bhatia 2000
Khan	$q_e = \frac{q_m b_k C_e}{(1 + b_k C_e)^{a_k}}$	b_k and a_k = model constant and model exponent	Khan et al. 1997
Radke-Prausnitz	$q_e = \frac{\alpha_R r_R C_e^{\beta R}}{\alpha_R + r_R C_e^{\beta R - 1}}$	β_R is the model exponent, and α_R and r_R are model constants.	Vijayaraghavan et al. 2006
Toth	$q_e = \frac{q_m C_e}{(b_T + C_e^{n})^{1/n}}$	q_e (mg.g^{-1}) = adsorption capacity at equilibrium; C_e (mg.L^{-1}) = metal concentration at equilibrium; b_T (mg.g^{-1}) = Toth maximum adsorption capacity; q_m = the Toth constant; n = the Toth model exponent	Toth 1971

netic data is the coefficient of determination R^2. Its value of close to 1 (R^2>0.98) shows the fitness of experimental data to the kinetic model. The ideal pseudo-second-order model indicates that there is a binding between one divalent metal and two monovalent binding sites (Salman et al. 2014). From the literature review, it is worth noting that numerous other studies have recorded the best fit of the pseudo-second-order model to biosorption kinetic data. (Salman et al. 2020, Sadeek et al. 2015, Saman et al. 2019, Santos et al. 2010, Chakravarty et al. 2010).

RECOVERY AND RESTORATION

Reuse of bio sorbent could be achieved by using restoration and regeneration for a low amount of pollutants (Khatoon & Rai 2016, Carolin et al. 2017). It is preferable that the desorbing medium should not be damaging to the biosorbent, but should help to recover, the loaded metals onto the surface of the biomass after biosorption (Gupta et al. 2015). The study of adsorbent reclamation can be utilized for the prevention of secondary pollution resulted due to waste adsorbents (Anirudhan & Sreekumari 2011). Literature reveals that Acids (such as HCl, H_2SO_4, and HNO_3) were mostly used in the case of recovery of heavy metal(s) from bio adsorbents (Lata et al. 2014).

The results derived from the study for the percentage recovery of Ni (II) and Cu (II) ions using the *Delonix regia* pods revealed that at different desorbing medium concentrations, the percentages recovery of metal ions was different. The studies also affirmed that a comparatively less concentration of acid is required to recover more than 50 % of the metal ions from the biomass (Babalola et al. 2020). An investigation was carried out to determine the reusability potential and stability of the pre-treated watermelon (*Citrullus lanatus*) rind showed 98.1% recovery of $Pb2^+$ ions (Lakshmipathya & Saradab 2015).

The study of Sorghum root biomass for removal of Cu(II) and Cr(VI) ions from an aqueous medium was carried out using HCl and HNO_3 as eluting agents. The formula used to calculate the desorption efficiency of biomass was,

$$desorption\ efficiency = \frac{amount\ of\ metal\ ions\ desorbed}{amount\ of\ metal\ ions\ adsorbed} \times 100$$

Using HCl as eluting agent desorption efficiency of Cu(II) and Cr(VI) ions from sorghum root biomass was shown to be 93 and 96%, whereas using HNO_3 desorption efficiency was 84 and 89% respectively (Choudhary et al. 2014).

In the study of the use of NaOH, HNO_3, and EDTA as eluting agents for desorption of Cr(III) ions from sorghum stalk biomass, EDTA showed high desorbing efficiency in comparison with NaOH and HNO_3 for Cr(III) ions due to the nature of metal-sorghum bonding. Desorption percentages for Cr(III) ions using 0.05 M EDTA and 0.1 M EDTA were shown to be 75% and 71%, respectively at 55°C (Bernardo et al. 2009)

CONCLUSION

Being the second-largest economy with year-round crop cultivation, India generates abundant agricultural waste including crop residue. Agricultural waste when not effectively used increases the burden of rural agricultural production and also cause pollution in the rural environment. Multiple-use of agro wastes can productively minimize air pollution by the burning of crops.

The utilization of agrowaste in environmental remediation furnishes an economical substitute for extracting toxic heavy metal ions from real wastewater and supports in recovering environmental damages. As a biosorbent shows an affinity for certain metals, a composite biosorbent containing more than one biosorbent can be tested for the removal of multiple metal ions from contaminated water.

From the literature review, it becomes clear that an appropriate modification method for the preparation of biosorbent can improve the adsorptive capacity of agricultural waste. Good removal efficiencies proved that; biomass-based adsorbent is an absolute solution to cope with heavy metal contamination.

Agricultural wastes-based biosorbent with uneven structures that contain high binding sites with metal craving functional groups like hydroxyl, carboxyl amine, and other active groups, that effectively remove pollutants.

The process of biosorption is influenced by pH, dose, temperature, concentration particle size, and other factors. The majority of the studies emphasized studying the biosorption process concerning kinetic, equilibrium, and thermodynamics, which proclaimed that Langmuir and pseudo-second-order models are dominant isotherm and kinetic models, respectively.

The study of regeneration of biosorbent unveiled that a single regenerating agent effective for one adsorbent was not necessarily efficacious for another adsorbent. Further exploration is desired to invent the best possible eluent that can be relevantly used for many adsorbents.

The development of effective green conversion and technology will be an indicator of the development of biological adsorption. Using agricultural waste as a biomass adsorbent can not only eliminate the damage to the current practice of agricultural waste but also are of significant economic benefits.

REFERENCES

Abbas, S.H, Ibrahim, M., Ismail, I.M., Tarek, M., Mostafa, T.M., Abbas, H. and Sulaymon, A.H. 2014. Biosorption of heavy metals: A review. J. Chem Sci. Technol., 3(4): 74-102.

Abdi, O. and Kazemi M. 2015. A review study of biosorption of heavy metals and comparison between different biosorbents. J. Mater. Environ. Sci., 6(5): 1386-1399.

Achak, M., Hafidi, A., Ouazzani, N., Sayadi, S. and Mandi, L. 2009. Low-cost biosorbent "banana peel" for the removal of phenolic compounds from olive mill wastewater: Kinetic and equilibrium studies. J. Hazard. Mater., 166(1): 117–125. doi: 10.1016/j.jhazmat.2008.11.036.

Agricultural and Processed Food Products Export Development Authority (APEDA), Department of Commerce and Industry, Union Budget 2018-19, Ministry of Agriculture and Farmers Welfare, Crisil.

Ahalya, N., Ramachandra, T.V. and Kanamadi, R.D. 2003. Biosorption of heavy metals. Res. J. Chem. Environ., 7: 71-79, 2003.

Ahluwalia, S.S. and Goyal, D. 2005. Removal of heavy metals by waste tea leaves from aqueous solution. Eng. Life Sci., 5(2): 158-162. DOI: 10.1002/elsc.200420066.

Ajmal, M., Rao, R.A.K., Ahmad, R. and Ahmad, J. 2000. Adsorption studies on *Citrus reticulata* (fruit peel of orange): Removal and recovery of Ni (II) from electroplating wastewater. J. Hazard. Mater., 79(1-2): 117-131. doi:10.1016/s0304-3894(00)00234-x.

Akpor, O.B., Nwonuma, C.O., Edewor-Kuponiyi, T.I. and Amira, O.J. 2013. The role of ripe *Musa sapientum* (plantain) peels in the removal of phosphorus and nitrogen from an aqueous solution. J. Biol. Agric. Healthcare, 3(13): 2013.

Aksu, Z. and Isoglu, I.A. 2005. Removal of copper (II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp. Process Biochem., 40(9): 3031-3044. doi: 10.1016/j.procbio.2005.02.004.

Alaa El-Din, G., Amer, A.A., Malsh, G. and Hussein M. 2017. Study on the use of banana peels for oil spill removal. Alex. Eng. J., 57(3): 2061-2068. http://doi.org/10.1016/j.aej.2017.05.020.

Alfarra, R.S., Ali, N.E. and Yusoff, M.M. 2014. Removal of heavy metals by natural adsorbent: Review. Int. J. Biosci., 4(7): 130-139.

Ali, A., Saeed, K. and Mabood, F. 2016. Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent. Alex. Eng. J., 55(3): 2933-2942. http://dx.doi.org/10.1016/j.aej.2016.05.011.

Amer, H., El-Gendy, A. and El-Haggar, S. 2017. Removal of lead (II) from aqueous solutions using rice straw. Water Sci. Technol., 76(5): 1011-1021.

Amin, M.N., Kaneco, S., Kitagawa, T., Begum, A., Katsumata, H., Suzuki T. and Ohta, K. 2006. Removal of arsenic in aqueous solutions by adsorption onto waste rice husk. Industrial & Engineering Chemistry Research, 45(24): 8105-8110. doi:10.1021/ie060344j.

Anirudhan, T.S. and Sreekumari, S.S. 2011. Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons. J. Environ, Sci., 23(12): 1989-1998. doi:10.1016/s1001-0742(10)60515-3.

Ansari, S.A., Khan F. and Ahmad, A. 2016. Cauliflower leave, an agricultural waste biomass adsorbent, and its application for the removal of mb dye from aqueous solution. Equilib. Kinetics Thermody. Stud., 54: 111. doi.org/10.1155/2016/8252354.

Apple, C. and Ma, L. 2002. Heavy metals in the environment concentration, pH, and surface charge effects Cd and Pb sorption in three tropical soils. J. Environ. Qual., 21: 581-589.

Araújo, C.S.T., Alves, V.N., Rezende, H.C., Almeida, I.L.S., de Assunção, R.M.N., Tarley, C.R.T. and Coelho, N.M.M. 2010. Characterization and use of Moringa oleifera seeds as biosorbent for removing metal ions from aqueous effluents. Water Sci. Technol., 62(9): 2198-2203. doi:10.2166/wst.2010.419

Ashrafi, S.D., Kamani, H., Jaafari, J. and Mahvi A.H. 2015. Experimental design and response surface modeling for optimization of fluoroquinolone removal from aqueous solution by NaOH-modified rice husk. Desalination and Water Treatment. doi:10.1080/19443994.2015.1080188.

Babalola, B.M., Babalola, A.O., Akintayo, C.O., Lawal, O.S., Abimbade, S.F., Oseghe, E.O., Akinola, L.S. and Ayanda, O.S. 2020. Adsorption and desorption studies of *Delonix regia* pods and leaves: removal and recovery of Ni (II) and Cu (II) ions from aqueous solution. Drink. Water. Eng. Sci., 16: 15-27. https://doi.org/10.5194/dwes-13-15-2020

Bamdad, H., Hawboldt, K. and MacQuarrie, S. 2018. A review on common adsorbents for acid gas removal: Focus on biochar. Renew. Sustain Energy, 81: 261. http://doi.org/10.1016/j.rser.2017.05.261

Bernardo, G.R.R., Rene, R.M. J. and Catalina, M.. 2009. Chromium (III) uptake by agrowaste biosorbents: Chemical characterization, sorption-desorption studies, and mechanism. J. Hazard. Mater., 170(2-3): 845-854. doi: 10.1016/j.jhazmat.2009.05.046

Bhatnagar, A. and Minocha, A.K. 2009. Biosorption optimization of nickel removal from water using *Punica granatum* peel waste. Coll. Surf B Biointerfaces, 76(2): 544-548. https://doi.org/10.1016/j.colsurfb.2009.12.016

Bulut, Y. and Baysal, Z. 2006. Removal of Pb (II) from wastewater using a wheat brand. J. Environ. Manag., 78(2): 107-113.

Carolin, C.F., Kumar, P.S., Saravanan, A., Joshiba, G.J. and Naushad, M. 2017. Efficient techniques for the removal of toxic heavy metals from the aquatic environment: A review. J. Environ. Chem. Eng., 5(3): 2782-2799. http://dx.doi.org/doi:10.1016/j.jece.2017.05.029

Chakravarty, P., Sarma, N.S. and Sarma, H.P. 2010. Biosorption of cadmium (II) from aqueous solution using heartwood powder of Areca catechu. Chem. Eng. J., 162(3): 949-955.

Choudhary, S., Goyal, V. and Singh, S. 2014. Removal of copper (II) and chromium (VI) from aqueous solution using sorghum roots (S. bicolor): a kinetic and thermodynamic study. Clean Technol. Environ. Policy, 17(4): 1039-1051. doi:10.1007/s10098-014-0860-2.

Creamer, A.E., Gao, B. and Zhang, M. 2014. Carbon dioxide capture using biochar produced from sugarcane bagasse and hickory wood. Chem. Eng. J., 249: 174-179. doi: 10.1016/j.cej.2014.03.105

Dai, Y., Sun, Q., Wang, W., Lu, L., Liu, M., Li, J., Yang, S., Sun, Y., Zhang, K., Xu, J., Zheng, W., Hu, Z., Yang, Y., Gao, Y., Chen, Y., Zhang, X., Gao, F. and Zhang, Y. 2018. Utilizations of agricultural waste as adsorbent for the removal of contaminants: A review. Chemosphere, 211: 235-253. DOI: 10.1016/j.chemosphere.2018.06.179

Deokar, S.K., Mandavgane, S.A. and Kulkarni, B.D. 2016. Adsorptive removal of 2,4-dichlorophenoxyacetic acid from aqueous solution using bagasse fly ash as an adsorbent in batch and packed-bed techniques. Clean Technol. Environ. Policy, 18(6): 1971-1983. doi:10.1007/s10098-016-1124-0

Dubinin, M.M. and Radushkevich, L.V. 1947. The equation of the characteristic curve of activated charcoal. Proceed. Acad. Sci. Phys. Chem. Section, 55: 331.

Farooq, U., Khan, M.A. and Athar, M.2007. *Triticum aestivum*: A novel biosorbent for lead (II) ions. Agrochimica, 51(6): 309-318.

Fawzy, M., Nasr, M., Abdel-Gaber, A. and Fadly, S. 2015. Biosorption of Cr (VI) from aqueous solution using agricultural wastes, with an artificial intelligence approach. Sep. Sci. Technol., 51(3): 416-426. http://dx.doi.org/10.1080/01496395.2015.1115068

Febrianto, J., Kosasih, A.N., Sunarso, J., Ju, Y.H., Indraswati, N. and Ismadji, S. 2009. Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. J. Hazard. Mater., 162(2-3): 616-645. doi: 10.1016/j.jhazmat.2008.06.042

Feng, N. and Guo, X. 2012. Characterization of adsorptive capacity and mechanisms on adsorption of copper, lead, and zinc by modified orange peel. Transact. Nonferr. Metals Soc. China, 22(5): 1224-1231. doi:10.1016/s1003-6326(11)61309-5

Feng, N., Guo, X., Liang, S., Zhu, Y. and Liu, J. 2011. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. J. Hazard. Mater., 8: 114. DOI:101016/jjhazmat2010.08.114

Fraissard, J.P. 1997. Physical Adsorption: Experiment, Theory, and Applications. Vol. 491. Springer Science & Business Media, Berlin, Germany.

Freundlich, H.M.F. 1906. Over the adsorption in solution. J. Phys. Chem., 57: 385-471.

Gadde, B., Bonnet, S., Menke, C. and Garivait, S. 2009. Air pollutant emissions from rice straw open field burning in India, Thailand, and the Philippines. Environ. Pollut., 157(5): 1554-1558. doi: 10.1016/j.envpol.2009.01.004.

Giwa, A.A., Bello, I.A., Oladipo, M.A. and Adeoye, D.O. 2013. Removal of cadmium from wastewater by adsorption using the husk of melon (*Citrullus lanatus*) seed. Int. J. Basic Appl. Sci., 2(1): 110-123.

Gourdon, P., Bhande, S., Rus, E. and Sofer, S.S. 1990. Comparison of cadmium biosorption by gram-positive and gram-negative bacteria from activated sludge. Biotechnol. Lett., 12: 839-842.

Goyal, N., Jain, S.C. and Banerjee, U.C. 2003. Comparative studies on the microbial adsorption of heavy metals. Adv. Environ. Res., 7: 311-319.

Guechi, E.K. and Hamdaoui, O. 2015. Evaluation of potato peel as a novel adsorbent for the removal of Cu (II) from aqueous solutions: equilibrium, kinetic, and thermodynamic studies. Desalin. Water Treat., 57(23): 10677-10688.

Guiza, S. 2017. Biosorption of heavy metal from aqueous solution using cellulosic waste orange peel. Ecol. Eng., 99: 134-140. doi: 10.1016/j.ecoleng.2016.11.043

Guo, L., Liang, L.Y., Wang, Y.J. and Liu, M.D. 2015. Biosorption of Pb2+ from aqueous solution by rice straw modified with citric acid. Environ. Prog. Sustain. 35(2): 359-367.

Gupta, V.K., Nayak, A. and Agarwal, S. 2015 Bioadsorbents for remediation of heavy metals: Current status and their prospects. Environ. Eng. Res., 20(1): 1-18. DOI: https://doi.org/10.4491/eer.2015.018

Gutha, Y., Munagapati, V.S., Alla, S.R. and Abburi, K. 2011. Biosorptive removal of Ni (ii) from aqueous solution by *Caesalpinia bonducella* seed powder. Sep. Sci. Technol., 46(14): 2291-2297. doi:10.1080/01496395.2011.590390

Hasan, S.H., Ranjan, D. and Talat, M. 2009. Rice polish for the removal of arsenic from aqueous solution: optimization of process variables. Ind. Eng. Chem. Res., 48(9): 4194-4201. doi:10.1021/ie801822d

Hill, A.V. 1910. The possible effect of aggregation of molecules of hemoglobin on its dissociation curve. J. Physiol,40(4), iv-vii.

Ho, Y.S., Ng, J.C.Y. and McKay, G. 2000. Kinetics of pollutant sorption by biosorbents: Review. Sep. Purif. Methods, 29(2): 189-232.

Hobbs, P. and Morris, M. 1996. Meeting South Asia's Future Food Requirements from Rice-Wheat Cropping Systems: Priority Issues Facing Researchers in the Post-Green Revolution Era. NRG Paper 96-01, CIMMYT, Mexico, pp. 1-56.

Horsfall, M. and Ayebaemi, I. 2005. Equilibrium sorption study of Al^{3+}, $Co^{2+,}$ and Ag^{+} in aqueous solutions by fluted pumpkin (*Telfairia Occidentalis* HOOK) Waste Biomass. Spiff Acta. Chim. Slov., 52: 174-181.

Hossain, M.A., Ngo, H.H., Guo, W. S. and Setiadi T. 2012. Adsorption and desorption of copper (II) ions onto garden grass. Bioresour. Technol., 121: 386-395. doi: 10.1016/j.biortech.2012.06.119.

Hossain, M.A., Ngo, H.H., Guo, W.S. and Nguyen, T.V. 2012. Palm oil fruit shells as biosorbent for copper removal from water and wastewater: Experiments and sorption models. Bioresour. Technol., 113: 97-101. doi: 10.1016/j.biortech.2011.11.111.

Huang, Y.F., Chiueh, P.T., Shih, C.H., Lo, S.L., Sun L., Zhong Y. and Qiu, C. 2015. Microwave pyrolysis of rice straw to produce biochar as an adsorbent for CO2 capture. Energy, 84: 75-82. doi: 10.1016/j.energy.2015.02.026.

Ibisi, N.E. and Asoluka, C.A. 2018. Use of agro-waste (Musa paradisiaca peels) as a sustainable biosorbent for toxic metal ions removal from contaminated water. Chem. Int., 4(1): 52-59.

Iqbal, M., Saeed, A. and Kalim, I. 2009. Characterization of adsorptive capacity and investigation of the mechanism of Cu^{2+}, Ni^{2+} and Zn^{2+} adsorption on mango peel waste from constituted metal solution and genuine electroplating effluent. Sep. Sci. Technol., 44(15): 3770-3791.

Ismadji, S. and Bhatia, S.K. 2000. Adsorption of flavor esters on granular activated carbon.Canad. J Chem. Eng., 78(5): 892-901. doi:10.1002/cjce.5450780506.

Jain, N., Bhatia, A. and Pathak, H. 2013. Emission of air pollutants from crop residue burning in India. doi: 10.4209/aaqr.2013.01.0031

Joo, J. and Hassan, S.H.A. 2010. Comparative study of biosorption of Zn (II) by *Pseudomonas aeruginosa* and *Bacillus cereus*.Int. Biodetere. Biodegrad., 64(8): 734-741. doi: 10.1016/j.ibiod.2010.08.007.

Kadirvelu, K. and Namasivayam, C. 2000. Agricultural by-product as metal adsorbent: sorption of lead (II) from aqueous solution onto coir pith carbon. Environ. Technol., 22(10): 1091-1097.

Kalaivani, S.S., Vidhyadevi, T., Murugesan, A., Baskaralingam, P., Anuradha, C.D., Ravikumar, L. and Sivanesan, S. 2014. Equilibrium and kinetic studies on the adsorption of Ni (II) ion from an aqueous solution using the cocoa shell. Desal. Water Treat., 54: 1629-1641.

Kaur, A. and Rani J. 2016. An approach to detect stubble burned areas in Punjab by digitally analyzing satellite images. J. Res., 2(6): 2395-3411

Khairia, M. and Al-Qahtani, M. 2015. Water purification uses different waste fruit cortexes for the removal of heavy metals. J. Taibah Univ. Sci., 10(5): 700-708. Doi: 10: 1016/j.jtusci.2015.09.001

Khan, A.R., Attaullah, R. and Al-Haddad, A. 1997. Equilibrium adsorption studies of some aromatic pollutants from dilute aqueous solutions on activated carbon at different temperatures. J. Coll. Interface Sci., 194(1): 154-165. doi:10.1006/jcis.1997.5041

Khatoon, H. and Rai, J.N. 2016. Agricultural waste materials as biosorbents for the removal of heavy metals and synthetic dyes: A review. Oct. Jour. Env. Res., 4(3): 208-229.

Koble, R.A. and Corrigan, T.E. 1952. Adsorption isotherms for pure hydrocarbons. Ind. Eng. Chem., 44(2): 383-387. doi:10.1021/ie50506a049.

Krishna, L.S., Yuzir, A., Yuvaraja, G. and Ashok Kumar, V. 2016. Removal of Acid Blue25 from aqueous solutions using Bengal gram fruit shell (BGFS) biomass. Int. J. Phytoremed., 19(5): 431-438. doi:10.1080/15226514.2016.1244161.

Kumar, P., Kumar, S. and Joshi, L.2015. Socioeconomic and environmental implications of agricultural residue burning: S case study of Punjab, India. Environ. Sci., 2015: 144.

Kutahyali, C., Sert, S., Cetinkaya, B., Inan, S. and Eral, M. 2010. Factors affecting lanthanum and cerium biosorption on *Pinus brutia* leaf powder.Sep. Sci. Technol., 45: 1456-1462.

Lakshmipathya, R. and Saradab, N.C. 2015. Metal ion-free watermelon (*Citrullus lanatus*) rind as adsorbent for the removal of lead and copper ions from an aqueous solution. Desal. Water Treat., 57(33): 1-11. DOI: 10.1080/19443994.2015.1072064.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica, and platinum. J. Am. Chem. Soc., 40(9): 1361-1403. doi:10.1021/ja02242a004.

Lata, S., Singh, P.K. and Samadder, S.R. 2014. Regeneration of adsorbents and recovery of heavy metals: a review. Int. J. Environ. Sci., 12(4): 741. DOI 10.1007/s13762-014-0714-9.

Lohan, S.K., Jat, H.S., Yadav, A.K., Sindhu, H.S., Jat, M.L., Choudhary, M., Peter, J.K. and Sharma, P.C. 2017. Burning issues of paddy residue management in northwest states of India. Renew. Sustain. Energy Rev., 81: 693-706. http://dx.doi.org/10.1016/j.rser.2017.08.057.

Malakootian, M., Hossein, K., Mahvi, A.H., Mansoorian, H.J. and Khanjani, N. 2018. Agrowaste-based eco-friendly bio-adsorbent for the removal of phenol: adsorption and kinetic study by *Acacia tortilis* pod shell. Chiang Mai J. Sci., 45(1): 355-368. http://epg.science.cmu.ac.th/ejournal.

Malkoc, E. and Nuhoglu, Y. 2005. Investigations of nickel (II) removal from aqueous solutions using tea factory waste. J. Hazard. Mater., 127(1-3): 120-128. doi: 10.1016/j.jhazmat.2005.06.030.

Mandal, A., Mukhopadhyay, P. and Das, S.K. 2019. The study of adsorption efficiency of rice husk ash for removal of phenol from wastewater with low initial phenol concentration. SN Appl. Sci., 129: 1992 |https://doi.org/10.1007/s42452-019-0203-3.

Manique, M.C., Faccini, C.S., Onorevoli, B., Benvenutti, E.V. and Caramão E.B. 2012. Rice husk ash is an adsorbent for purifying biodiesel from waste frying oil. Fuel, 92(1): 56-61. http://doi.org/http://dx.doi.org/10.1016/j.fuel.2011.07.024.

Martín-Lara, M.A., Blázquez, G., Ronda, A., Pérez, A. and Calero, M. 2013. Development and characterization of biosorbents to remove heavy metals from aqueous solutions by chemical treatment of olive stone. Ind. Eng. Chem. Res., 2(31): 10809-10819. doi:10.1021/ie401246c.

Mathew, B.B., Jaishankar, M., Biju, V.G. and Nideghatta, K. 2016. Role of Bioadsorbents in Reducing Toxic Metals. Beeregowdahttp://dx.doi.org/10.1155/2016/4369604

Mishra, A. and Tripathi B.D. 2008. Utilization of fly ash in adsorption of heavy metals from wastewater. Toxicol. Environ. Chem., 90(6): 1091-1097. doi:10.1080/02772240801936786.

Modak, J.M. and Natarajan, K.A. 1995. Biosorption of metals using non-living biomass-a review. Miner. Metall. Proc., 12: 189-199.

Mohammed, T.J. and Ibrahim, R.I., 2016. Remediation of Cu (II) from well water of Iraq by using cortex of fruits and agricultural waste. Chem. Eng., 41(2): 345-355.

Mor, S., Chhoden, K. and Khaiwal, R. 2016. Application of agro-waste rice husk ash for the removal of phosphate from the wastewater. J. Clean. Prod., 129: 673-680. DOI: 10.1016/j.jclepro.2016.03.088.

Mor, S., Negi, P. and Ravindra, K. 2019. Potential of agro-waste sugarcane bagasse ash for the removal of ammoniacal nitrogen from landfill leachate. Environ. Sci. Pollut. Res., 7: 52. doi:10.1007/s11356-019-05563-7.

Naiya, T.K., Bhattacharya, A.K. and Das, S.K. 2008b. Adsorption of Pb (II) by sawdust and neem bark from aqueous solutions. Environ. Prog., 27(3): 313-328. doi:10.1002/ep.10280.

Naiya, T.K., Chowdhury, P., Bhattacharya, A.K. and Das, S.K. 2008a. Sawdust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn (II) and Cd (II) ions from aqueous solutions doi: 10.1016/j.cej.2008.08.002.

Netzahuatl-Muñoz, A.R., Guillén-Jiménez, F., de, M., Chávez-Gómez, B., Villegas-Garrido, T.L. and Cristiani-Urbina, E. 2011. Kinetic study of the effect of ph on hexavalent and trivalent chromium removal from aqueous solution by *Cupressus lusitanica* Bark. Water Air Soil Pollut., 223(2): 625-641. doi:10.1007/s11270-011-0888-4.

Nguyen, T.H. 2017. An overview of agricultural pollution in Vietnam: The crop sector 2017. World Bank, Washington DC.

Obi, F.O., Ugwuishiwu, B.O. and Nwakaire, J.N.2016. Agricultural waste concept, generation, utilization, and management. Nig. J. Technol., 35(4): 34 http://dx.doi.org/10.4314/njt.v35i4.34.

Okoye, A.I., Ejikeme, P.M. and Onukwuli, O.D.2010. Lead removal from wastewater using fluted pumpkin seed shell activated carbon: adsorption modeling and kinetics. Int. J. Environ. Sci. Technol., 7(4): 793-800.

Owalude, S.O. and Tella, A.C. 2016. Removal of hexavalent chromium from aqueous solutions by adsorption on modified groundnut hull. Beni-Suef Univ. J. Basic Appl. Sci., 5(4): 377-388. http://dx.doi.org/10.1016/j.bjbas.2016.11.005.

Pandey, M.M.. 2009. Indian agriculture: An introduction Submitted to Fourth Session of the Technical Committee of APCAEM 10-12 February 2009, Chiang Rai, Thailand.

Pappu, A., Saxenaa, M. and Asolekar, S. R. 2006. Solid wastes generation in India and their recycling potential in building materials. Buil. Environ., 42(6): 2311-2320. doi: 10.1016/j.buldenv.2006.04.015.

Park, D., Yun, Y.S. and Moon Park, J.2010. The past, present, and future trends of biosorption. Biotechnol. Bioprocess. Eng., 15: 86-102.

Parlayıcı, ε and Pehlivan, E., 2017. Removal of metals by Fe3O4 loaded activated carbon prepared from plum stone (Prunus nigra): Kinetics and modeling study. Powder Technol., 317: 23-30.

Pino, G.H., de Mesquita L.M.S., Torem M.L. and Pinto G.A.S. 2006. Biosorption of Heavy Metals by Powder of Green Coconut Shell. Sep. Sci. Technol., 41(14): 3141–3153. doi:10.1080/01496390600851640.

Qiu, H., Lv, L., Pan, B., Zhang, Q., Zhang, W. and Zhang, Q. 2009. Critical review in adsorption kinetic models. J. Zhejiang Univ. Sci. A, 10(5): 716–724. doi:10.1631/jzus. a0820524.

Rafique, U. and Zulfiqar, S. 2014. Synthesis and technological application of agro-waste composites for treatment of textile wastewater. Int. J. Agric. Innov., Res., 3(3): 2319-1473.

Rai, M.K., Shahi, G., Meena, V., Meena, R., Chakraborty, S., Singh, R.S. and Rai B.N. 2016. Removal of hexavalent chromium Cr (VI) using activated carbon prepared from mango kernel activated with H_3PO_4. Resour. Efficient Technol., 2(1): 63-70. http://dx.doi.org/10.1016/j.reffit.2016.11.011.

Rao, C.N., Subbarayudu, K., Vijaya, Y. and Subbaiah, M.V. 2014. Adsorption of Ni (II) from aqueous solution by activated carbons derived from tobacco stem. Desalin. Water Treat. 54(12): 3392-3399.

Redlich, O. and Peterson, D.L. 1959. A useful adsorption isotherm. J. Phys. Chem., 63(6): 1024–1024. doi:10.1021/j150576a.5

Sadeek, S.A., Negm, N.A., Hefni, H.H.H. and Wahab, M.M.A. 2015. Metal adsorption by agricultural biosorbents: Adsorption isotherm, kinetic and biosorbents chemical structures. International J. Biol. Macromol., 81: 400-409. doi: 10.1016/j.ijbiomac.2015.08.031

Safa, Y. 2015. Utilization of mustard and linseed oil cakes: novel biosorbents for removal of acid dyes. Desal. Water Treat., 57(13): 5914-5925. doi:10.1080/19443994.2015.1007087

Sahai, S.C., Sharma, C., Singh, S.K. and Gupta, P.K. 2010. Assessment of trace gases, carbon, and nitrogen emissions from field burning of agricultural residues in India. Nutr. Cycl. Agroecosys., 89: 143-157. DOI 10.1007/s10705-010-9384-2.

Sahota, S., Vijay, V.K., Subbarao, P.M.V., Chandra, R., Ghosh, P., Shah, G., Vijay, V., Vaibhav Koutu, V. and Thakur, I.S. 2017. Characterization of leaf waste-based biochar for cost-effective hydrogen sulfide removal from biogas. Bioresour. Technol., 250: 635-641. doi.org/10.1016/j.biortech.2017.11.093.

Salman, M., Athar M. and Farooq U. 2015. Biosorption of heavy metals from aqueous solutions using indigenous and modified lignocellulosic materials. Reviews in Environmental Science and Bio/Technology, 14(2), 211-228. doi:10.1007/s11157-015-9362-x

Salman, M., Athar, M., Farooq, U., Rauf, S. and Habiba, U. 2014. A new approach to modification of an agro-based raw material for Pb (II) adsorption. Korean J. Chem. Eng., 31(3): 467-474. doi:10.1007/s11814-013-0264-8

Salman, M., Rehman, R., Farooq, U., Tahir, A. and Mitu, L. 2020. Biosorptive removal of cadmium (ii) and copper (ii) using microwave-assisted thiourea-modified sorghum bicolor agrowaste. J. Chem., 43: 1643. https://doi.org/10.1155/2020/8269643.

Saman, N., Kong, H., Mohtar, S.S., Johari, K., Mansor, A.F., Hassan, O., Ali N. and Mat, H. 2019. A comparative study on dynamic Hg (II) and MeHg (II) removal by functionalized agrowaste adsorbent: breakthrough analysis and adsorber design. Korean J. Chem. Eng., 36(7): 1069-1081. DOI: 10.1007/s11814-019-0285-z

Santos, V.C.G.D., Tarley, C.R.T., Caetano, J. and Dragunski, D.C. 2010. Assessment of chemically modified sugarcane bagasse for lead adsorption from aqueous medium Water Sci. Technol., 62: 201.

Saqib, A.N.S., Waseem, A., Khan, A.F., Mahmood, Q., Khan, A., Habib, A. and Khan, A.R. 2013. Arsenic bioremediation by low-cost materials derived from Blue Pine *(Pinus wallichiana)* and Walnut *(Juglans regia).* Ecol. Eng., 51: 88-94. doi: 10.1016/j.ecoleng.2012.12.063

Sarath Babu, B. and Yamini, G. 2020. Removal of methylene blue dye by using lemon leaf powder as an adsorbent. Water Resour. Manag., 11(2): 341-359. https://doi.org/10.1007/978-981-15-0706-9_10

Shafique, U., Ijaz, A., Salman, M., Zaman, W., Jamil, N., Rehman, R. and Javaid A. 2012. Removal of arsenic from water using pine leaves. J. Taiwan Instit. Chem. Eng., 43(2): 256–263. doi: 10.1016/j.jtice.2011.10.006

Shahkarami, S., Dalai, A.K., Soltan, J., Hu, Y. and Wan, D. 2015. Selective CO_2 capture by activated carbons: Evaluation of the effects of precursors and pyrolysis process. Energy Fuels, 29(11): 7433-7440. doi: 10.1021/acs.energy fuels.5b00470.

Shakoor, M.B., Niazia, N.K., Bibia, I., Shahidd, M., Saqiba, Z.A., Nawaze, M.F., Shaheenf, S.M., Wangh, H., Tsangj, D.C.W., Bundschuhk, J., Okl, Y.S. and Rinklebe J. 2018. Exploring the arsenic removal potential of various biosorbents from water. Compare. Stud. Environ. Int., 123: 567-579. https://doi.org/10.1016/j.envint.2018.12.049.

Silva, C.R., Gomes, T.F., Andrade, G.C.R.M., Monteiro, S.H., Dias, A.C.R., Zagatto, E.A.G. and Tornisielo, V.L. 2013. Banana peel as an adsorbent for removing atrazine and ametryne from waters. J. Agric. Food Chem., 61(10): 2358-2363. doi:10.1021/jf304742h.

Sips, R. 1948. combined form of Langmuir and Freundlich equations. J. Chem. Phys., 10

Smitha, T., Santhi, T., Prasad, A.L. and Manonmani, S. 2012. Cucumis sativus is used as an adsorbent for the removal of dyes from an aqueous solution. Arab. J. Chem., 10(1): 244-251. http://dx.doi.org/10.1016/j.arabjc.2012.07.030

Taha, G., Arifien, A.E. and Elnahas, S. 2011. The removal efficiency of potato peels as a new biosorbent material for uptake of Pb(II) Cd(II) and Zn(II) from their aqueous solutions. J. Solid Waste Technol. Manag., 37(2): 128-140. https://doi.org/10.5276/JSWTM.2011.128.

Tempkin, M. and Pyzhev, V. 1940 Kinetics of ammonia synthesis on promoted iron catalysts. Acta Physicochim., 12: 217-222.

Toth, J. 1971. State equation of the solid-gas interface layer. Acta Chim. Acad. Sci. Hungar., 69(3): 311-328.

United Nations, Glossary of Environment Statistics, Studies in Methods, Series F, 67, Department for Economic and Social Information and Policy Analysis, Statistics Division, New York, USA, 1997.

Vieira, M.G.A., Almeida Neto, A.F., de Silva, M.G.C., Nóbrega, C.C. and Melo Filho, A.A. 2012. Characterization and use of natural and calcined rice husks for biosorption of heavy metal ions from aqueous effluents. Brazil. J, Chem. Eng., 29(3): 619-634. doi:10.1590/s0104-66322012000300019.

Vijayaraghavan, K. and Yun, Y.S. 2008. Bacterial biosorbents and biosorption. Biotechnol. Adv., 26(3): 266-291. doi: 10.1016/j.biotechadv.2008.02.002.

Vijayaraghavan, K., Padmesh, T., Palanivelu, K. and Velan, M. 2006. Biosorption of nickel (II) ions onto Sargassum wightii: Application of two-parameter and three-parameter isotherm models. J. Hazard. Mater., 133(1-3): 304-308. doi: 10.1016/j.jhazmat.2005.10.016.

Volesky, B. 1994. Advances in biosorption of metals: Selection of biomass types. FEMS Microbiol. Rev., 14(4): 291-302. doi:10.1111/j.1574-6976.1994.tb00102.x

White, C., Sayer, J.A. and Gadd, G.M. 1997.Microbial solubilization and immobilization of toxic metals: key biogeochemical processes for treatment of contamination. FEMS Microbiol. Rev., 20: 503-516.

Witek-Krowiak, A. and Reddy H.K. 2013. Removal of micro elemental Cr (III) and Cu (II) by using soybean meal waste – Unusual isotherms and insights of binding mechanism. Bioresour. Technol., 127: 350-357. doi: 10.1016/j.biortech.2012.09.072

Witek-Krowiak, A., Szafran, R.G. and Modelski, S. 2010. Biosorption of heavy metals from aqueous solutions onto peanut shells as a low-cost biosorbent. Desalination, 7: 042. doi: 10.1016/j.desal.2010.07.042

Zein, R., Suhaili, R., Earnestly, F., Indravati, M. and Munaf, E. 2010. Removal of Pb (II), Cd (II), and Co (II) from aqueous solution using Garcinia mangostona L. fruit shell. J. Hazard. Mater., 4: 76. DOI: 10.1016/j.jhamat.2010.04.076.

Zhang, X., Wu, J., Yang, H., Shao, J., Wang, X., Chen, Y. and Chen, H. 2016. Preparation of nitrogen-doped microporous modified biochar by high-temperature CO_2–NH_3 treatment for CO_2 adsorption: Effects of temperature. RSC Adv., 6(100): 98157-98166. doi:10.1039/c6ra23748g

Zouboulis, A.L., Matis, K.A. and Hancock, I.C. 1997. Biosorption of metals from dilute aqueous solutions. Sep. Purif. Meth., 26: 255-295.