

PAPER • OPEN ACCESS

Adsorption mechanisms for heavy metal removal using low cost adsorbents: A review

To cite this article: E I Ugwu *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **614** 012166

View the [article online](#) for updates and enhancements.

EXTENDED ABSTRACT DEADLINE: DECEMBER 18, 2020



239th ECS Meeting

with the 18th International Meeting on Chemical Sensors (IMCS)



May 30-June 3, 2021

SUBMIT NOW →

Adsorption mechanisms for heavy metal removal using low cost adsorbents: A review

E I Ugwu^{1*}, O Tursunov^{2,3,4}, D Kodirov², L M Shaker⁵, A A Al-Amiery⁵, I Yangibaeva⁴, and F Shavkarov⁶

¹Department of Civil Engineering, College of Engineering and Engineering Technology, Michael Okpara University of Agriculture Umudike, P.M.B.7267 Umuahia Abia state, Nigeria

²Department of Power Supply and Renewable Energy Sources, Tashkent Institute of Irrigation and Agricultural Mechanization Engineers, 100000 Tashkent, Uzbekistan

³School of Mechanical and Power Engineering, Shanghai Jiao Tong University, 200240 Shanghai, China

⁴Research Institute of Forestry, 111104 Tashkent, Uzbekistan

⁵Department of Applied Science, University of Technology, 10001 Baghdad, Iraq

⁶Department of Accounting and Audit, Tashkent Institute of Irrigation and Agricultural Mechanization Engineers, 100000 Tashkent, Uzbekistan

*Email: emmanuelugwu@mouau.edu.ng

Abstract. A review of adsorption mechanisms for heavy metal removal using low cost adsorbents has been carried out in this article. Some metal ion sequestration techniques used over the years have some demerits, ranging from generation of sludge to high operational cost. Adsorption process using low cost adsorbents has been found cost effective and environmentally nuisance-free. In this review, various low cost adsorbents for heavy metal sequestration have been studied. The application of some adsorption models such as single and multi-component isotherms, adsorption thermodynamics, and kinetics as well as the effect of process parameters on heavy metal sequestration using low cost adsorbents has also been reviewed so as to better understand the adsorption process. From the literature reviewed, the percentage removal of chromium, copper and zinc was favoured by an increase in contact time, temperature, initial concentration, adsorbent dosage as well as a decrease in pH.

1. Introduction

High quality portable water is very necessary for domestic, industrial, agricultural and commercial purposes. Things provided by the environment in order to meet our desires and needs, which can be depended on with time are known as resources [1]. Water is the most essential of all the resources on earth and needs urgent attention. The major quantity of portable water is polluted as a result of industrialization. Water pollution



refers to any human activity which contaminates water and thereby, making it unfit for use as a resource. The rapid growth in urbanization as well as industrialization has brought about aquatic environmental degradation owing to sporadic discharge of effluents. As a result, heavy metals are deposited into the terrestrial and aquatic habitat, and this has equally brought about the biological cycling of hazardous heavy metals [2]. Heavy metals refer to any metallic element which has a density that is greater than 5.0g/cm^3 , hence, density which is five times greater than the density of water. They are toxic even with minute concentrations ranging from 1.0-10mg/l. However, some metal ions such as copper, mercury, zinc, chromium, lead, nickel, Arsenic, cobalt, Tin and cadmium are toxic even when present in a very minute quantity in the range of 0.001-0.1 mg/l concentration [3, 4]. The presence of metal ion in industrial wastewater or water is an environmental issue of global concern [5, 6]. They are of great concern owing to their non-biodegradability as well as their prevalence. Nnaji et al (2017) [7] pointed out that heavy metals are pollutants of priority owing to their persistence in the environment and their high mobility. A significant increase in industrial use of metals together with the discharge of same over the years has unavoidably brought about an increase of metallic substances in water bodies [8]. Heavy metals can equally occur through contamination in water from soil as well as through precipitation and ground water systems [4, 9, 10, 11].

Several conventional methods which include ion exchange, chemical precipitation, reverse osmosis, electrochemical methods and carbon sorption [12, 13, 14, 15, 16] are available for sequestration of heavy metals from water. However, they are not cost-effective. Adsorption has been found very effective in sequestration of heavy metals, owing to the fact that it is efficient in reducing metal ions to minute concentrations, cheap, affordable, profitable and very easy in operation [17].

The primary objective of this review work is to give an overview of the adsorption mechanisms using low cost adsorbents. Several sections relating to heavy metal adsorption such as the health effects, the permissible limits, the adsorption isotherms, kinetics, thermodynamics and the process parameters were highlighted for description of the adsorption process.

2. Adsorption Techniques

Adsorption is defined as the mass transport of substances from either gas or liquid state to a solid interface, which gets attached by physical and/or chemical interactions [18]. It is a mechanism where molecules move out of the solution and, thereby get attached to the surface of the chemical through physical and chemical bonding [19]. Adsorption differs from absorption in that adsorption is based on surface whereas, absorption is based on volume. A concept known as “sorption” is used for both absorption and adsorption whereas desorption refers to the opposite of adsorption.

2.1. Adsorption Models and Isotherms

Adsorption process does not have a specific mechanism. However, the mechanism of action which exists between the adsorbent surface and the heavy metal ions can be described with the use of adsorption isotherms [20]. The adsorption models for both single and many component systems were studied by several researchers [21, 22, 23, 24, 25, 26, 27].

Adsorption process does not have a specific mechanism. However, the mechanism of action which exists between the adsorbent surface and the heavy metal ions can be described with the use of adsorption isotherms [20]. Adsorption isotherms can be described as the relationship obtained when the adsorbed material is determined as a function of the concentration of the adsorbent at a fixed temperature [19]. It is very important to analyze the isotherm data because it helps in developing equations that describe the results accurately. The equations, so developed also, help in the design and optimization of the process parameters. The most widely used isotherms for liquid/solid phase systems are the Langmuir and

Freundlich Isotherms, which are known as the two-parameter-theoretical isotherms [28, 29]. The major reasons behind their usage are likened to their easy interpretability as well as simplicity.

2.1.1. Langmuir Isotherm

The assumption of the Langmuir isotherm is based on the fact that the attainment of equilibrium is achieved when there is saturation of the adsorbent by the monolayer adsorbate substances [23].

The Langmuir isotherm is shown thus:

$$q_e = Q \frac{b C_e}{1 + b C_e} \quad (1)$$

The linearized form of the Isotherm is:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \left(\frac{1}{Q_m}\right) C_e \quad (2)$$

Where Q_e = the quantity of the adsorbed adsorbate per unit mass of the adsorbent (mg/l)

C_e = the adsorbate equilibrium concentration (mg/l)

b = a constant which is related to the affinity existing between the adsorbate and the adsorbent.

Q_m = the saturation ability of the monolayer which is expressed theoretically.

2.1.2. Freundlich Isotherm

The Freundlich isotherm is an empirical model which takes the adsorbent mono molecular layer interference of the solute into consideration. Nevertheless, it is based on the assumption that there is a heterogenous surface possessed by the adsorbent, such that the binding sites are not similar [22]. For a single component system, the isotherm is described thus; [26].

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

The linear form of the Isotherm is;

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

K_F and n in the equation are the known as the Freundlich constants, where n gives the favourability of the adsorption technique and K_F is the adsorption capacity. K_F and n can be determined by plotting $\ln q_e$ versus $\ln C_e$.

2.1.3. Dubinin-Radushkevich Isotherm (DR)

The Dubinin-Radushkevich Isotherm is another Isotherm that is used for single component adsorption. It has the form:

$$q_e = q_m e^{-\beta \varepsilon^2} \quad (5)$$

The linear of Dubinin–Radushkevich isotherm is shown thus:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (6)$$

Where q_m =Dubinin–Radushkevich monolayer capacity (mmol / g),

B = a constant which is sorption energy-related, and ε =the Polanyi potential which is equilibrium concentration-related. Hence,

$$\varepsilon = R T \ln \left(1 + \frac{1}{C_e}\right) \quad (7)$$

R =gas constant (8.31J/mol K), T =the absolute temperature, b = a constant and E = the mean free energy, E which can be computed thus;

$$E = \frac{1}{\sqrt{2\beta}} \quad (8)$$

2.1.4. Temkin Model

Temkin isotherm model takes the interaction of the adsorbent and the adsorbing species into consideration. It is described as;

$$q_e = \frac{RT}{b} \ln (K_t C_e) \quad (9)$$

The linear form of the isotherm is:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (10)$$

Thus, $B_1 = \frac{RT}{b}$, R = the universal constant (8.314 KJ/mol.K) and T is the absolute temperature (K). q_e (mg/g)=amount of metal ion adsorbed/unit weight and C_e (mg/l=) amount of metal ion that is not adsorbed at equilibrium when in solution. K_T and B_1 are the Temkin constants.

2.1.5. Radke-Praunsitz Model

The Radke–Praunsitz isotherm is shown thus;

$$q_e = \frac{K_{RP} C_e}{1 + \left(\frac{K_{RP}}{F_{RP}}\right) C_e^{1-N_{RP}}} \quad (11)$$

Where K_{RP} (L/mg), F_{RP} and N_{RP} are the model parameters, which are obtained by a non-linear statistical fit of the equation to the experimental data.

The Radke–Praunsitz equation has several important properties making it suitable for use in many adsorption processes. At low concentration it reduces to a linear isotherm. At high concentration it becomes Freundlich isotherm and for the special case of $N_{RP} = 0$, it becomes Langmuir isotherm.

2.1.6. Redlich-Peterson Model

The Redlich–Peterson model is expressed by the following equation;

$$q_e = \frac{A_R C_e}{1 + B_R C_e^{mR}} \quad (12)$$

Where, A_R (L/mg), B_R (L/mg) and mR are the model parameters. This model expresses the adsorption process when dealing with a certain pollutants at high concentration.

2.1.7. Multi-component Isotherm Models

The experimental measurement of multi-component adsorption isotherm is time consuming because of large number of variables involved. Thus, the problem of predicting multi-component adsorption isotherm from single component adsorption data has attracted a lot of attention. Several isotherms have been proposed to describe the competitive adsorption. Most of these isotherms are based on single component isotherm parameters and correction factors extracted from the experimental competitive data [30].

2.1.8. Extended Langmuir Model

The Langmuir isotherm can be extended for multi-component system to give the following form;

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{k=1}^n b_k C_{e,k}} \quad (13)$$

Where $C_{e,i}$ is the equilibrium concentration of the component i in the multi-component solution, $q_{e,i}$ is the equilibrium uptake of the component i , $q_{m,i}$ and b_i are the single component Langmuir parameters for component i .

This model is applicable when each single component obeys the Langmuir model in a single component system [30].

2.1.9. Combination of Langmuir-Freundlich Model

The competitive Langmuir-Freundlich model related to the individual isotherm parameters is expressed in the following equation.

$$q_{e,i} = \frac{K_{R,i} (b_{R,i}) C_{e,i}}{1 + \sum_{k=1}^N b_{R,k} (C_{e,k})} \quad (14)$$

Where $C_{e,i}$ is the equilibrium concentration of the component i in the multi-component solution, $q_{e,i}$ is the equilibrium uptake of the component i , $q_{m,i}$ and b_i are the single component Langmuir parameters for component i .

2.1.10. Competitive Redlich-Peterson Model

The competitive Redlich-Peterson model related to the individual isotherm parameters is given by the following equation;

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{k=1}^n b_k (C_{e,k})} m_{R,k} \quad (15)$$

Where $K_{R,i}$ (L/mg), $b_{R,i}$ (l/mg) m_R and $m_{R,i}$ are the Redlich-Peterson single component parameter for component i .

2.1.11. Kinetic Models

The kinetics of adsorption can be studied by using three kinetic models, first order and second order kinetic models. These models take into account the adsorbed quantities that will enable us in determining the reactor volume.

2.1.11.1. First Order Rate Equation

The first order kinetic models usually take the form;

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (16)$$

Where q_e and q_t are the sorption capacities at equilibrium and at time t , respectively (mg/g) and k_1 is the rate constant of first order rate adsorption, (1/min). After integration and applying boundary conditions, $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$.

The integrated form of equation (16) becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (17)$$

2.1.11.2. Second Order Rate Equation

If the rate of sorption is a second order mechanism the second order kinetic rate equation is expressed as

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (18)$$

Where q_e and q_t are the sorption capacities (mg/g) at equilibrium and at time t , respectively and k is the rate constant of pseudo-second order sorption, g/mg.min). For the boundary conditions, $q_t = 0$ to q_t at $t = 0$ to t .

The integrated form of Equation 18 gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (19)$$

Equation 19 can be rearranged to get:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (20)$$

Where t is the contact time (min), q_e (mg/g) and q_t (mg/g) is the amount of the solute adsorbed at equilibrium and at any time, t respectively. Equation (20) does not have the problem of assigning an effective q_e . If pseudo-second order kinetics is applicable, the plot of $\frac{t}{q_t}$ against t of Equation (20) should give a linear relationship, from which q_e and k can be determined from the slope and intercept.

2.1.11.3. Weber and Morris Intra-particle Diffusion Model

Weber and Morris proposed intra-particle diffusion model, which can be written as;

$$q_t = K_{id} t^{\frac{1}{2}} + C \quad (21)$$

Where q_t (mg/g) is the amount adsorbed at time t (s), K_{id} (mg/g s^{1/2}) is the rate constant of intra-particle diffusion, C is the value of intercept which gives an idea about the boundary layer thickness, i.e. the larger intercept; the greater is the boundary layer effect.

2.1.11.4. Elovich Kinetic Model

A widely used equation to describe the kinetics of chemisorption is the Elovich equation:

$$\frac{dq}{dt} = a \exp(-bq) \quad (22)$$

Where a (mg/g.s) and b (g/mg) are parameters of the equation. The parameter (a) is regarded as the initial rate because $dq/dt \rightarrow a$ as $q \rightarrow 0$ and parameter b is related to the extent of surface coverage and activation energy for chemisorption. Given that $q = 0$ at $t = 0$, the integrated form of Equation (22) becomes:

$$qt = \frac{1}{b} \ln(t + t_0) - \frac{1}{b} \ln t_0 \quad (23)$$

Where $t_0 = 1/ab$. If $t \gg t_0$, Equation (23) is simplified as:

$$qt = \frac{1}{b} \ln ab + \frac{1}{b} \ln t \quad (24)$$

3. Adsorption Thermodynamics

The changes in the reaction expected during the sorption process require a brief idea of thermodynamic parameters. Thermodynamics parameters characterizing the equilibrium of the system are Gibbs free energy change ΔG , enthalpy change ΔH and entropy change ΔS . They are determined using the following equation,

$$\Delta G^0 = -RT \ln K_a \quad (25)$$

Where ΔG^0 (J/mmol) is Gibb's energy change which is normally used to determine the feasibility and spontaneity of the adsorption process and is given as Equation 26, R is the universal gas constant (8.314 J/mol/k), T is the absolute temperature (K) and K_a is the thermodynamic equilibrium constant.

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (26)$$

Substituting Equation 25 into Equation 26 yields Equation 27

$$\ln k_a = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (27)$$

Where ΔH° (J/mol) represents enthalpy change, which indicates whether the process is exothermic($\Delta H^\circ < 0$) or endothermic ($\Delta H^\circ > 0$) and ΔS° (J/mmol/k) is the change in entropy.

The thermodynamic equilibrium constant is taken as the Langmuir equilibrium constant, K_L .

4. Process Parameters for Adsorption of Heavy Metals

Process parameters to be considered in heavy metal sequestration include the following; temperature, pH, particle size, contact time, adsorbent dosage and initial metal concentration. Usually, adsorption isotherms are used to describe the mechanism involved in adsorption process. The final residual metal concentration after adsorption is measured with the aid of Atomic absorption Spectrophotometer. In order to estimate the percentage removal of metal ions from aqueous solution, the following equation is used [31]

$$\% \text{ Rem.} = \frac{C_0 - C_e}{C_0} \times 100 \quad (28)$$

The metal uptake (q_e) at equilibrium time can be calculated using equation (29)

$$q = \frac{(C_0 - C_e)V}{m} \quad (29)$$

Where C_0 and C_e are the initial and equilibrium adsorbate concentrations in solution(mg/l), respectively, V is a known volume of adsorbate solution (l), and m is a known mass of dry adsorbent (g).

4.1. Effect of pH

The pH value of the metal solution plays a major role in heavy metal adsorption. It contributes so much in adsorption capacity. The pH affects the behavior of the aqueous solution as well as the points of attachment for the surface [32]. The pH effect is dependent on the adsorbent surface charge. The pH contributes to the adsorbent surface charge, ionization potential and distribution of metal ions [33]. For a negatively charged adsorbent surface, at a decreased pH, the negatively charged surface is neutralized by the H^+ ions which are observed in large number, and in turn reduce the obstacle to diffusion with an increased adsorption rate. Previous studies showed that at lower pH values, the adsorption efficiency decreases while it increases at higher pH [32, 34]. Several authors have studied the effect of pH on heavy metal adsorption and they reported different optimum pH values for adsorption of copper, zinc and chromium. Tang et al. (2009) [35] studied the adsorption of chromium (VI) using activated carbon derived from coconut shell at a pH range of 2.0 to 8.0. Their result showed that the adsorption of Cr (VI) reduced with the increase in pH while the maximum adsorption was observed at a pH of 2. Bhatti et al. (2007) [36] also investigated the adsorption capacity of activated carbon derived from almond shells. They observed a higher adsorption capacity at an acidic pH ($pH < 5$). Hossain et al. (2012) [37] investigated the effect of pH on banana peel. Their results showed that the adsorption capacities of Cu (II) increased from 0.7 mg/g to 1.76 mg/g when the pH was increased from pH 2 to pH 6. This was as a result of the free hydrogen ion present for a pH less than 6. But the adsorption capacity reduced from pH 6 to pH 12. This is due to the fact that at low pH, copper ions tend to be in competition with the hydrogen ion for the adsorbent surface attachment site and at a high pH, copper ions form precipitate in the solution [20]. The adsorption of copper, chromium and zinc was investigated by Kaakani (2012) [34] using palm tree leaves. In his result, he found out that the optimum adsorption occurred at pH 5, 3 and 9 for copper, chromium and zinc respectively. Wan Ngah and Hanafiah (2008) [38] on the other hand, obtained an optimum pH value of 4 for adsorption of copper using Rubber. Banu (2006) [39], in his research on the adsorption of zinc using maize cob, got an optimum pH of 5.0. Other works include Tamarind Seed [40] with optimum pH of 3, Coconut shell [41] with optimum pH of 2, Hazelnut shell [42] with optimum pH of 1, Saw dust [43] with optimum pH of 2, *Terminalia arjuna* nuts [44] with optimum pH of 1 and Ground nut husk [45] with optimum pH of 7.

4.2. Effect of Contact Time

For adsorption to be complete, equilibrium between the adsorbent and the solute of the solution should be attained. Thus, a particular time is required for the interactions of the equilibrium in order to ensure that the adsorption is achieved. The time required for the equilibrium to be attained is known as the contact time. Several authors have studied the effect of contact time on adsorption. Their results showed that the rate of adsorption of metal ions increases with time, after a certain time, an optimum value is reached after which no more removal of metal ion takes place [26, 46, 47]. The amount of metal ion adsorbed at the contact time is a reflection of the maximum adsorption capacity achieved by the adsorbent under the operating conditions. The result obtained by Ushakumary (2013) [32] using milled adsorbents of mango peel and *Alisma plantago aquatica* showed that the rate of metal binding with biomass is more pronounced during the starting stages and it decreases and remains constant after 120min. Ngugi (2015) [48] studied the adsorption capacity of Mangroves from Kenyan coast and his result showed that equilibrium was achieved after 10 minutes. After that, the rate of copper removal became stagnant as a result of the reduction in copper concentration together with the number of adsorption sites [49]. The same trend was observed in the adsorption of Cr (III) onto biogas residual slurry [50]. Similar result was obtained by Attahiru et al. (2003) [51] in the sequestration of copper (II) ions from aqueous solution using micaceous mineral of Kenyan origin. Brahmaiah et al. (2015) [52] in their research using rice straw observed that at 40 min, the chromium removal was found to be optimum at 65%. There was a high increase in the rate of adsorption of Cr(VI) using tamarind wood activated carbon within 20 minutes, which decreased as the time was increased, thus attaining equilibrium within 40 minutes [53]. Similar results were equally obtained by Attia et al. (2010) [54], Selomulya et al. (1999) [55] and Khezami and Capart (2005) [56].

4.3. Effect of Initial Metal Concentration

The rate of Adsorption depends on the initial concentration of solution. Previous studies on adsorption showed that the rate of adsorption increases at a lower concentration. Ushakumary (2013) [32] reported higher rate of adsorption for Cd(II), Pb(II), Zn(II), Cr(III) and Cu(II) using milled adsorbents of mango peel and *Alisma plantago aquatica* when the concentration was low. This is because when the concentration was high, saturation of adsorption sites occurred which left most metal ions un-adsorbed [26, 47]. Hence, at lower concentration, the rate of adsorption increased due to the availability of a larger surface area of the adsorbent [57]. Batch and column adsorption were conducted using coconut shell as an adsorbent to remove the chromium (Cr^{6+}) from the effluent [58, 59, 60]. Their results showed that when the initial concentration was adjusted to 5-100 gm/L, the optimum removal efficiency was 87.3% with the concentration of 50 mg/L. With the decrease in concentration, the removal efficiency was reduced. Babu and Suresh (2009) [61] on the other hand, carried out adsorption of hexavalent chromium using sawdust. They reported that, as the concentration was adjusted to 50-500 mg/g, the removal efficiency reduced from 99.9% to 89% and equally attained the maximum adsorption capacity from 4.98 to 41.45 mg/g. Abdulrasaq and Basiru (2010) [62] investigated the use of coconut husk for Cu(II) removal from simulated industrial waste effluent. They reported that the adsorption of Cu (II) the metal ion adsorbed increased with increase in concentrations.

4.4. Effect of Temperature

Temperature can affect the adsorption capacity of the adsorbent depending on the types of adsorbent used. Temperature can change the adsorption equilibrium depending on whether the process is exothermic or endothermic. In order to find out the spontaneity of the process, the enthalpy, entropy and Gibbs free energy must be determined. Ho and Ofomaja (2006) [28] pointed out that Gibbs free energy (G°) is considered as the spontaneity indicator of a chemical reaction. The effect of temperature on adsorption rate is such that it

alters the molecular interaction and the solubility of the adsorbate [63]. With an increase of temperature the uptake of Cr(VI) increases continuously [64]. Kartikeyan et al. (2005) [43] reported that the adsorption of Cr(VI) on activated carbon increases as the temperature increases and thus the adsorption reaction is endothermic in nature. The enhancement of adsorption capacity may be due to the chemical interaction between adsorbate ions and adsorbent, creation of some new adsorption sites or increase in the intraparticle diffusion of Cr(VI) into the pores of adsorbent at high temperatures [50]. Ngugi (2015) [48] carried out adsorption studies at varying temperatures (25 to 70 °C) and he reported that the percentage removal of copper increased from 92.5% to 99.4% with an initial concentration of 200 ppm with a temperature rise from 20°C to 70 °C. The increase in percentage removal of the metal ions with temperature increase depicts that the adsorption process is an endothermic reaction. Park et al. (2010) [65] reported similar observation and argued that adsorption of heavy metals was endothermic in nature. Kashif et al. (2016) [66] studied the effect of temperature on Cu²⁺ adsorption on rice husk ash at various temperature ranges. Effect of temperature on 20 ppm, 30 ppm and 40 ppm copper standards was studied. In case each of copper standards (20 ppm, 30 ppm, 40 ppm), the maximum adsorption was noted at 50 °C. However as the temperature increased beyond 50 °C, desorption of Cu²⁺ was observed. Therefore, an increase in temperature after certain limit, decreased the adsorption of Cu²⁺ and favored desorption from rice husk ash.

4.5. Effect of Particle Size

The particle size is an important parameter in adsorption process. The smaller the particle sizes of the adsorbent, the higher its adsorption rate. As the particle size decreases, the adsorption increases. This is because the surface area increases as the particle size decreases [32]. Several authors have studied the effect of particle size on adsorption. Amarasinghe and Williams (2007) [6] studied the effect of particle size on the adsorption of Cu(II) ions using tea waste. They obtained percent removal of 57%, 53%, and 41% for 575 µm, 925 µm and 1250 µm particle sizes respectively. Vijayaraghavan et al. (2006) [67] utilized crab shell for adsorption of copper (II). They reported maximum copper uptake of 243.9 at optimum particle size of 0.767 mm, pH of 6 and adsorbent dosage of 5g/l. Eze et al. (2013) [68] investigated the effect of particle size on the bioremediation of Zn(II) using unmodified and carboxymethylated fluted pumpkin and broad-leaved pumpkin pods. The results showed that the amount of metal ions adsorbed by individual particle size revealed optimum particle size ranges from 400-600 µm on unmodified adsorbent, and optimum particle size ranges of 850-1200 µm for the modified adsorbent.

4.6. Effect of Adsorbent Dosage

The adsorbent dosage is an important parameter because this determines the capacity of an adsorbent. The removal of metal ions increases with an increase in the adsorbent dosage. Ushakumary (2013) [32] investigated Cd(II), Pb(II), Zn(II), Cr(III) and Cu(II) adsorption using milled adsorbents of mango peel and *Alisma plantago aquatic*. His result showed that the adsorption of metal ions increased with the adsorbent dosage. Hence, with an adsorbent dosage above 0.4g/100ml, equilibrium was reached. The metal removal percentage thus, increases with the increasing amount of adsorbent dosage [26, 69, 70]. The adsorption of Cr(VI) ions using Bael fruit shell was investigated by Ramakrishna (2012) [71]. He reported that the Cr(VI) removal efficiency increased with the increase of adsorbent dose. Further increase in adsorbent dose did not produce any remarkable change [45, 72]. The trend of increase in removal capacity can be associated with the availability of more adsorption sites for the metal ions [44]. Brahmaiah et al. (2015) [52] on their research, investigated the effectiveness of untreated and treated rice straw for removal of Chromium. They reported an increase in percent removal of chromium for both treated and untreated adsorbent with increase in adsorbent dosage. The optimum dosage for treated as well as untreated rice straw was 8g/100ml.

5. Perspectives for Future Studies

- (1). There is a need to explore the efficiency of some locally available plant waste-based adsorbents for sequestration of heavy metals.
- (2). Extensive comparative study between physical, chemical and physical/chemical activation using various adsorbents for chromium, zinc and copper adsorption are required.
- (3). Further research on the effect of adsorbent dosage, metal concentration, temperature, and contact time and particle size on the adsorption of heavy metals is required.
- (4). It is necessary to study both the single and competitive adsorption of two or more heavy metals, and also, to quantify the interference between one metal ion with the sorption of another. Thus, the equilibrium and kinetic studies of the adsorption of heavy metals from both single as well as multi-component systems are necessary.
- (5). More studies on improved method of process parameters optimization for heavy metal sequestration are recommended.
- (6). The fitting of the adsorption data with different single and multi-metal system isotherms, kinetics as well as thermodynamics is required.

6. Conclusions

The adsorption mechanisms for heavy metal removal using low cost adsorbents have been studied in this research. From the review conducted, the low cost adsorbents showed high metal sequestration capacities. Moreover, the isotherms, kinetics and thermodynamics play important role in the sorption of metal ions. The adsorption is also dependent on the process parameters such as contact time, particle size, temperature, initial concentration, and adsorbent dosage.

Conflict of Interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

References

- [1] Dobrowolski JW, Bedla D, Czech T, Gambus F, Gorecka K, Kiszczak W, Kuzniar T, Mazur R, Nowak A, Sliwka M, Tursunov O, Wagner A, Wieczorek J, Swiatek M 2017 Integrated Innovative Biotechnology for Optimization of Environmental Bioprocesses and a Green Economy *Optimization and Applicability of Bioprocesses* eds Purohit H, Kalia V, Vaidya A, Khardenavis A (Singapore: Springer) chapter 3 pp 27-71.
- [2] Nilanjana D, Karthika P, Vimala R, Vinodhini V 2008 *Natural Product Radiance* **7**(2)133 – 138.
- [3] Kapoor AT, Viraraghavan T, Cullimore DR 1999 *Bioresource Technology* **70** 95-104.
- [4] Wang JL, Chen C 2009 *Biotechnology Advances* **27** 195–226.
- [5] Axtell NR, Sternberg SPK, Claussen K 2003 *Bioresource Technology* **89** 41-48.
- [6] Amarasinghe BMWPK, Williams RA 2007 *Chemical Engineering Journal* **132** 299–309.
- [7] Nnaji CC, Ebeagwu CJ, Ugwu EI 2017 *Bioresources* **12**(1)799-818.
- [8] Olukanni DO, Agunwamba JC, Ugwu EI 2014 *American Journal of Science and Industrial Research*. **5**(2) 81-87.
- [9] Wang J, Chen C 2006 *Biotechnology Advances* **24** 427 – 451.
- [10] Vijayaraghavan K, Yun YS 2008 *Biotechnology Advances* **26** 266-291.
- [11] Olukanni DO, Ugwu NC 2013 *International Journal of Water resources and Environmental Engineering* **5** 262-271.
- [12] Igwe JC, Abia AA 2003 *The Physical Sciences* **2** 83-94.
- [13] Babel S, Kurniawan TA 2003 *Journal of Hazardous Materials* **97** 219-243.
- [14] Mohan D, Pittman Jr C 2007 *Journal of Hazardous Materials* **142** 1-53.

- [15] Chiban M, Soudani A, Sinan F, Persin M 2011 *Journal of Environmental Management* **95** 561-565.
- [16] Chiban M, Soudani A, Sinan F, Persin M 2011b *CLEAN - Soil Air Water* **39**(4) 376-283.
- [17] Demirbas A 2008 *Journal of Hazardous Materials* **157** 220-229.
- [18] Kurniawan TA, Chan GYS, Lo WH, Babel S 2006 *Chemical Engineering Journal* **118** 83-98.
- [19] Agunwamba JC 2001 Waste engineering and management tools, *Immaculate Publishers Ltd.* Enugu.
- [20] Abas SNA, Ismail MHS, Kamal M, Izhar S 2013 *World Applied Science Journal* **28**(11) 1518-1530.
- [21] Lagergren S 1898 *K. Sven. Vetenskapsakad. Handl.* **24**(4) 1-39.
- [22] Freundlich HMF 1906 *Journal of Physical Chemistry* **57** 385-470.
- [23] Langmuir I 1918 *Journal of the American Chemical Society* **40**(9) 1361-1403.
- [24] Aksu Z, Kabasakal E 2004 *Separation and Purification Technology* **35** 223-240.
- [25] Kumar U, Bandyopadhyay M 2006 *Bioresource Technology* **97** 104-109.
- [26] Azouaou N, Sadaoui Z, Djaafri A, Mokaddem H 2010 *Journal of Hazardous Materials* **184** 126-134.
- [27] Ahmaruzzaman M 2011 *Advances in Colloid and Interface Science* **166**(1-2) 36-59.
- [28] Ho YS, Ofomaja AE 2006 *Biochemical Engineering Journal* **30** 117-123.
- [29] Jeppu GP, Clement TP 2012 *Journal of Contaminant Hydrology* **129-130** 46-53.
- [30] Al-Rub FA, Kandah M, Al-Dabaybeh N 2003 *Sep. Sci. Technol.* **38** 483-497.
- [31] Luukkonen T, Sarkkinen M, Kempainen K, Rämö J, Lassi U 2016 *Applied Clay Science* **119**(2) 266-276.
- [32] Ushakumary ER 2013 Waste water treatment using low cost natural adsorbents, PhD Thesis, Cochin University of Science and Technology, India.
- [33] Park D, Yun YS, Park JM 2010 *Biotechnology and Bioprocess Engineering* **15**(1) 86-102.
- [34] Kaakani MW 2012 Heavy Metal removal from Wastewater using novel Adsorbent, Master's Thesis, American University of Sharjah.
- [35] Tang C, Zhang R, Wen S, Li K, Zheng X, Zhu M 2009 *Water Environment Research* **81**(7) 728-734.
- [36] Bhatti I, Qureshi K, Kazi RA, Ansari AK 2007 *World Academy of Science, Engineering and Technology* **34** 199-204.
- [37] Hossain MA, Ngo HH, Guo WS 2012 *International Journal of Geomate* **2** 227-234.
- [38] Wan Ngah WS, Hanfiah MAKM 2008 *Bioresource Technology* **99** 3935-3948.
- [39] Banu I 2006 *Scientific Study & Research* **VII** 2.
- [40] Babu BV, Gupta S 2008 *Adsorption* **14**(1) 85-92.
- [41] Mohan D, Singh KP, Singh VK 2005 *Industrial Engineering and Chemical Research*. **44** 1027-1042.
- [42] Koby M 2004 *Bioresource Technology* **91** 317-321.
- [43] Karthikeyan T, Rajgopal S, Miranda LR 2005 *Journal of Hazardous Materials* **124** 192-199.
- [44] Mohanty K, Jha M, Meikap BC, Biswas MN 2005 *Chemical Engineering Science* **60** 3049-3059.
- [45] Dubey SP, Gopal K 2007 *Journal of Hazardous Materials* **145**(3) 465-470.
- [46] Martinez ML, Torres MM, Guzman CA, Maestri DM 2006 *Industrial Crops and Products* **23** 23-28.
- [47] Mohammad MMR, Parisa R, Atefeh A, Ali RK 2011 *Journal of Hazardous Materials* **185** 401-407.
- [48] Ngugi F 2015 Adsorption of heavy metals from aqueous solutions using mangroves from Kenyan coast, Master's Thesis, University of Nairobi.
- [49] Kumar PS, Ramalingam S, Sathyaselvabala V, Kirupha SD, Murugesan A, Sivanesan S 2012 *Korean Journal of Chemical Engineering* **29** 756-768.
- [50] Namasivayam C, Yumuna RT 1995 *Bioresource Technology* **52** 125-131.
- [51] Attahiru S, Shiundu PM, Onyari JM, Mathu EM 2003 *Adsorption Science Technology* **21**(3) 269-283.
- [52] Brahmaiah T, Spurthi L, Chandrika K, Ramanaiah S, Prasad KSS 2015 *World Journal of Pharmacy and Pharmaceutical Sciences* **4**(11) 1600-1610.

- [53] Acharya J, Sahu JN, Sahoo BK, Mohanty CR, Meikap BC 2009 *Chemical Engineering Journal* **150**(1) 25-39.
- [54] Attia A, Khedr SA, El-Kholy SA 2010 *Brazilian Journal of Chemical Engineering* **27**(1) 183-193.
- [55] Selomulya C, Meeeyoo V, Amal R 1999 *Journal of Chemical Technology and Biotechnology* **74** 111-122
- [56] Khezami L, Capart K 2005 *Journal of Hazardous Materials B* **123** 223-231.
- [57] Senthil KP, Ramalingam S, Senthamarai C, Niranjanaa M, Vijayalakshmi P, Sivanesan S 2010 *Desalination* **261** 52-60.
- [58] Sandhya B, Tonni AK 2004 *Chemosphere* **54** 951- 967.
- [59] Ravi K, Dinesh KA, Nouratan S, Hirdayesh K 2017 *IOSR Journal of Applied Chemistry* **10** 76-79.
- [60] Parineeta P, Subhangi N 2013 *International Journal of Chemical and Physical Sciences*.
- [61] Babu BV, Suresh G 2009 *Chemical Engineering Journal* **150** 352-365.
- [62] Abdulrasaq OO, Basiru OG 2010 *African Journal of Environmental Science and Technology* **4**(6) 382-387
- [63] Singh P, Singh TS, Pant KK 2001 *Research Journal of Chemistry and Environment* **5** 25-28.
- [64] Hu Z, Lei L, Li Y, Ni Y 2003 *Separation and Purification Technology* **31** 13-18.
- [65] Park YY, Tran T, Lee YH, Nam Y, Senanayake G, Kim MJ 2010 *Hydrometallurgy* **104**(2) 290-297.
- [66] Kashif I, Dildar A, Naseem Z 2016 *International Journal of Research – Granthaalayah* **4**(2) 52-61.
- [67] Vijayaraghavan K, Palanivelu K, Velan M 2006 *Bioresource Technology* **97** 1411-1419.
- [68] Eze SO, Igwe JC, Dipo D 2013 *International Journal of. Biology and Chemical. Science* **7**(2) 852-860.
- [69] El-Said AG, Badaway NA, El Pasir AA 2010 *Journal of Nature and Science* **8** 86-94.
- [70] Saifuddin MN, Kumaran P 2005 *Electronic Journal of biotechnology* **1** 43-53.
- [71] Ramakrishna G 2012 Preparation and characterization of microporous activated carbon from biomass and its application in the removal of chromium (vi) from aqueous phase, PhD Thesis, National Institute of Technology Rourkela, Odisha.
- [72] Ranganathan K 2000 *Bioresource Technology* **73** 99-103.