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Bio-sorbents from Agricultural Wastes for Eradication of Heavy Metals: A Review

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Abstract

Pollution of water by heavy metals is an emergent anxiety in the all over the world. Insufficient aquatic system treatments, attached with augmented industrial activity, have led to augmented heavy metal pollution in lakes, rivers, and other aquatic sources in different countries. However, common approaches for eliminating heavy metals from aquatic sources, including membrane filtration, activated carbon adsorption, and electrocoagulation, are not feasible especially for developing countries. Due to this reason, an important number of researches have been done on low-cost adsorbents like agricultural wastes to remove heavy metals from aquatic media. Thus, this review article summarizes the efficient removal of heavy metals with an emphasis on low-cost adsorbents (agricultural wastes). It evaluates the use of different agricultural waste adsorbent materials such as potato waste, peanuts waste, maize cob waste and tea waste. Along with a summary of the use of these adsorbents in the removal of heavy metals, this article provides a summary of the isotherms and kinetics of these adsorbents with its maximum adsorbate uptake capacities. The different biosorption mechanisms for the efficient removal of heavy metals are also discussed.

1. Introduction

Water is a fundamental prerequisite for all living things. In order to have safe and healthy life pure and uncontaminated drinking water is very much significant throughout the world. Even though, world water mandate enhanced per year, countless contamination have conceded possible marine sources [1]. In developing countries, the influence of augmented contamination is predominantly challenging since these contaminations do not have the resources to efficiently treat polluted water that can supply water to drinking and other uses. According to the World Health Organization (WHO) assumption 844 million people suffer from having a fundamental clean drinking water source and that 230 million people devote more than 30 min/d fetching water from an amended water source, which may include pipeline water, bore wells, threatened wells and coils, freshwater, and enveloped water [1,2]. The incapability for individuals in undeveloped countries to have reliable admittance to an amended clean drinking water source enhances the water borne diseases. In line to this WHO estimates, nearly 1.6 million people die per year from water borne diseases, such as diarrhea, mostly 90% of these are below 5 years of age [3].

The proliferation of heavy metals in drinking water sources is also a growing concern. Table 1 provides the characteristics of common heavy metals found in the developing world.

Recently, industrial, agricultural and urban developmental activities have increased all over the world, which has consequently involved to enhanced pollution of aqueous body with toxic heavy metals [4]. Heavy metals present in marine systems are non-biodegradable and extremely toxic even at low levels. Metal ions such as, lead, mercury, cadmium, chromium, zinc, copper and nickel present in maximum concentration are considered to be toxic. They are not decomposed under normal circumstances, their growth in ecological systems (e.g. air, soil and waters) in increased manner results in accumulation in foodstuff and aqueous body intended for human being utilization [5]. It might cause several sicknesses and infections by accumulating in living cells [6-10]. Also, they directly or indirectly affect the human and environmental health throughout the world [11]. Due to this reason, the efficient removal of heavy metal ions from the surroundings has become a paramount important.

In order to remove these heavy metal ions from aqueous media, numerous predictable methods, including adsorption, electrochemical coagulation, oxidation, flocculation, membrane separation, and others, have been investigated [12,5,13]. Among these, adsorption using activated carbon proved to be more advantageous with high heavy metal uptake capacity, high rate removal efficiency, and ease of working principle [14-17]. But, recent developments in the field of green chemistry resulted in alternative materials. There are some Green chemistry concepts including materials that substitute the use of dangerous chemicals such as, commonly used organic solvents and keep away from the generation of wastes that cannot be re-obtained and reused for future. Therefore, it is paramount important to generate low cost, effective, and eco-friendly materials for the adsorption of heavy metal ions from aqueous media [18].

Green processes are environment friendly and involves application of naturally available waste materials for heavy metal pollutant remediation. Green processes are known to involve biosorption and classified as a subdivision of bioremediation that has been significant in providing knowledge regarding the processes of environmentally friendly concept [19,20]. Application of biological materials as adsorbents for water purification purpose has got an enhanced merit to conventional chemical adsorption systems. These materials are considered as biocompatible under normal circumstances, easily available throughout the world and simple collection and preparation methods [21]. Biological adsorbents include fungi (moulds, fungi, and yeasts), algae (microalgae, macro algae, and seaweed), bacteria (Gram positive, Gram negative and cyanobacteria), natural, industrial, agricultural wastes, and others (e.g. materials made from chitosan and cellulose) [5]. These provide an increased surface area to volume ratio and have many reactive binding places on their surface to which pollutants can be effectively adsorbed under normal circumstances (e.g. -COOH, $-NH_2$, -OH, -SH groups) [22].Therefore, the present review is focused on application of agricultural wastes as bio-based adsorbents for the efficient heavy metal eradication from aqueous media.

2. Agricultural waste materials for heavy metal removal

2.1. Background

Agricultural wastes materials have exhibited a significant ability for adsorbing heavy metals and precious minerals, but needs chemical or thermal activation. The gold may be adsorbed from pregnant solution using cheap agricultural waste and the loaded adsorbent is then collected and smelted with flux to recover the solid precious metal. Low cost bio-sorbents derived from agricultural waste also have the advantage of good adsorption characteristics. The wastes constitute a significant proportion of worldwide agricultural productivity. It has been estimated by various sources that these wastes can account for over 30% of worldwide agricultural productivity. When discharged to the environment, agricultural waste can be both beneficial and detrimental to living matter. Bio-sorption is a metabolism independent process that occurs in the cell wall [17] and the mechanism responsible for the metal uptake may differ according to the biomass type. Cost effectiveness is the main attraction of metal bio-sorption. Since biosorption often employs dead biomass, this eliminates the need of nutrient requirement and can be exposed to environments of high toxicity [4].A major advantage of bio-sorption is that it can be used in situ, and with proper design may not need any industrial process operations with the ability of integration with many systems in the eco-friendliest manner [23].

2.2. Different Types of Agricultural Wastes used as Heavy Metals Removal

A large number of agricultural residues such as potato wastes, maize wastes, peanut wastes, tea wastes**,** etc. can be potentially used to remove toxic heavy metals from aqueous media [4].The details are presented in the following section.

2.2.1. Potato waste-based bio sorbents

Potato peels are largely available agricultural solid residue mostly used for pollutants removal applications throughout the world. Firstly, potato peels were used for the preparation of a charcoal and the material's adsorptive competence of Cu(II) in industrial wastewater samples were indicated [24]. Potato peels were first subjected cleaning and then thermally treated in a furnace for 2 h at 700 ℃ or (973 K). The obtained potato peels charcoal (PPC), was ground and sieved to get the particles of 0.2mm. It has been proved that one gram of PPC has an ability to remove approximately, 99.8% of Cu(II) (150 mg/L, 100 mL) at pH 6 after shaking for 20 min at 30 ℃. Even though the Langmuir maximum Q_o value was very low (0.3877 mg/g) as presented in this report, the negative value of ΔG^o confirmed that the uptake capacity was spontaneous and PPC indicated the similar uptake performance through 5 cycles. Moreover, PPC powder (particle size of 0.147 mm) adsorbent was prepared after treating it with HCl followed by washing with distilled water, drying at 60 ℃, and sieving for the nickel removal from water [25]. The up take capacity confirmed greater solution pH dependence and the optimum up take capacity was near to pH value of 9. At these optimum dose (1.4 g/L) and optimum pH the adsorbent confirmed the up take capacity of nearly 90% in 250 mg/L Ni(II) solution after 50 min shaking time. It has been reported that these materials after modification by HCl as an adsorbent material with particle size < 75 mm were effective for hexavalent chromium remediation [26]. Quantitatively, 100% uptake capacity of Cr(VI) observed at low concentration of 4 g/L in acidic conditions.

Secondly, potato peels in dry form could be used without further treatment for Cu(II) removal applications [27]. From this report it is possible to understand that the optimal values of various factors were observed at the dosage of the sorbent is 0.15 g/400mL and the particle size is in the range of 0.16-0.63 mm, concentration of the copper solution is 300 mg/L, solution pH nearly neutral, at room temperature, agitation speed at 800 rpm, and without the of addition NaCl. The pollutant uptake capacity decreases with increasing the particle size, ionic strength, or temperature. Also, fitting of the equilibrium data to Langmuir, Freundlich, isotherm models indicated that the adsorption process was much better. The stated Langmuir adsorption capability in the above circumstances was found to be 84.74 mg/g, which is a greater value compared to other similar low-cost biosorbents.

Furthermore, potato peels charcoal adsorbent in which the powder was chemically treated with HCl was prepared to remove Fe(II) ions from aqueous media [28]. Here, the thermal effect was found to be a crucial factor for binding processes. The maximum Fe(II) ions uptake capacity was reached at 20 ℃ (293 K), while increasing to 60 ℃(333 K) led to removal decrease the Fe(II) ions uptake capacity, because of the enhanced reverse processes for adsorption and the non-endothermic nature of the binding action. The untreated PPC revealed that the uptake capacity of 36.1% and 21.8% corresponds to 50 mg/L and 250 mg/L iron solution, respectively, at 20 ℃. Chemical modification with HCl provides more significant uptake capacity of 90.4 and 78.0% in 50 and 250 mg/L, respectively. Here, the Freundlich model was found not suitable for adsorption, while the Langmuir model indicated better fitting with its R^2 value was above 0.999 in all cases. The highest uptake capacity of 121.95 mg/g based on the Langmuir model for PPC was resulted. In addition to this, the pseudo-second order kinetic models describe better binding process for all samples, compared to the pseudo-first order [28].

The past studies reported the use of activated carbons as remediation agent prepared from biomass byproducts for removal of different pollutants, such as, toxic heavy metal ions, dyes, and pharmaceuticals remains to breed powerfully [29-38].The elimination of Co(II) using chemically modified (H_3PO_4 and pyrolysis) activated carbons prepared from potato peels shows a good up taking capacity [39]. Here the most significant of using biomass for the preparation of adsorbents (porous carbons) is the great products of the process. The maximum product reported was 55% from the pyrolysis modification at the lowest temperature (400 ℃) and the lowest product reported was 49% from the highest temperature (800 ℃). In addition to this, the metal removal efficiency of carbonaceous adsorbents, is dependent on their textural structures and their superficial areas.

In addition, activated carbon adsorbents synthesized via hydrothermal treatment of potato peels followed by chemical activation was reported for the elimination of Co(II) ions. Concisely, washed and dry potato peels undergoing a hydrothermal action in an autoclave at 200 ℃ for 4 hrs in heating rate of 4 ℃ per min, a pressure of around 580 psi at 200 ℃, and mixing at a rate of 150 rpm. The resulted residue was washed using hot deionized water as well as ethanol and was dried at 100 ℃. Following, it was chemically modified with H_3PO_4 and finally subjected to carbonization at 400 ℃, 600 ℃, and 800 ℃ under nitrogen atmosphere.The resulting material after Soxhlet washing, freeze-drying, and grinding/sieving was evaluated as adsorbent and its relative removing capacity was found to be around 32.5%.

Recently, the usage of potato peels as a non-economic security impact for activated carbon adsorbent preparation for Pb(II) elimination was reported [40]. This adsorbent was prepared using the hydro carbonization process and the specific surface area obtained based on N_2 sorption was 625 m^2/g, which is an acceptable worth aimed at carbon resources obtained from bio wastes and a comparatively trifling activation/ carbonization way. The optimum solution pH was established to be 6 and estimation of the equilibrium statistics showed an improved fitting to the Langmuir rather than to Freundlich isotherm model. The q_m was found to be 217 mg/g at 20 ℃ and 262 mg/g at 50 ℃. The thermodynamic studies suggested that the adsorption was a spontaneous and endothermic process. Stimulatingly, the researchers offered also approximations concerning the actual cost-effectiveness of the hydrothermal produced activated carbon adsorbent materials.

2.2.2. Peanut waste-based bio-sorbents

Based on the database of Scopus more than 180 research articles, considering the elimination of different pollutants such as, toxic heavy metals, dyes, etc. using peanut plant-based adsorbents including activated carbon, bio char and ashes, have been reported since 1972, when the usage of peanut husks, between other resources, were established for the eradication of mercury [41].

According to the reported results, peanut husks can be implemented as an economical and environmentally welcoming bio-sorbent for the eradication of different toxic heavy metal ions. For instance, Witek-Krowiak et al. [42] reported that the high pollutant uptake capability of peanut husks of 25.39 mg/g and 27.86 mg/g for Cu(II) ions and Cr(III) ions, respectively. The heavy metal uptake capacity enhances at its equilibrium value within 20 min and its temperature of 50 ℃. Though, the adsorption capability diminished at 60 ℃ and it was accredited to the credible damage of active adsorbing sites of the biomass. Furthermore, they implemented four rate models to determine the kinetic parameters and five adsorption isotherm models to describe the biosorption equilibrium.

The main shortcoming of the formerly reported removal investigation is that most of the studies are still in the lab-scale, therefore they have taken industrial wastewater to examine the effect of peanut husks for the eradication of different metal ions [43]. The eradication capacity was 100%, 41%, 38%, 30%, and 24% for Pb(II), Cd(II), Mn(II), Co(II) and Ni(II) ions, respectively. According to the calculated results and running costs of the resulted pilot scale treatment plant, the peanut husks proved to be an economical heavy metal removal agent. In addition to this, the estimated costs (including electrical energy, treatment, transportation, reagents, drying would be nearly 10 EUR (11.35 USD) per ton) of the peanut husks have also been reported [44]. Generally, this indicates a good example of a well-organized biosorption study. Remarkably, certain investigators have selected to customize exclusively the term "groundnut" in the place of the more common term "peanut", and it would be recalled when penetrating for applicable publications. A good example of this study was the sorption performance comparison of the raw groundnut husks and citric acid modified groundnut husks [45]. The highest uptake capacity of Cu(II) ions obtained from the Langmuir isotherm was 33.49 and 15.36 mg/g for raw and modified husks, respectively.

Liu, Sun and Li [46]. compared that, the sorption efficiency between pristine and chemically modified peanut shells. Even though, the highest up taking capacity of epichlorohydrin/ ethylenediamine modified shells compared to the pristine one, the potential health and environmental hazards associated with the use of these toxic substances was not mentioned. Due to this reasons, A. Kausar et al., [47] reported an environmentally-friendly modification method including the use of weak acids and base solutions, where peanut shells and sugarcane bagasse for the removal of Sr(II) ions. Here the metal removing mechanism involves complexation of metal ions with oxygen-containing functional groups of the biomass.

2.2.3. Maize waste-based bio-sorbents

Maize is one of the largest production crops in the world and their cob is one type of agricultural wastes having natural ion-exchange capability [48]. Due to this reason, it is used mostly for heavy metal removal purposes. The enhanced removal capacity would be achieved through chemical modification enhancing their natural ion-exchange capability and add value to the by-products [49]. Achanai Buasri et al., [50] treated corn cobs with phosphoric acid (PA) to modify the biosorbents and analyzed their property. The biosorption capacity of the modified corn cob to remove zinc(II) from wastewater was evaluated as a function of initial solution concentration, initial biomass concentration and temperature. The adsorption equilibrium was expressed using Langmuir, Freundlich and Temkin models. Furthermore, two adsorption kinetic models were calculated to analyze the experimental data.

The other type of maize based wastes involved is maize tassel, which is the male part of the maize plant. Its major purpose is the production of pollen grains which fertilize the female part of the maize flower which then develops into a cob. Pollination and fertilization in a maize field covers a period of not more than 21 days if the plants germinate within 1 week. This means tassel has no production value after fertilization. The aim of this study was to optimize the removal of Pb(II) from simulated aqueous solutions by maize tassel powder and to apply the optimized method for the removal of lead and other heavy metals from environmental aqueous solutions [51].

Also, maize stover is the other major crop wastes in Ethiopia, Nigeria, Zimbabwe and other African countries. It is characterized by a low protein and high fiber content. It consists of the wastes of maize which was left in a field following the harvest of the grain. It includes stalks, leaves, husks, and cobs. It is either grazed in situ or removed from the land prior to livestock feeding. It can be used as an adsorbent material for water purification, energy sources etc. In this regards, Mambo Moyo et al., [52] performed a research to compare and evaluate raw and acid treated maize stover as biosorbents for enhanced removal of Pb(II) from aqueous solutions and wastewaters. The removal efficiency was investigated by a series of experiments under different experimental conditions such as solution pH, contact time, initial Pb(II) concentration, temperature and biosorbent dosage. The adsorption isotherm and sorption kinetics of Pb(II) ions onto raw and acid treated maize stover are presented.

Maize is a Pakistan's third most important cereal crops after wheat and rice. It is used as food, feed as well as wet milling industrial agent. Pakistan environmental conditions are very favorable and for domestic need, surplus amount of maize is produced [34]. Corn cob is produced as a waste material from maize during processing. Small amount of corn cob waste is used as a fuel (in kitchen for cooking purpose) and other is wasted in huge quantity [35].In view of current scenario of heavy metals contamination of water bodies, there is a need to explore alternate adsorbents for the remediation purposes. So far, the possibility to use modified corn cob waste biomass as adsorbent is of great interest, which has not been studied previously for Cr ions adsorption. In the present investigation, corn cob powder was immobilized in Ca–alginate beads and adsorption efficiency of prepared adsorbent was evaluated for Cr ions. Various process variables such as Cr ions initial concentrations, contact time, pH and adsorbent dosage were also studied. Equilibrium and kinetic models were employed to evaluate the adsorption behavior of Cr(III) and Cr(VI) on to modified corn cob adsorbent [53].

2.2.4. Tea waste waste-based adsorbents

Tea waste is another agricultural waste and considered as bio-waste. Due to the outstanding level of aromatic, carboxylate, hydroxyl and phenolic groups in its leaves, it exhibits prolonged ion replacement characteristics which intern increases its pollutant uptake capacity as presented in the review [54,55].

The high uptake ability of tea waste for different pollutants was indicated (Table 1). Here, K.L. Wasewar [56] reported approximately 99% of Zn(II) (50 mg/dm^3 initial concentration) was found to get adsorbed onto tea factory waste at pH of 4.2 under batch conditions. From this point view, it is possible to conclude that it is not only environmentally friendly but also having high pollutant uptake capacity. Currently, mixed waste tea resulted in comparatively higher Cr(VI) eradication (with uptake capacity of 94 mg/g) than coffee ground (uptake capacity of 87 mg/g) under same laboratory situations (Cr(VI) concentration of 250 mg/L, pH of 2) [57].

Table. 1. A list of adsorption isotherms and kinetics for the adsorption of potentially toxic heavy metals on agricultural waste derived biosorbents.

Biosorbents	Adsorbate	Adsorbent maximum capacity (mg/g)	Dominant isotherm/kinetic model	Refs
Potato peels HCl activated	Cr(VI)	3.28	Langmuir and pseudo-first order	[26]
Potato peels charcoal	Fe(II)	121.95	Langmuir and pseudo-second order	[28]
Hydrothermally and H_3PO_4 activated carbon derived from Potato Peels	Pb(II)	217	Langmuir and pseudo-first order	[40]
Peanut shells	Cr(III)	27.86	Langmuir and pseudo-second order	[42]
Peanut shells	Cu(II)	25.39	Several models (Langmuir, Sips and Redliche Peterson) /pseudosecond order	[41]
Corn cob	Ni(II)	12	Langmuir and Pseudo-second order	[43]
Corn cob	Pb(II)	32.4	Langmuir and Pseudo-second orde	[43]
Corn cob	Cd(II)	24		[43]
Peanut shells	Cd(II)	6.00	Langmuir/pseudo-second order	[46]
Peanut shells	Hg(II)	1.90	Langmuir/pseudo-second order	[46]
Tea waste	Zn(II)	8.9 mg/L	Langmuir	[56]
Alkali treated tea residue	Pb (II)	64.10	Langmuir and Pseudo-second order	[60]
Alkali treated tea residue	Cu(II)	43.18	Langmuir and Pseudo-second order	[61]
Magnetite-decorated tea waste	Cu(II) And Zn(II)	95.44 68.78	Langmuir and Pseudo-second order	[63]
Peanut shells	Cu(II)	30.59	Langmuir/modified dose response model	[65]
Black tea waste	Cu(II) Pb (II)	48 65	Langmuir and Freundlich Pseudo-second order	[66]

Different methods have been used to advance the pollutant uptake capacity of tea waste such as, before treating it with Trichodermareesei cellulases Bacillus sp. [58,59], alkali [60,61]. $Ca(OH)_2$ [62], magnetite [63,64]. For instance, the adsorption efficiency of agricultural tea waste to adsorb Cr(VI) was increased due to the presence of cellulosic material in trichodermareesei cellulases that provides more accessible area for metal adsorption. Hydrolysis using this enzyme provides acceptable structure, supplementary attacked carbon sites and exhaustive modification in the conformation of tea waste. In addition to this, green tea waste was soaked in heated water and immersed in 0.05 mol/L $Ca(OH)_2$ solution. The resulting material was used for the uptake of As (III) and Ni(II) in both single and binary systems. At acidic pH value (pH=3) the maximum uptake capacity was observed (for As) and at neutral pH (7) (for Ni) and their values were 0.42 and 0.31 mg/g for As(III) and Ni(II), respectively [60].

3. Mechanisms of heavy metal removal from water using agricultural waste

Several mechanisms were reported by different scholars in the past, which involves processes such as ion exchange, chemical precipitation, oxidation-reduction, flocculation, and adsorption [67-69].Among these, adsorption is the significantly used heavy metal eradicating mechanism from water by using different adsorbents such as, agricultural wastes, clay, nanomaterials and defined as a process in which adsorbate or pollutants accumulates on the adsorbent surface either chemically or physically. From all these adsorbent materials, this review focuses on agricultural waste based adsorbent materials due to its biodegradable and non-toxicity nature. During the eradicating process, there are many things disturbing the heavy metal removing mechanism such as, the particle size of adsorbent materials, affinity of the adsorbate for the adsorbent, the surface area of adsorbent, degree of ionization of the adsorbate molecule (more highly ionized molecules are adsorbed to a smaller extent than neutral molecules), solution pH etc. The heavy metal uptake capacities were greatly enhanced through the optimization of these things. The quantity of adsorbed heavy metal is calculated by the difference between the original and equilibrium quantity of pollutants in solution divided by the weight of the adsorbent. The number of pollutants can be calculated from mass balance:

$$m(q-qe)=(Co-Ce)v \qquad (1)$$

Where m stands for mass of adsorbent, v stands for volume of liquid, C_o stands for the initial adsorbate concentration in solution (mg/L), C_e stands for the adsorbate residual concentration in solution, q_o designated for the initial amount of adsorbate per unit mass of adsorbent (mg/g)

From which a relationship between the value of C and the corresponding equilibrium value of q can be established. To determine equilibrium relationship, $q_o = 0$:

$$qe=\frac{v}{m}(Co-Ce) \qquad (2)$$

During binding, dissolved substances are passed into adsorbent constituent parts by dissemination and are then trapped onto surfaces of biding materials. Both chemisorption and physisorption interaction is participated during the adsorption process. In chemisorption, the contaminant binds with the surface to form covalent or ionic binding leads in binding energies of >80 kJ/mol. In physisorption, a rapid process is caused by nonspecific binding mechanisms such as van der Waals forces and results in bonding energies of 4 - 40 kJ/mol. Generally, physical adsorption is less specific for which compounds bound, has weaker forces and energies of bonding, works over longer distances (multiple layers) and is more reversible [70].

In contrast to the binding of organic contaminants from water (polar solvent) onto a nonpolar binding species (carbon-based materials), where van der Waals forces are predominating, binding of ionic species (metal ions), onto cellulose nanomaterial surfaces is driven by electrostatic attraction, which is highly dependent on solution pH and ionic strength because of the charge differences. The affinity of the heavy metal for binding species is quantified using adsorption isotherms, which are used to describe the amount of adsorbate that can be adsorbed onto an adsorbent at equilibrium and are usually a function of the liquid phase concentration. To develop isotherms, a known quantity of adsorbate in a fixed volume of liquid is exposed to various dosages of the adsorbent.

Here, one can consider the significant differentiation between adsorption of a solitary and of multiple compounds. In the first case, the dissimilar adsorbates are competing for binding places and the adsorption equilibrium, as well as the isotherm, can be significantly dissimilar than without antagonism. In the second situation, the initial concentration of the target adsorbate influences the consequential isotherm. For the mathematical description of the adsorption equilibrium, one can consider the existence of different models, differing in complexity and in the number of parameters. Mostly, for practical importance, the two main parametric isotherms (Langmuir isotherm and Freundlich isotherm) are formulated [71].

The Langmuir isotherm is important for the binding of a solute from a liquid solution as monolayer adsorption on a surface containing a fixed number of similar sites. This model describes the equilibrium between the adsorbent surface and adsorbate as a reversible chemical equilibrium between. It assumes homogeneous energies of binding onto the surface of the adsorbent without the interaction of adsorbate in the plane of the surface where adsorbate molecules can be chemically bound. Its equation assumes that uniform arrangement of the adsorbent surface, i.e. all binding sites are energetically identical. Due to these reasons, the Langmuir equation is in most situations only relevant for small level ranges. Equilibrium parameter (RL) indicates the isotherm shape and whether the binding is possible or not possible. The Langmuir nonlinear equation is commonly expressed as follows [71]:

$$qe = \frac{Q_o Ce}{1 + bCe} \tag{3}$$

To derive the model parameters Q_o and b, equation 3 can be linearized. The linear Langmuir isotherm allows the calculation of adsorption capacities and is equated by the equation 4:

$$\frac{Ce}{qe} = \frac{1}{bCo} + \frac{Ce}{Qo} \tag{4}$$

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L (Table 2), which is defined by equation 5:

$$RL = \frac{1}{1 + bCe} \tag{5}$$

Where Q_o designated for the maximum uptake concentration and b designated for the ratio of adsorption and desorption rates.

Table. 2. Type of isotherm for various R_L.

R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L=0$	irreversible

The second important isotherm is Freundlich isotherm and can be obtained assuming a logarithmic decrease in the enthalpy of binding with an increase in portions of engaging places. This isotherm is generally improved to describe adsorption in water media compared with the Langmuir isotherm. This isotherm is commonly given by equation 6 which is non-linear [70];

$$qe = Kf C_n^{\frac{1}{n}} \tag{6}$$

K_f represents an adsorption coefficient which reveals the number of contaminants bound to binding material surface for unit equilibrium concentration, called a constant for system related to bonding energy. 1/n is representing an empirical constant associated with the degree for adsorption driving force to binding material, becoming more heterogeneous as its value gets closer to zero. The Freundlich istherm that determines both K_f and n was earlier reported in equation 7 [72]:

$$\log qe = \log Kf + \frac{1}{n}\log Ce \tag{7}$$

In addition to this, B. U. Ugi [73].tested graphically for the values of surface coverage (ϴ), in order, to fit with different isotherms using equation 8 and confirmed that the adsorption behavior follows whether Langmuir isotherm or Freundlich isotherm.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{8}$$

where ϴ is the degree of surface coverage, k the equilibrium constant of the adsorption – desorption process and C the concentration of the inhibitor in the electrolyte.

Next to the adsorption isotherms, the adsorption kinetics gives the statement of adsorption rates and significant information for scheming and modeling of the progressions. A significant benefit for pollutant binding processes is difficulty in minimization of expensive resources with cheap, easily available and plentiful adsorbents of known kinetic parameters and sorption characteristics. Until now, numerous kinetic models (pseudo-first- and second-order equations, intra-particle diffusion and Elovich equations) are implemented to construe time-dependent experimental data as well as inspect the controlling mechanism of pollutant binding process [74]. The Pseudo-first order model [74] is given by equation 9:

$$\log(qe - qt) = \log Qe - \frac{K1t}{2.303} \tag{9}$$

The pseudo-second-order kinetic model equation (Ho and McKay, 1998) is given by equation 10,

$$\frac{t}{qt}=\frac{1}{K2qe^{2}}+\frac{t}{qe} \tag{10}$$

Also, the spontaneous action of binding processes was easily determined by obtaining information from the thermodynamics concept. Therefore, concepts of standard Gibb's free energy change (ΔG^o) predict whether spontaneous or non-spontaneous actions are implemented. If the value of ΔG^o is negative, then the reactions occur spontaneously at a given temperature. Change in standard free energy ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) can be calculated by using the following equation 11,12 &13 [74];

$$\Delta G^{\circ} = -nRTlnK_C \tag{11}$$

$$lnK_C = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{12}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{13}$$

Where R (8.314 J/molK) is the gas constant, T (K) is the absolute temperature and K_c is the standard thermodynamic equilibrium constant defined by q_e/C_e. By plotting the graph of lnK_c versus T^{-1}, the value of ΔH^o and ΔS^o can be estimated from the slopes and intercept, respectively.

Generally, the adsorption mechanism of heavy metals onto the agricultural waste adsorbent was investigated as the schematic representation (Figure 1):

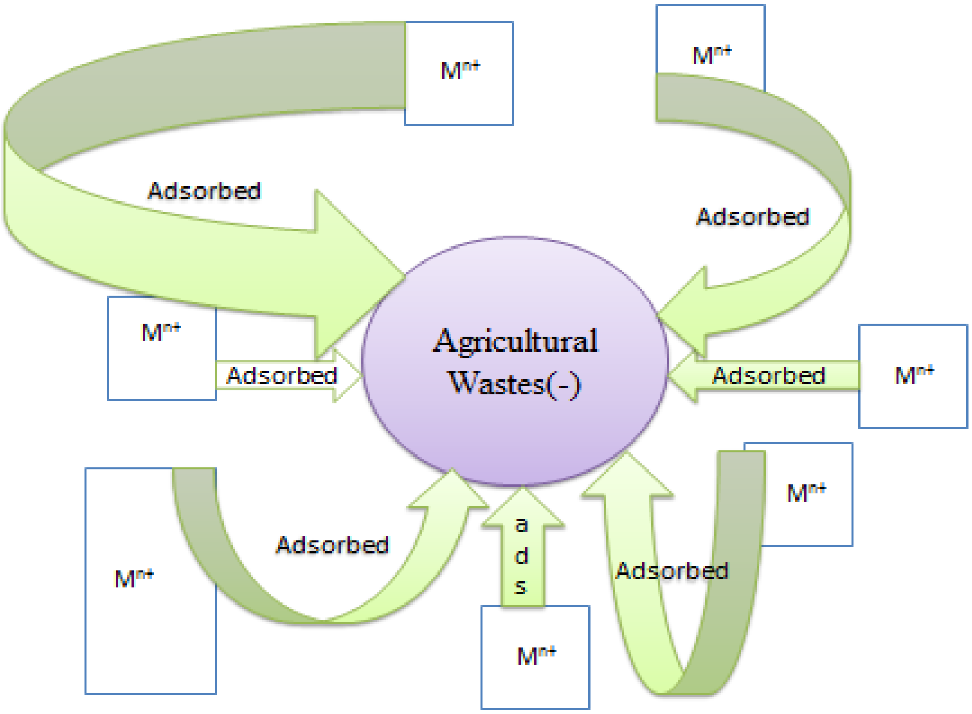

Figure. 1. The schematic representation of M^{n+} ions adsorbed onto the Agriculture waste adsorbent.

From the schematic representation one can understood that the adsorption mechanisms are dependent on the degree of adsorbate-adsorbent interaction and the adsorbate-solvent interactions. This point view was supported researches reported by [74,75]. Therefore, it shows the adsorbate has positive charge and the adsorbent has the negative charge on the surface and the adsorption process enhances greatly.

Finally, an important mechanism is recycling adsorbents implemented by acid washing. If a binding process is thought of as surface complexation reaction, a high concentration of H^+ ions shifts the equilibrium so that less adsorbate (pollutants) is bound to the surface. In addition to this, the surface acid/base reaction is shifted more towards positively charged species, which hinders the absorption of cations such as metal ions. As a result, a pH decreases due to the use of HCl shifts the adsorption equilibrium and can result in desorption of adsorbed solute (metal ions). If the adsorption capacity can be regained in this process, the adsorbent was regenerated. In many studies, hydrochloric acid (HCl) solution has been shown as a suitable regenerant for cellulose-based adsorbents as well as hybrid anion exchange resins. The pollutants-desorb ability was represented by equation 14:

$$\text{Percent of desorption } (\%) = \frac{desorbed}{adsorbed} * 100\%\ldots(14)$$

Where, Desorbed: the concentration of the metal ions after the desorption process Adsorbed: $(C_o - C_e)$ for each recovery process.

4. Conclusion

In this study, the efficient removal of heavy metals using bio-sorbents from agricultural waste as eradicating agent has been reviewed. Agricultural wastes have great potential for eradication of heavy metals due to their distinctive physical and chemical properties. Agricultural waste prioritization for the efficient removal of heavy metals and its adsorption mechanisms was discussed briefly. Most of the past reports revealed that agricultural wastes proved to be efficient biosorbents after chemical or thermal treatment and their implication in heavy metal adsorption is one of the most proficient and flourishing applications due to their biodegradable and biocompatible nature. In the concluding lines, it is summarized that there is much recent interest in the utilization of agricultural wastes which is relatively a non-invasive tool in varied applications including water treatment. Therefore, using agricultural wastes as adsorbent for water treatment especially for developing country like Ethiopia was multidirectional benefits including cost effective, clean and safe environment and high uptake pollutant capacity.

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