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AGRICULTURAL WASTE MATERIALS AS BIOSORBENTS FOR THE REMOVAL OF HEAVY METALS AND SYNTHETIC DYES– A REVIEW

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Abstract: This review discusses the potential use of agricultural waste based bio-sorbents for sequestering heavy metals and synthetic dyes in terms of their adsorption capacities, cost effectiveness, binding mechanisms, operating factors and pre-treatment methods. Agricultural wastes are known to be rich in functional carboxyl and hydroxyl groups which facilitate binding of cation on to the surface. Adsorption by using low cost alternative adsorbent is a fascinating area as it has dual benefits *i.e.* water treatment and waste management. The literature survey indicates that agricultural waste based bio-sorbents have shown equal or even greater adsorption capacities compared to conventional adsorbents. In most cases, chemical pre-treatments bring about an obvious improvement in metal uptake capacity. However, there are still several gaps, which require further investigation, such as (i) searching for novel, multi-function agricultural waste based bio-sorbents, (ii) developing cost-effective modification methods and (iii) assessing agricultural waste based bio-sorbents under multi-metal and real wastewater systems. Once these challenges are addressed, the replacement of traditional adsorbents by agricultural waste based bio-sorbents in decontaminating heavy metals and dyes from wastewater more efficiently could be achieved.

Keywords: Adsorption capacities; Agricultural wastes; Bio-sorbents; Heavy metals; Synthetic dyes.

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INTRODUCTION

Water is vital requirement of life and used for various household as well as industrial activities. The rapid and continuous growth of industries over the last few decades has increased fresh water demand and thereby also the amount of waste water discharged. This waste water contains many heavy metals and synthetic dyes, which often have been regarded as hazardous pollutants because of their potential toxicity to human health. Many methods available for the removal of pollutants from aqueous solution, include chemical precipitation, ion exchange, membrane separation process, biological degradation, chemical oxidation, solvent extraction, and adsorption. However, these methods have several disadvantages such as limited metal concentrations specificity, generation of huge toxic sludge and high capital costs. On the contrary, adsorption is found to be the most effective and prolific technique due to its convenience, cost effectiveness, ease of operation, high adsorption capacities and versatility, which explain why the adsorption method is more economical for heavy metals and dyes removal (Yildiz, *et al.,* 2005; Yan, *et al.*, 2007). Recently scientists have paid much attention on the use of biological-based materials for pollutants removal from different waste waters because of presence of several carboxyl, hydroxyl and amino groups over their surface, which facilitates the biosorption process (Ay, *et al.,* 2012). Potential applications of agricultural wastes as low-cost biosorbents are (1) abundant availability, (2) low cost, (3) good adsorption capacity, (4) easy-to-make chemical modification, (5) easy regeneration and (6) less disposal problem after adsorption. Keeping this in view many researchers have used agriculture-based biomass such as hazelnut and coconut shell, rice husk, peanut shell, jackfruit peel, sugarcane bagasse, water chestnut shell, and peels of various fruits (Kamala, *et al*., 2005; Kamsonlian, *et al*., 2012; Marín-Rangel, *et al*., 2012; Shafique, *et al*., 2012; Jiménez-Cedilloa, *et al*., 2013) as potential biosorbents for the removal of heavy metals, whilst cocoa shells (Meunier *et al*. 2003), rice husk (Malik, 2003, Safa and Bhatti, 2011), barely husk (Haq, *et al*., 2011), coirpith (Namasivayam and sangeetha, 2006), for synthetic dyes removal from industrial waste water. In current years, attention of chemists has been focused on agricultural waste based biosorbents as cost-effective and eco-friendly. This paper attempts to review agricultural waste as capable biosorbent for removal of heavy metals and dyes from contaminated water.

HEAVY METALS AND SYNTHETIC DYES

Heavy metals in the aquatic medium may originate from wastewater of many industries, such as batteries, tanneries, electrical, electroplating, fertilizers, pesticides, mining, refining ores, etc. (Banerjee, *et al.,* 2012; Manzoor, *et al*., 2013). Due to their hazardous effects, persistency, non-degradability and accumulation tendency, heavy metals can pose a risk to the human and environmental health (Marin, *et al*., 2010; Kumar, *et al*., 2012). Heavy Metals like Pb, Cr, Hg, U, Se, Zn, As, Cd, Co, Cu, and Ni are classified as toxic (Johnson, *et al*., 2008). Typical poisoning symptoms and maximum contaminants levels of the most common heavy metals are described in Table 1 (Barakat, 2011). Synthetic dyes are widely used to color the substrate like textile fiber, paper, leather, hair, fur, plastic material, wax, a cosmetic base and food stuff. The classification of various dyes according to their chemical structure is revealed in Table 2. Dyes are highly visible even at very trace concentrations due to their coloring properties and toxic effects such as mutagenic, allergenic, and carcinogenic on aquatic life and humans, also cause some ecological problems to the aquatic ecosystem (Kannan and Sundaram, 2001; Robinson, *et al.,* 2002; Mittal, *et al.,* 2007). A wide variety of biological, physical and chemical methods for synthetic dyes removal from waste water include photocatalytic degradation (Mahmoodi, *et al*., 2005), coagulation (Bozdogan and Goknil, 1987) and microbiological degradation (Pearce, *et al*., 2003). All these methods have different color removal abilities, capital costs and operating rates (Amin, *et al.,* 2009). Amongst them, adsorption is one of the best removal techniques which have gained utmost attention mainly because of its simplicity and insensitivity to toxic pollutants including heavy metals and dyes (Crini, *et al*., 2006; Boddu, *et al*., 2008; Cheraghi, *et al.,* 2013, Bhatnagar, *et al*., 2015).

CONVENTIONAL METHODS FOR HEAVY METALS AND DYES REMOVAL FROM INDUSTRIAL EFFLUENTS

Numerous treatments on the heavy metal removal from contaminated water have already been applied years ago which can be divided into biological, chemical and physical processes. The Comparison of different technologies for removing pollutants from waste water is shown in Table 3. Some conventional methods for heavy metal and dyes removal are described as follows:

(i) Precipitation is the most common method for removing toxic heavy metals up to parts per million (ppm) levels from water. Although the process is cost effective its efficiency is affected by low pH and the presence of other salts (ions). The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive.

(ii) Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluents. Though it is relatively expensive as compared to the other methods, it has the ability to achieve ppb levels of clean up while handling a relatively large volume. An ion exchange is a solid capable of exchanging either cations or anions from the surrounding materials. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater.

(iii) Electro-winning is widely used in the mining and metallurgical industrial operations for cheap leaching and acid mine drainage. It is also used in the metal transformation and electronics and electrical industries for removal and recovery of metals. Metals like Ag, Au, Cd, Co, Cr, Ni, Pb, Sn and Zn .

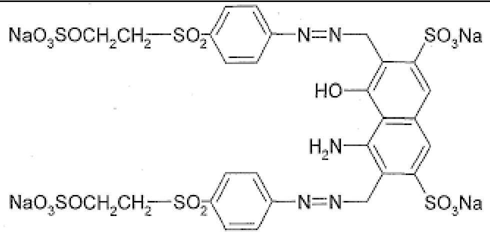
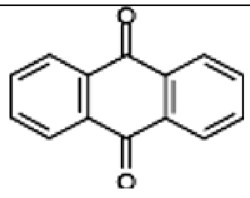
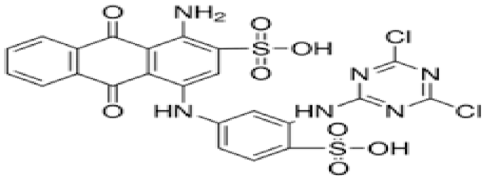
(iv) Electro-coagulation is an electrochemical approach, which uses an electrical current to remove metals from solution. Electro-coagulation system is also effective in removing suspended solids, dissolved metals, tannins and dyes. The contaminants presents in wastewater are maintained in solution by electrical charges. When these ions and other charged particles are neutralized with ions of opposite electrical charges provided by electro coagulation system, they become destabilized and precipitate in a stable form.

(v) Reverse osmosis and electro-dialysis involves the use of semi-permeable membranes for the recovery of metal ions from dilute wastewater. In electro-dialysis, selective membranes (alternation of cation and anion membranes) are fitted between the electrodes in electrolytic cells, and under continuous electrical current the associated ion migrates, allowing the recovery of metals.

Table 1. Maximum Contaminant Levels (MCL) for the most common heavy metals (Barakat, 2011)

Heavy metal	Toxicities	MCL (mg/L
Arsenic (As)	Skin manifestations, visceral cancers, vascular disease	0.05
Cadmium (Cd)	Kidney damage, renal disorder, human carcinogen	0.01
Chromium (Cr)	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper (Cu)	Liver damage, Wilson disease, insomnia	0.25
Nickel (Ni)	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc (Zn)	Depression, lethargy, neurological signs and increased thirst	0.80
Lead (Pb)	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury (Hg)	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

Table 2. Classification of dyes according to the chemical structure adapted from (Ali, 2003)

Class	Chromospheres	Example
Azo dyes	$-N{=}N-$	 Reactive Black 5
Anthraquinone dyes		 Reactive Blue 4

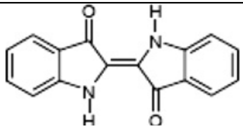
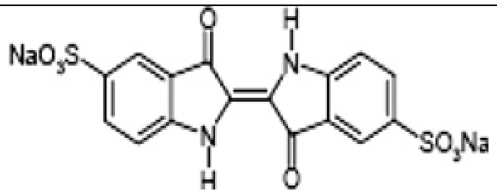
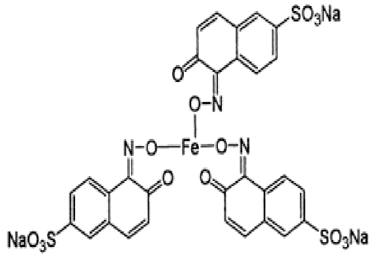
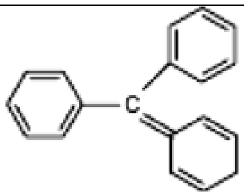
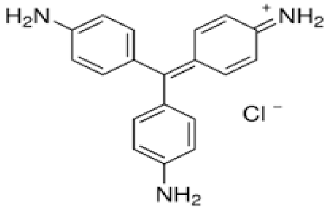
Indigoid dyes		 Acid Blue 71
Nitroso dyes	$-N{=}O$	 Acid green 1
Triarylmethane dyes		 Basic Red 9

Table 3. Comparison of different technologies for removing heavy metals from wastewater

S.No.	Methods	Disadvantages	Advantages
1.	Chemical precipitation	Large amounts of sludge, Extra operational cost for sludge disposal,	Simple operation, inexpensive, can remove most of metals
2.	Chemical coagulation	High cost Large consumption of chemicals	Sludge settling Dewatering
3.	Ion-exchange	High cost Less number of metal ions removed	High regeneration of materials Metal selective
4.	Electrochemical methods	High capital and running cost Initial solution pH and current density	Metal selective No consumption of chemicals Pure metals can be achieved
5.	Adsorption using activated carbon	Cost of activated carbon	No regeneration Performance depends upon adsorbent Most of metals can be removed High efficiency (>99%)
6.	Biosorption	Early saturation, limited potential for biological process improvement, no potential for biologically altering the metal valence state	Low cost, high efficiency, minimization of sludge, regeneration of biosorbents, no additional nutrient requirement, metal recovery
7.	Membrane filtration	High operational cost due to membrane fouling	Small space requirement, low pressure, high separation Selectivity
8.	Electro dialysis	High operational cost due to membrane fouling and energy consumption	High separation selectivity
9.	Photo catalysis	Long duration time, limited applications	Removal of metals and organic pollutant simultaneously, less harmful by-products

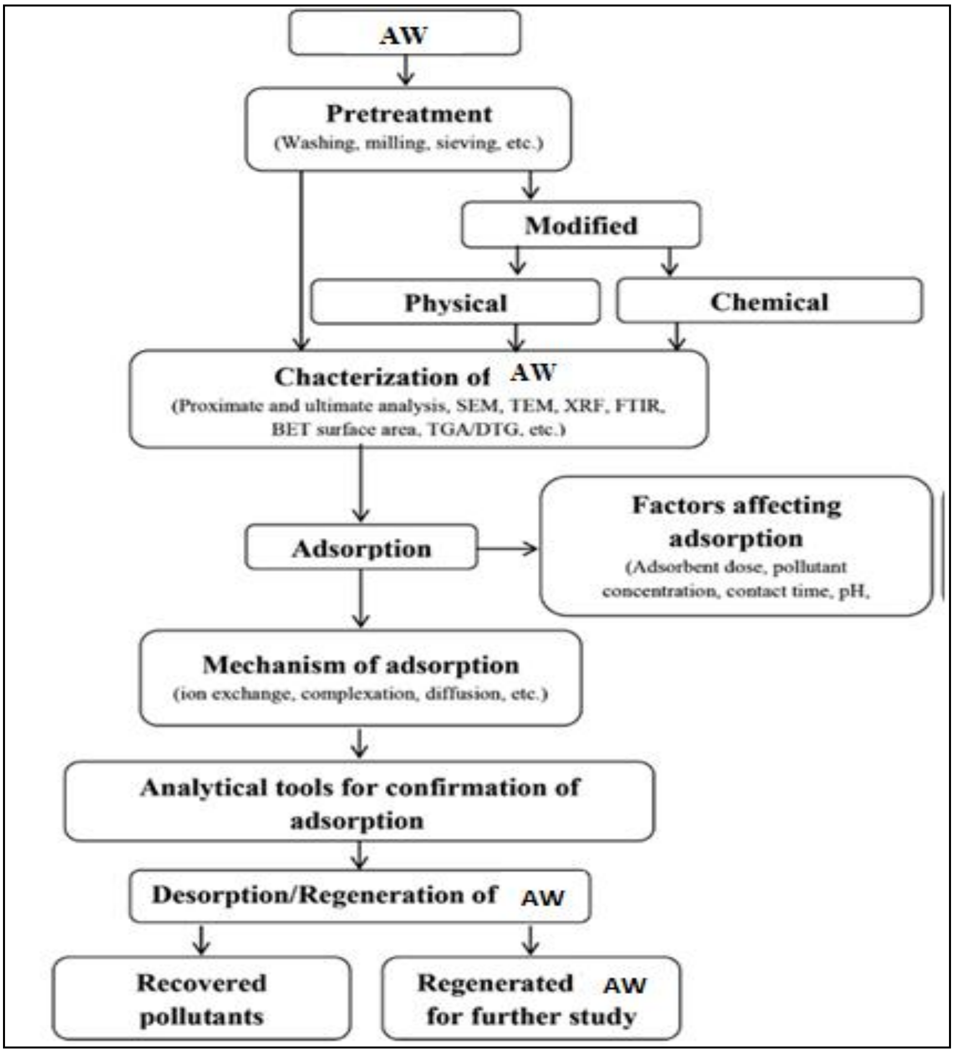


Figure. 1. Overall adsorption process using agricultural wastes (AW)

ADSORPTION PROCESS

Recently the adsorption process has gained interest as a more promising method for the long term as it is seen to be a more effective and economic approach for heavy metals and dyes removal. Adsorption is a fundamental process today due to its flexibility in design and simple operation. The term adsorption refers as a mass transfer process by which a substance is transformed from the liquid phase to the surface of the solid and becomes bound by physical and/or chemical interactions (Babel and Kurniawan, 2003). In general, the overall adsorption process is illustrated in Figure 1.

AGRICULTURAL WASTES AS LOW COST ADSORBENTS

Agricultural wastes and by products were found to be low cost and alternate adsorbents for heavy metals and synthetic dyes removal. Agro wastes are rich in organic contents with variety of functional groups which can cooperate binding of cations and anions. The other advantages of agricultural wastes are easily available, non-hazardous and no disposal problems. The conversion of these materials into adsorbents can help to reduce the cost of waste disposal and provide an alternative treatment to replace the commercial activated carbon (Kurniawan, 2006). Various researchers used different agricultural wastes as adsorbents for heavy metals removal which is described in Table 4. Several agricultural wastes have been studied and reported for heavy metals and dyes removals, some of them are as follows:

(i) Rice husk

Rice husk, a major agricultural by product was found to have affinity towards heavy metal ions and synthetic dyes. (Bishnoi, *et al*., 2004) studied the removal of Cr^{6+} from aqueous solution by rice husk activated carbon and the removal efficiency was found to be high compared to raw husk. (Ajmal, *et al*., 2003) studied the feasibility of pretreated rice husk. Various pretreatment of rice husk was studied by many researchers for enhancing the loading capacity of rice husk towards metal ions. The removal of methylene blue and basic red from aqueous solution with raw rice husk was studied by (Mckay, *et al*., 1999) and they found the loading capacity 312 mg/g. The use of activated carbon rice husk for the removal of methylene blue was reported by (Kannan and Sundaram, 2001) and they found higher loading capacity compared to raw husk.

(ii) Sugarcane bagasse

Sugarcane bagasses abundant by product obtained from sugar industries are found to have 50% cellulose, 27% ployoses and 23% lignin. These biopolymers make sugarcane bagasse a rich adsorbent with variety of functional groups. The possibilities of sugarcane dust as low cost adsorbent for the removal of crystal violet, rhodamine B and methylene blue form aqueous solution explored by Khattri and Singh (1999). The Sugarcane bagasses were found to show 94-95% removal efficiency for Basic blue 9 removal from industrial effluents (Zhang, *et al.,* 2013).

(iii) Saw dust

Saw dust, an abundant agro waste was explored for the removal of metal ions and dyes. Saw dust from different sources have been researched for their capability to act as an adsorbent. The phosphate treated saw dust from mango tree as potential sorbent for the removal of Cr^{6+} ions from electroplating effluents, investigated by Ajmal et al. (1999). The pre-treated saw dust was found to show 100% removal efficiency for Cr^{6+} ions from industrial effluents. The use of saw dust from various sources for the removal of polar blue and methylene blue from aqueous solution reported by Ferrero (2007).

(iv) Peanut shell

The peanut shell based activated carbon was reported by (Wilson, *et al*., 2006 and Romero, *et al.,* 2004) for the removal of various heavy metal ions. (Chamarthy, *et al*., 2001) reported the use of activated peanut shell for the removal of five heavy metal ions and found that the efficiency was higher than many commercial adsorbents. (Kannan and Sundaram, 2001) studied the use of peanut shell carbon for the removal of methylene blue along with rice and coconut shell carbons. The peanut shell showed lowest loading capacity compared to rice and coconut shells. The removal of malchanite green by activated carbon from peanut shell and found to be effective by (Malik, *et al*., 2007).

(v) Coir pith

The use of coirpith as low cost adsorbent was investigated by Namasivayam and Kadirvelu (1997, 1999) for the removal of Hg^{2+}, Ni^{2+} and Cu^{2+} ions. (Namasivayam and Sangeetha, 2006) reported the use of $ZnCl_2$ as activating agent for coirpith and the removal efficiency was found to be very high compared to untreated coirpith. The increased efficiency was found to be due to high surface area of coir pith after activation. (Namasivayam, *et al.,* 2001) reported the use of coir pith raw and activated for the removal of acid brilliant blue, rhodamine B and acid violet. It was observed that with activation the loading capacity increased and rate of adsorption was found to be spontaneous.

Table 4. Summary of work done by Various Researchers using low cost agricultural waste materials for Heavy metals Removal

S. No.	Agricultural waste	Metal ions	Results	Reference
1.	Oat biomass	Cr (III), Cr (VI)	>80%	Gardea-Torresdey *et al.* (2000)
2.	Beech saw dust	Cr (VI)	100%	Acar and Malkoc (2004)
3.	Wheat bran	Cr (VI)	>82%	Farajzadeh and Monji (2004)
4.	Coconut shell fibers	Cr (VI)	>80%	Mohan *et al*. (2006)

5.	Raw rice bran	Cr (VI),	40–50%	Oliveira *et al.* (2005)
6.	Sugarcane bagasse, maize corn cob, jatropha oil cake	Cr (III)	Upto 97%	Garg *et al.* (2007)
7.	Agro waste of black gram husk	Pb (II)	Upto93%	Saeed *et al.* (2005)
8.	Rice bran	Pb (II), Cd (II), Cu (II), Zn (II)	>80.0%	Montanher *et al.* (2005)
9.	Saw dust of Pinus sylvestris	Pb (II), Cd (II	96%, 98%	Taty-Costodes *et al.* (2003)
10.	Rice straw, soybean hulls, sugarcane bagasse, peanut shells, pecan and walnut shells	Pb (II), Cu (II), Cd (II), Zn (II), Ni (II)	Pb > Cu > Cd > Zn > Ni	Johns *et al.* (1998)
11.	Rice husk	Cd (II)	80–97%	Kumar and Bandyopadhyay (2006)
12.	Bagasse	Cd (II), Zn (II)	90–95%	Mohan and Singh (2002)
13.	Bagasse fly ash	Cd (II), Ni (II)	65 & 42%	Srivastava *et al.* (2007)
14.	Rice bran	Cd (II), Cu (II), Pb (II), Zn (II)	>80.0%	Montanher *et al.* (2005)
15	Wheat bran	Cd (II), Hg (II), Pb (II), Cr (VI),Cu (II)	>82%	Farajzadeh and Monji (2004)
16.	Hazelnut shell, orange peel, maize cob, peanut hulls, soyabean hulls treated with NaOH	Cd (II), Cr (VI), Cu (II), Ni (II), Zn (II)	High metal adsorption	Kurniawan *et al.* (2006)
17.	Sugarcane bagasse	Ni (II)	>80%	Garg *et al.* (2007)
18.	Saw dust	Cr(VI)	>100%	Ajmal *et al.* (1996)
19.	Waste tea leaves	Ni (II), Pb (II), Fe (II), Zn (II)	>92%	Ahluwalia and Goyal (2005)
20.	Wheat stem (raw)	Cd(II)	>72%	Tan and xiao (2009)
21.	Activated carbon of peanut shells	Pb (II), Cd (II), Cu (II), Ni (II), Zn (II)	Upto 75%	Wilson *et al.* (2006)
22.	Barley straw (raw)	Cu(II)	>80 %	Pehlivan (2012)

PRETREATMENT/MODIFICATION OF AGRICULTURAL WASTES FOR BIOSORPTION

Pretreatment of biosorbent can result in opening of biopolymer rings; enhance porosity and stability, thereby improving heavy metal removal efficiency of the sorbent material (Dod, *et al.,* 2012; Khosa, *et al.*, 2013; Okoro and Okoro, 2011). In addition, modified/pretreated biosorbents could also be helpful to diminish the problem of coloration and addition of some dyes in the water (Rahaman, *et al.,* 2008). The physical and chemical pretreatment methods and coating with various Fe oxide mineral nano-particles can be used for modification of the biosorbents. Physical modifications (steam activation, drying or heating) are simple and less costly, but they are not extensively used due to their low effectiveness in enhancing the heavy metals sorption on the biosorbent surface (Okuo, *et al.,* 2006; Rahaman, *et al.,* 2008). On the contrary, chemical modifications are given priority because they are efficient to increase the biosorbent stability and metals sorption capacity (Park, *et al.,* 2010). The process pathways to modify raw agricultural wastes material are shown in figure 2. Adsorption is affected by the physico-chemical and surface properties of the adsorbent, like elemental composition, porosity, particle density, bulk density, surface pH, surface area, functional groups present on the surface, and thermal properties. Chemical treatment is used to alter properties like water sorbency, ion exchange capability, conductivity, hydrophilicity, or hydrophobicity of cellulosic materials. To enhance adsorption capacity of agricultural wastes, most of the researchers prefer only washing with acid, alkali, or some other solvent (Ngah and Hanafia, 2008; O'Connell, *et al.*, 2008; Park, *et al.,* 2010; Patel, 2012).

CHARACTERIZATION OF BIOSORBENTS USING VARIOUS TECHNIQUES

Agricultural waste has basic chemical constituents like cellulose, hemicellulose, lignin, lipids, proteins, sugars, starch, polysaccharides, and pigments. These constituents contain different functional groups such as carboxyl, hydroxyl, and amino. These groups are present on their surfaces and have ability to bind the sorbate ions and molecules (Qin, *et al.*, 2012; Huang and Zhu, 2013; Meisam, *et al.*, 2013). The characterization of surface chemistry and structure of the biosorbent is essential for the development of adsorption and separation processes. Agricultural waste was characterized to understand surface morphology and physico-chemical properties by using sophisticated analytical tools like infrared absorption spectroscopy or Fourier transformed infrared spectroscopy (IR or FTIR), scanning electron microscopy (SEM), energy dispersive X-ray (EDS), x-ray fluorescence (XRF), X-ray diffraction (XRD), nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) surface area, elemental analysis, proximate analysis, energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), and vibrating sample magnetometer (VSM) of agricultural waste (Memon, *et al.*, 2009; Marín, *et al.*, 2010; Ning-Chuan, *et al.,* 2010; Ay, *et al.*, 2012; Gupta and Nayak, 2012; Lugo-Lugo, *et al.*, 2012; Lim, *et al.*, 2014). Figure 3 shows various techniques for characterization of the adsorbent and their outcomes.

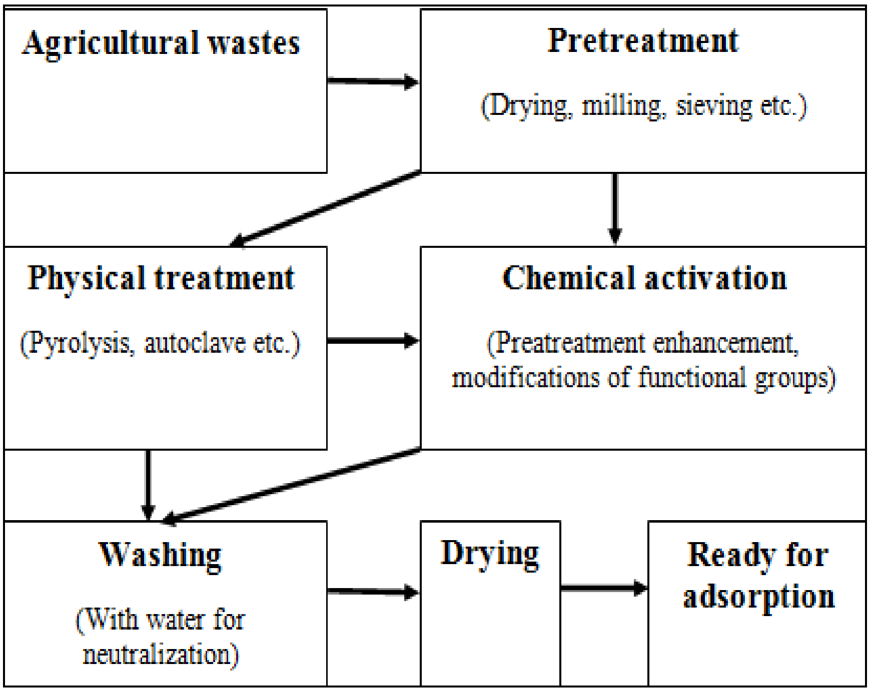


Figure 2. Schematic diagram for processing of Agricultural wastes for adsorption

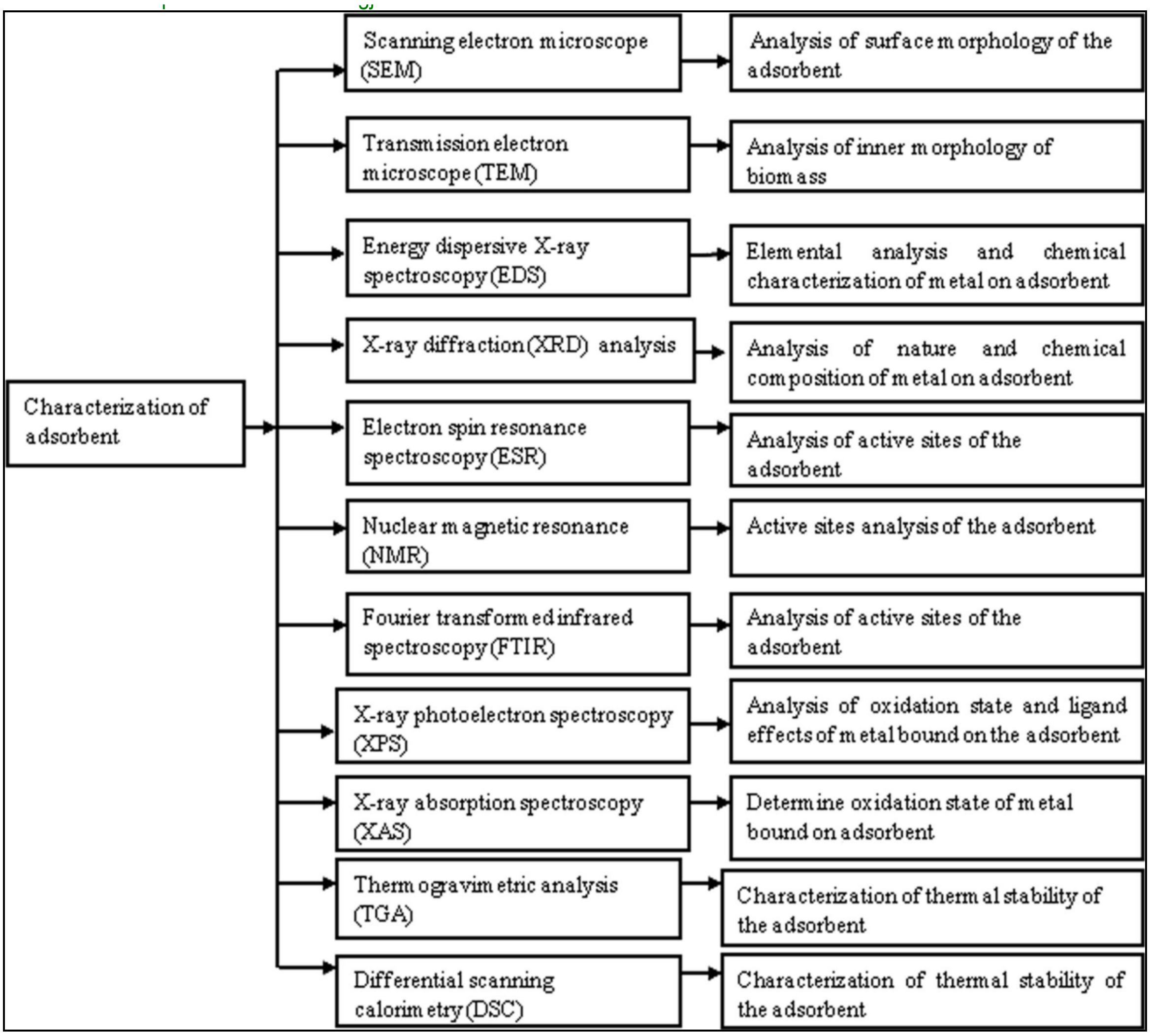


Figure 3. Instrumental analysis for characterization of the adsorbents and their outcomes

FACTORS AFFECTING ADSORPTION

Adsorption on agricultural wastes depends on different parameters and some major factors affecting adsorption process are as follows:

(i) Adsorbent dose

Adsorbent dosage is an important parameter to determine the capacity of an adsorbent. Generally the percentage of dye removal increases with increasing adsorbent dosage (salleh, 2011). The amount of adsorbent decides the extent of available surface binding sites for adsorption. Hence, the percentage removal of adsorbate increases with adsorbent dosage. The amount of adsorbent is sufficient for the maximum removal of adsorbate ions from the solution at a given concentration. Sorption capacity of different biosorbents has been observed to reduce with increasing biosorbent dose. Table 5 shows the reported studies on the effect of adsorbent dosage on the percentage of dye removal.

(ii) Contact time

Contact time is the time required for the system to reach equilibrium. This solid/liquid heterogeneous system frequently undergoes different mass transfer steps, some of which could be comparatively slow. Therefore, it is necessary to determine the contact time to make sure that the equilibrium is reached. Biosorption of heavy metals can increase with increasing contact time. This could be attributed to the transfer of higher amount of metal ions from solution phase to the biosorbent active sites as contact time increases (Okafor, *et al*., 2012; Pehlivan, *et al*., 2012; Rahaman, *et al*., 2008).

(iii) Solution pH

The pH is considered to be the most important parameter in the adsorption process. It affects the solution chemistry, functional group activity on the agricultural waste surface, and the composition of the adsorbate. As the pH varies from acidic to basic, it enhances adsorptive removal of basic dyes or cationic metals. The solution pH is considered to be one of the most critical factors in controlling heavy metals biosorption (Anirudhan and Unnithan, 2007; Baig, *et al*., 2012; McAfee, *et al*., 2001, Zafar, *et al*., 2007). The adsorption of anionic dyes by modified barley straw was studied by (Ibrahim, 2010) and he found that anionic dyes gives a complete removal of 100% at pH 3 and decreased value below 50% as the pH was increased. Table 6 reported the compilation of different studies on the effect of solution pH on dye adsorption.

Table 5. Effect of adsorbent dosage on the percentage of dye Removal

Adsorbents	Dye name	Adsorbent dosage	Percentage Removal range (%)	References
Modified sawdust	Methylene blue	1.5–5 g	34.4–96.6	Zou, 2013
Modified mango seed	Methylene blue	0.1–1.2 g	99.8–79	Senthil kumar 2013
Cashew nutshells	Congo red	5–30 g/L	56.3–99.3	Senthil kumar 2010
Treated sawdust	Brilliant Green	1–30 g/L	61–99.9	Mane *et al*., 2011
Raw mango seed	Methylene blue	0.1–1.2 g	99.5–68	Senthilkumar 2013
Treated sawdust	Malachite Green	0.2–1.0 g/100 mL	18.6–86.9	Garg, 2003
Rice hull	Reactive Orange 16	0.02–0.08 g	21.7–56.2	Ong *et al.,* 2007
Orange peel	Acid Violet 17	50–600 mg/50 mL	15–98	Sivaraj *et al.,* 2001

Table 6. Effect of solution pH on the adsorption of dyes by different Adsorbents

Adsorbents	Dye name	pH	% removal range	References
Activated-rice husk	Acid Yellow 36	2–9	80–45	Imam *et al.,* 2003
Fly ash	Methylene blue	2–8	36–45	Kumar *et al.,* 2005
Tobacco Stem Ash	Methylene blue	2.08–7.93	60–81	Ghosh and Reddy, 2013
Modified sawdust	Methylene blue	2–11	Increase	Zou, 2013

(iv) Initial Adsorbate Concentration

Higher initial concentrations give higher loading capacity. Biosorption capacity of a particular biosorbent increases with increasing initial heavy metal concentration and reaches at maximum. Most of the heavy metals can transfer from the aqueous solution to biosorbent surface as a result of a driving force produced by initial concentration of analyte in aqueous solution (Sahmoune, *et al.,* 2011; Taha, *et al*., 2011; Okafor, *et al.,* 2012). The effect of initial dye concentration depends on the immediate relation between the concentration of the dye and the available sites on an adsorbent surface. In general, the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. On the other hand the increase in initial dye concentration will cause an increase in the capacity of the adsorbent and this may be due to the high driving force formass transfer at a high initial dye concentration (Bulut and Aydin, 2006). Table 7 presented the results of various reported studies on the effect of initial dye concentration on adsorption.

(v) Temperature

Effect of temperature is another significant physico-chemical process parameter because temperature will change the adsorption capacity of the adsorbent (Argun, 2008). The temperature can affect biosorption in several ways based on the endothermic or exothermic nature of the biosorption process (Kamsonlian, *et al*., 2012). Rate of adsorption increases with temperature, as higher temperature enhances the mobility of adsorbate ions and decreases the viscosity of the solution. A temperature study also helps in understanding thermodynamic parameters such as enthalpy, entropy, and free energy involved in the adsorption process. The effect of temperature on the sorption capacity of biosorbents depends on surface functional groups. However, it is recognized from many studies such as rice husk (Kamsonlian, *et al*., 2012), mango leaf powder, (Kamsonlian, *et al*., 2012), orange peel (Khaskhel, *et al.,* 2011) and coconut shell (Okafor, *et al.*, 2012) that the influence of temperature is often in a particular temperature range (25-40^{0}C). Kumar, *et al.,* (2012) found that the biosorption of Cd(II) by cashew nut shell decreased from 80.13% to 74.32% with the rise in temperature from 30^{0}C to 60^{0}C. They attributed this to the decrease in surface activity of agricultural wastes adsorbents. Moreover, (Tavlieva, 2013) highlighted how the temperature increase favoured the removal, and the brilliant green adsorption was a fast process at 47 °C, as it reached equilibrium within 90 min. Table 8 shows the compilation of results of various studies on the effect of temperature on the dye adsorption by various adsorbents.

Table 7. The results of various reported studies on the effect of initial dye concentration on dye adsorption by various adsorbents

Adsorbents	Dye name	Initial dye Concentration (mg/L)	Removal Range (%)	References
Sawdust	Direct brown 2	600–850	99.6–99.1	Kannan and Sundaram, 2001
Sugarcane bagasse	Rhodamine B	100–500	99.1–87.1	Zhang, 2013
Sugarcane bagasse	Basic Blue 9	250–500	94–55.5	
Modified sawdust	Methylene blue	25–500	91.2–66.3	Zou, 2013
Rice husk	Malachite Green	10–30	82.5–71	Ramaraju *et al.,* 2013
Raw mango seed	Methylene blue	50–250	99.1–92.5	Senthilkumar 2013
Modified mango seed	Methylene blue	50–250	99.9–96.9	

Table 8. Effect of temperature on the adsorption of dyes using various adsorbents

Adsorbents	Dye name	Temperature range (K)	Type of process	References
Sugarcane bagasse	Rhodamine B	303–323	Endothermic	Zhang, 2013
Sugarcane bagasse	Basic Blue 9	303–323	Endothermic	
Treated rice husks	Methylene blue	293–313	Endothermic	Lin, 2013
Peanut husk	Indosol Black	303–333	Exothermic	Sadaf *et al.,* 2013

(vi) Particle Size/surface area

Surface area increases with a decrease in particle size and gives more number of binding sites for adsorption. Surface area is one of the key factors for adsorption. Adsorption is directly proportional to the surface area. Agricultural waste surface is porous and may contain micro pores, mesopores, and/or macro pores. Along with area, pore volume and pore diameter are also influencing factors. Pore volume and pore diameter determine the degree or extent of diffusion of pollutant molecules into the pores. Depending upon the size of the molecule and pore diameter, pore diffusion can be estimated. If the diameter of the pore is larger than the diameter of the adsorbate molecule, then the molecule diffuses deeper into the pore. Biosorbent particle size has a pronounced influence on the number of available sorption sites of biosorbent material, which could cause a change in total surface area. Surface area of biosorbent is enhanced with decreasing particle size and vice versa, hence it plays a potent role for heavy metal sorption at the surface of biosorbents (Nguyen, *et al*., 2013).

(vii) Speed of agitation

Agitation speed helps the adsorbate overcome the boundary layer mass transfer resistance. Higher agitation speed results in higher rate of adsorption (Marín, *et al*., 2010, Mishra, *et al*., 2010, Dod, *et al*., 2012, Lim, *et al.,* 2014). The adsorption kinetics of brilliant green onto white rice husk was studied by (Tavlieva, 2013) in aqueous solutions. They showed that the maximum adsorption capacity at 47°C was 85.56 mg/g. Further, considering a contact time of 60 min and an adsorbent dosage of 5 g/L, the adsorption capacity related to an initial adsorbate concentration of 3, 6, 8, 20, 40 and 100 mg/l was about 0.8 mg/g, 0.9 mg/g, 1.0 mg/g, 3.0 mg/g, 7.0 mg/g and 18 mg/g, respectively.

MECHANISMS OF BIOSORPTION

In biosorption, adsorption is a result of the interactions of weak forces, chemical reactions, and ionic strength leading to stronger binding (Achak, *et al.,* 2009). These interactions may occur inside the pores, outside the pores, or on the surface of agricultural wastes (Silva, *et al*., 2013). The adsorption mechanism depends on the physico- chemical characteristics of agricultural wastes as well as on some mass transport processes (Lasheen, *et al*., 2012). Usually, for the adsorption of pollutants onto agricultural waste, carboxylic and hydroxyl groups are found to be more responsible than the other groups (sulfhydryl, thio, aldehyde, ketones, amino, etc.) present on the surface. Carboxylic groups are mainly responsible for metal binding. Biosorption involves various mechanisms for heavy metals and dyes removal; all are represented in figure 4 and 5. The mechanism responsible for the adsorption of different organic compounds onto lignocellulosic waste like agricultural waste is tough to predict. The chemical structure and the functional groups present on the agricultural waste surface are difficult to fix due to their different origins, types, seasonal variations, and geographic locations. Particularly acid base functional groups present on the adsorbent surface might play a vital role in ionic interactions taking place during adsorption. These interactions help to postulate the involved mechanisms such as chemisorption, complexation reactions, surface adsorption, ion exchange, diffusion through pores and electrostatic interactions, or some other. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm according to the general Eq. (i):

$$\mathbf{qt = (C0-Ct).V/m \quad \text{--------} \ (i)}$$

where qt (mg/g) is the amount of adsorbate per mass unit of adsorbent at time t, C0 and Ct (mg/l) is the initial and at time t concentration of adsorbate, respectively, V is the volume of the solution (l), and m is the mass of adsorbent (g) (coonery, *et al*., 1999).

Agricultural wastes contain different types of functional groups on its surface, like carboxyl, hydroxyl, amino, thiol, etc. Removal of anionic pollutants is much challenging than removal of the other pollutants. For anionic pollutants removal, a cationic adsorbent is needed. Therefore, sometimes, surface modification is required for better efficiency (Silke and Ankit, 2009, Kosasih, *et al.,* 2010, Mallampati and Valiyaveettil, 2013). When the heavy metal ions in the solution pass through the cations column, they would be exchanged for the hydrogen ions which serve as exchangeable ions with metal cations in the sulfonic group or carboxylic group of the resin with the following Eq. (ii) to (iii) (Zeng and Li, 2014).

$$\mathbf{nR{-}SO_3H + M^{n+} \rightarrow (R{-}SO^-_3)_nM + nH^+ \quad (M{=}Metal) \ \text{----} \quad (ii)}$$

$$\mathbf{nR{-}COOH + M^{n+} \rightarrow (R{-}COO^-)_nM + nH^+ \quad (M{=}Metal) \ \text{----} \quad (iii)}$$

For dye removal, several mechanisms are proposed, like ion exchange, chemisorption, and ionic exchange. Hydroxyl and poly-phenolic groups on agricultural wastes are the main binding sites for dyes. Khaled, *et al.* (2009b) and Inbaraj and Sulochana (2006) concluded the possibility of ion exchange mechanism for dye adsorption, while Amin (2009) and Khaled *et al.* (2009a) assume electrostatic interaction and chemical reaction between the dye and agricultural waste.

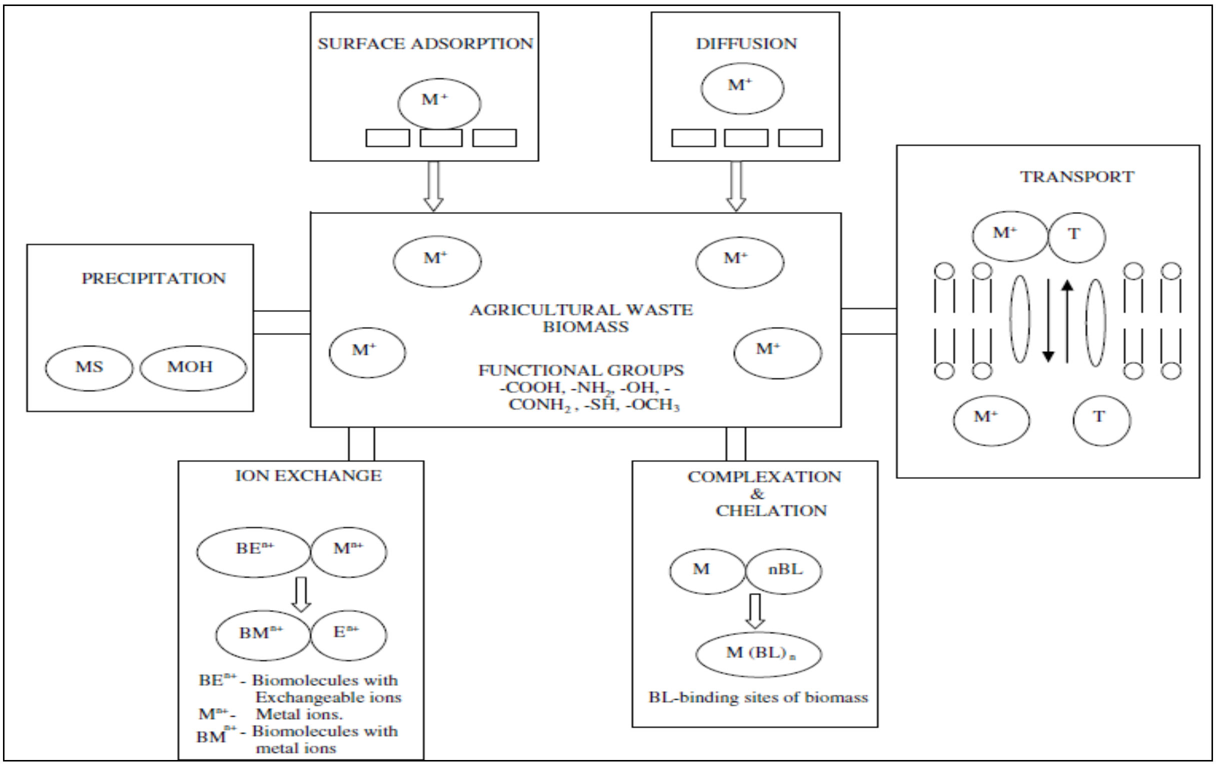


Figure 4. Various mechanisms of biosorption (Sud *et al.*, 2008)

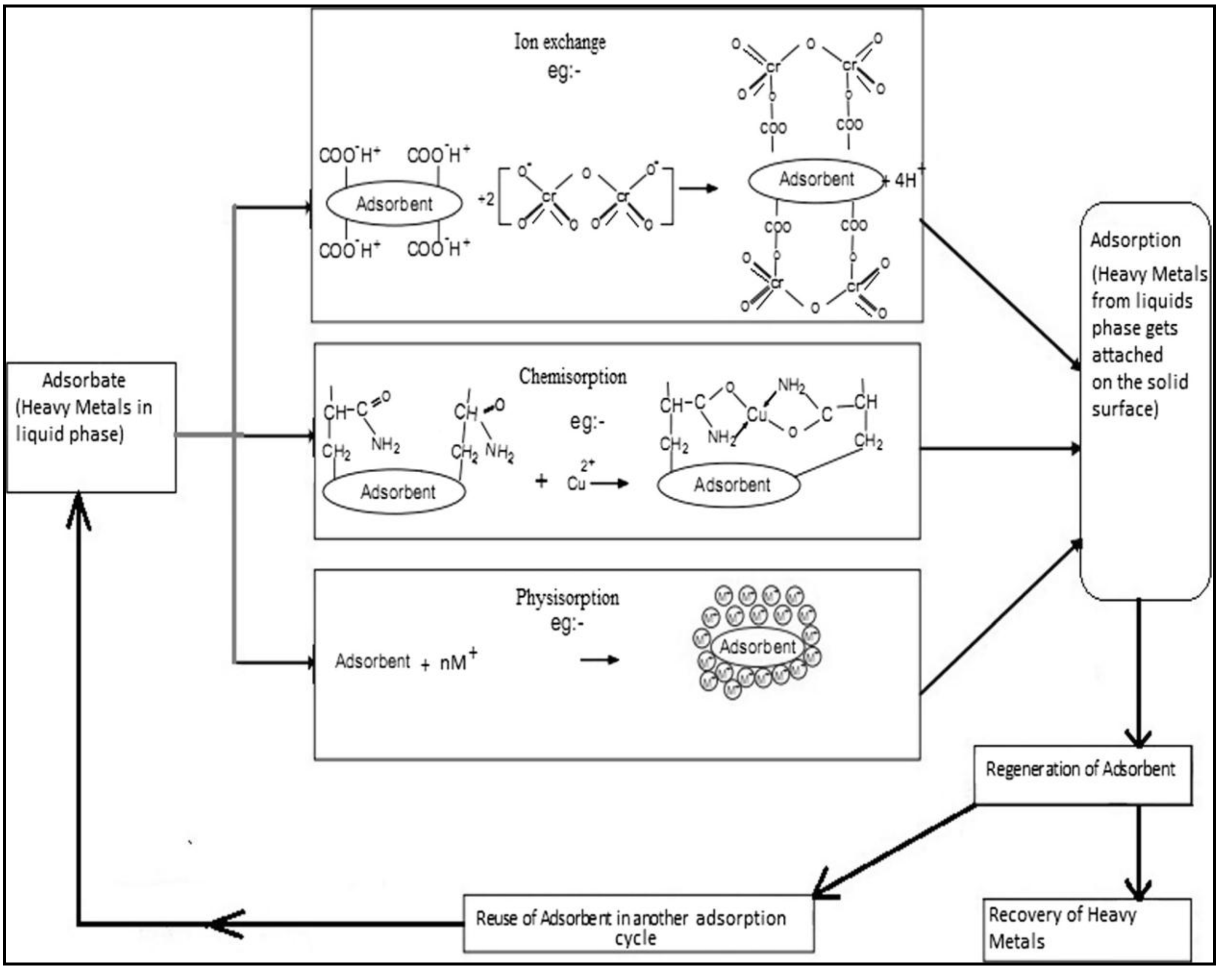


Figure 5. Mechanism of heavy metal adsorption on the surface of adsorbent

ADSORPTION ISOTHERM

Adsorption isotherm is used to describe the mechanism of how adsorbate ions interact on the surface of adsorbent. There are several isotherm equations available to analyze the experimental sorption equilibrium parameters, but the well known adsorption isotherm models used for single solute systems are Langmuir (1918) and Freundlich isotherms (1906). Both adsorption isotherm models are found to be more suitable to describe the relationship between q (quantity adsorbed at equilibrium, mg/g) and C (concentration of adsorbates remained in the bulky solution at the equilibrium, mg/L). Some other adsorption isotherm models are described as follows:

(i) Langmuir Isotherm: Based on Langmuir adsorption theory, molecules are adsorbed at a fixed number of well-defined active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between the adsorbed molecules (Langmuir, 1918). The Langmuir adsorption isotherm has been successfully used in many monolayer adsorption processes. The adsorption isotherm data were analysed by the Langmuir isotherm model in the linearised form,

$$Ce/qe = Ce/qmax + 1/(b\ qmax)$$

Where qe is the equlibrium adsorption capacity of the adsorbent (mg/g), Ce is the equilibrium metal ion concentration in solution (mg/l), qmax is the maximum amount of metal ion that could be adsorbed on the adsorbent (mg/g) and KL is the Langmuir adsorption equilibrium constant.

(ii) Freundlich Isotherm: Freundlich isotherm model interprets the adsorption on heterogeneous surfaces with interactions occurring between the adsorbed molecules and is not restricted to the formation of a monolayer. This isotherm is commonly used to describe the adsorption of organic and inorganic compounds on a wide variety of adsorbents (Febrianto, 2009). The experimental data were analysed by Freundlich isotherm model in the linearised form:

$$\log qe = 1/n \log Ce + \log KF$$

Where KF is the Freundlich adsorption constant and it is the maximum adsorption capacity of metal ions (mg/g) and n is the constant illustrates the adsorption intensity (dimensionless).

(iii) Temkin Isotherm: The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The adsorption experiment data were analysed by Temkin isotherm model in the linearised form,

$$qe = B\ \mathrm{In}\ Ce + B\ \mathrm{In}\ A$$

where B = RT/b, b is the Temkin constant related to heat of sorption (J/mol), A is the equilibrium binding constant corresponding to the maximum binding energy (L/g), R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K). The plot of *qe* against *In Ce* is given below.

(iv) Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich isotherm equation is generally used to distinguish between physical and chemical adsorption. It is given in the linearised form as,

$$\mathrm{In}\ qe = KDR\ \epsilon2 + \mathrm{In}\ qmax$$

where qe is the equilibrium adsorption capacity of the adsorbent (mg/g), qmax is the maximum adsorption capacity (mg/g), KDR is the Dubinin-Radushkevich constant (mol2/kJ2) and ϵ is Polanyi potential given by,

$$\epsilon = RT\ \mathrm{In}\ (1 + 1/Ce)$$

where R is the gas constant (8.314 * 10-3 kJ/molK), T is the temperature in Kelvin and Ce is the equilibrium concentration of metal ions (ppm). Thus the plot of *In qe* against *ϵ2* gives a straight line with a slope of KDR and an intercept of qmax. The Dubinin-Radushkevich isotherm also gives the mean energy of adsorption by the equation,

$$E = (-2\ KDR)-1/2$$

If the E value is less than 8 kJ/mol, the process follows physical adsorption, and if the E value lies between 8 and 16 kJ/mol, the process follows chemical adsorption. The Dubinin-Radushkevich isotherm plot for the experimental data as follows. From the Dubinin-Radushkevich isotherm plot, the linear regression value R2 was 0.791. The mean energy of adsorption was found to be 0.0535 kJ/mol which is less than 8 kJ/mol, and hence it is clear that the adsorption of Copper ions by

Chitosan–Red Soil beads was physical adsorption.

BIOSORPTION EFFICIENCY DETERMINATION SYSTEMS

The efficiency of heavy metals biosorption can be evaluated by using two different methods: (1) batch and (2) column. The best biosorbent material can be selected by using these two methods-

(i) Batch adsorption method

In this method, predetermined mass of biosorbent is mixed with a known concentration of heavy metals solution for a specific contact time (Loganathan, *et al.,* 2014). Batch sorption method is commonly used to evaluate maximum sorption capacity of various biosorbents, as this process is easy-to-operate and information about the impact of various solution parameters on biosorption process can be attained by carrying out several batch experiments simultaneously (Ghimire, *et al*., 2002; Kamsonlian, *et al.,* 2012; Khaskheli, *et al*., 2011; Niu, *et al.,* 2007).

(ii) Column adsorption method

Batch adsorption studies are used for the treatment of small volumes of effluents or for laboratory purposes. It is, however, not suitable to use at industrial scale, where large volumes of wastewater are continuously generated. So, for practical and large-scale operations, a packed column (fixed-bed) is preferred. Packed column is generally considered as the best reactor type for wastewater treatment, where fresh adsorbent is always in contact with wastewater, providing the essential concentration gradients between adsorbate and adsorbent for adsorption. This permits far more effective utilization of adsorbent capacity and also results in improved effluent quality. The performance of packed column is described by the theory of the breakthrough curve (Zou, *et al.,* 2013, Chatterjee and Schiewer, 2014, Simate and Ndlovu, 2015). The adsorption capacity by treatment of solvent extraction and alginate-immobilization of Citrus peel was enhanced by Chao, *et al.* (2014) and Chatterjee and Schiewer (2014) respectively. Though the uptake capacity in column is less than in the batch, residence time in column is much less than that in batch. Thus, column removes pollutants faster than batch.

REGENERATION OF ADSORBENT

Regeneration is a process in which adsorbent loaded agricultural wastes are eluted by using appropriate solvent to recover a small volume of concentrated pollutants (especially metals). One of the important industrial applications of adsorption is recovery of loaded pollutants from the adsorbent and simultaneous regeneration of the adsorbent for reuse. The usefulness of any adsorbent depends parameters in each case also vary depending on the active functional group (Kosasih, *et al.,* 2010, Palma*, et al*., 2011). Various chemicals like NaOH, HNO_3, H_2SO_4, and HCl were used in different concentrations to desorb metal ions from agricultural waste. Arsenic desorption from the biomass could be done by using suitable efluents including alkali and acid solutions (e.g. NaOH, KOH, H_3PO_4) (Pehlivan*, et al*., 2013; Pehlivan, *et al*., 2012).

FUTURE PROSPECTIVE

This review has focused on the recent evidence that identifies potential use of biosorbents like agricultural wastes for removal of heavy metals and dyes from contaminated water.

Biosorbents could also offer commercial purpose in the future therefore; further research should be focused on filling the following gaps:

- A detailed research is required for the characterization of novel biosorbents from agriculture/food-industry with maximum heavy metals sorption capacities to promote large-scale use of biosorbents.
- Studies are required to increase the understanding about the adsorption mechanism at the biosorbent-water interface.
- Various pre-treatment methods (as discussed above) should be explored to make the biosorbents efficient during the heavy metal remediation process.
- Diverse techniques are available for the characterization of biosorbents, however a combination of these

techniques is essential to acquire a complete description of the structure, morphology and surface functional groups.

- The idea of using biosorbents could be helpful in the development of an affordable 'green' filtration technology for purification of heavy metals-contaminated drinking water which would provide low income communities to enjoy heavy metals-free drinking water to protect them from health hazards.

CONCLUSION

Heavy metal contamination of water is a major health and environmental concern at global level due to its toxic and carcinogenic nature. For the treatment of heavy metal contaminated water, the process of biosorption can play a vital role by providing a low–cost and eco-friendly solution. Biosorption using agricultural wastes is a new process that has shown good promise for the removal of heavy metals and synthetic dyes from aqueous effluents. The use of these low cost biosorbents like agricultural waste is suggested since they are relatively cheap and easily available, renewable, can be easily modified, and show no waste disposal problem with good adsorption capacity for wide range of pollutants. Different surface modification methods as employed by researchers are useful for enhancement of adsorption capacity. The non-conventional, inexpensive and locally available effective biosorbents could be used instead of commercially available inorganic sorbents.

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