

State of Art on Modelling Approaches of Adsorption Techniques for Removal of Heavy Metals

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Abstract

The objective of this study is to contribute in the search for low-cost adsorbents and investigate the parameters that influence the adsorption of heavy metals on adsorbents using various Adsorption Isotherm Models. The large industries mainly chemical industries discharge these heavy metal ions in the form of chemicals directly into the water of river, lake, sea. They cause health issues for living beings specially flora and fauna which survives into the water. So, it is compulsory to remove those toxic metal ions to illuminate the health risk of living beings and plant as well. There are lots of techniques present to remove that heavy metal ion like ion-exchange, chemical precipitation, coagulation-flocculation & flotation, adsorption, membrane filtration. Among all of the process, adsorption is the best suitable method for illumination of toxicity of heavy metal ions from industrial waste water effluent. Here adsorption performs a useful method for removal process with lots of advantages because this is the low cost method with eco-friendly in nature. Biosorption is an environmental friendly method for metal removal as it can be used as a cost effective and efficient technique for heavy metal removal. A lot of biomass can be choosen as biosorbent such as waste material from food processing and agriculture. Ent. Biosorption offers the advantages of low cost, good efficiency and production of sludge with high metal content is possible to avoid by the existence of metal recovery method from metal loaded biosorbent.

Keywords: *Adsorption, Heavy metals, Biosorption, Isotherm, Biosorbent*

INTRODUCTION

Water pollution is the major concern nowadays and it also affects the health of living organism. The excessive use of chemicals which present in the contaminated water are directly flow into the rivers which endanger the life of aquatic organism as well as human beings (Jaya Mishra et. al, 2021). Rapid industrialization and development released excessively heavy metals into the environment. Industries such as mining, metal plating and battery manufacturing, result in the release of heavy metals to aquatic ecosystem (Lokendra Singh Thakur et. al, 2013). The most toxic form of these heavy metals in their ionic species. In the environment, the heavy metals are generally more persistent than organic contaminants such as pesticide or petroleum byproducts.

The heavy metals can become mobile in water and soil depending on water and soil specification (Shyam R. Khairkar et. al, 2014). Heavy metals are non-biodegradable, entry into the food chain can result in accumulation through the food chain and biomagnifications, which increases the toxicity, thus increasing its

threat to the ecosystem and human health (Saravanan M et. al, 2020).

Industrial waste water contains polluting substances such as inorganic, organic, elemental and polymeric products (Renu et. al, 2016). The major heavy metal comes out from industries which are hazardous are nickel (Ni), iron (Fe), cadmium (Cd) and chromium (Cr), zinc (Zn), lead (Pb) and mercury (Hg). In India, the current maximum contaminant level (ppm – mg/L) for heavy metals is 0.20, 0.1, 0.01, 0.05, 0.80, 0.006, 0.00003 for nickel (Ni), iron (Fe), cadmium (Cd), chromium (Cr), zinc (Zn), lead (Pb) and mercury (Hg) respectively (Feng et al., 2009) (Renu et. al, 2016). Nickel can cause lung cancer, asthma, allergic reactions and heart disorders, Iron can cause conjunctivitis, choroiditis and retinitis if it contacts and remains in the tissue, cadmium (Cd) accumulate in human body, bones and kidney and it cause cancer.

Past disaster due to contamination of cadmium in wastewater are " itai itai " in Jintsu river of Japan. Chromium exists in two oxidation forms trivalent and Hexavalent form. Hexavalent chromium is

more harmful than trivalent chromium. Zinc is essential for human health but large quantities of zinc can cause skin irritation, stomach cramps, vomiting and anemia (Renu et. al, 2016). Similarly, lead is harmful to human health and can damage to kidney, liver, reproductive system and brain functions. Mercury is also harmful and it is a neurotoxin that can affect the central nervous system. If it is exceeded in concentration it can cause pulmonary, chest pain and dyspnea. Conventional treatment technologies for removal of heavy metals are chemical precipitation, ion exchange, chemical oxidation/reduction, reverse osmosis, electro dialysis, ultrafiltration but they are not economical.

Different metals have different toxicity or toxic profiles depending upon their chemical form (Jaya Mishra et. al, 2021). The source of heavy metal includes natural source, mining, smelting, agrochemicals and sewage sludge applications, and livestock manure uses (Shraddha Rani Singh et. al, 2017). Exposure to heavy metals may occur through inhalation or ingestion through food, drink, fume or dust which leads to affect the human health (Patiha et. al, 2016).



Fig 1. Heavy metal ions illuminate through conventional process

There are various techniques which are used for the separation of heavy metals from the contaminated water and that techniques are adsorption, oxidation, coagulation, ion-exchange, bio-remediation, Nano-filtration, solvent, - extraction, reverse-osmosis (Arshad I. Esmael et. al, 2014). Among all of the above techniques adsorption is chosen for the best removal process from the waste water effluent because adsorption is low cost process, easy removal as well as recovery rate, most efficient technique because of its easy operation, high efficiency and the operation perform is sludge free (Shaymaa I. Saeed et. al, 2017). If we talk about the adsorption process then we have concern about the properties of adsorbent because it play major role in adsorption, a good adsorbent for removal of heavy metal ions must possess these characteristic like high

adsorption capacity, pore volume and size, large surface area, compatibility, cost effectiveness, mechanical stability environment friendly, high selectivity, ease of regeneration, simple processing (Vinaykumar S N et. al, 2019)

BIOSORPTION

The need for more economical and effective method for metal removal from wastewater, have initiated all researchers world widely to search for efficient eco-friendly and cost-effective remedies (N. Yuvaraja et. al, 2019). Hence, this search has directed to the discovery of biosorption. Biosorption is a technique that employs inactive non-growing biomass for the recovery of heavy metals from aqueous solutions. Biosorption offers the advantages of low cost, good efficiency and production of sludge with high metal content is possible to avoid by the existence of metal recovery method from metal loaded biosorbent through elution or incineration treatment. Therefore, a low cost sorbent with high metal binding need to be investigated (M.S. Mansour et. al, 2011).

Biosorption is defined as “ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated (by the use of

ATP) or spontaneous physicochemical pathways of uptake (not at the cost of ATP), or as a property of certain types of inactive, non- living microbial biomass which bind and concentrate heavy metals from even very dilute aqueous solutions” (Sureshkumar Halnor et. al, 2013). It is a complex process that depends on different-factors like cell physiology, physicochemical factors such as pH, temperature, contact time, ionic strength, and metal concentration, chemistry of the metal ions, cell wall composition of microorganisms. Biosorption of different heavy metals e.g. cadmium, silver, lead, nickel etc. by using microorganisms like fungi, algae or bacteria was studied by different groups (Sunil H et. al, 2014).

FACTORS AFFECTING BIOSORPTION

Biosorption process is affected by following factors:

Temperature: For efficient removal of metal ions from environment, the optimum temperature needed to be investigated. It is generally assumed that biosorption is carried out between 20 and 35°C. High temperatures above 45°C may results in damage to proteins which in turn affects metal uptake process (Renu et. al, 2016).

pH: It is a very important parameter. It affects solubility of metal ions and binding sites of biomass. At lower pH, the biosorption of metals is affected. General range of pH for metal uptake is 2.5–6. Above this limit, metal uptake ability of biosorbent gets compromised (Renu et. al, 2016).

Nature of biosorbents: Metal uptake is reported in different forms like biofilms, freely suspended microbial cells or immobilization of microbial cells. It can be altered by physical or chemical treatments (Renu et. al, 2016). Physical treatments include autoclaving, drying, boiling, sonication, etc. Chemical treatment as the name indicates involves chemicals like acid or alkali to improve biosorption capacity (Jaya Mishra et. al, 2021). The fungal cells are deacetylate which affects the structure of chitin resulting in the formation of chitosan- glycan complexes which have results high metal affinities (Ajay K. Agarwal et. al, 2014).

Surface area to volume ratio: This property plays an important role in efficient removal of heavy metal from medium. The surface area property plays a significant role in case of biofilms. The binding of metal ions with microbial cell wall is previously reported. Although

intracellular metal adsorption is energy-consuming process but still microorganisms prefer it over wall adsorption (Jaya Mishra et. al, 2021).

Concentration of biomass: The concentration of biomass is directly proportional to the metal uptake. It is reported that electrostatic interaction between the cells plays an important role in metal uptake. At a given equilibrium, the biomass adsorbs more metal ions at low cell densities than at high densities. Metal uptake depends on binding sites. More biomass concentration or more metal ions restricts the access of metal ions to binding sites (Renu et. al, 2016).

Initial metal ion concentration: The initial concentration provides an important driving force to overcome all mass transfer resistance of metal between the aqueous and solid phases (Aparna Bhawnani et. al, 2017). Increasing amount of metal adsorbed by the biomass will be increased with initial concentration of metals. Optimum percentage of metal removal can be taken at low initial metal concentration. Thus, at a given concentration of biomass, the metal uptake increases with increase in initial concentration (Renu et. al, 2016).

Metal affinity to biosorbent:

Physical/chemical pretreatment affects permeability and surface charges of the biomass and makes metal binding groups accessible for binding. It can be manipulated by pretreating the biomass with alkalis, acids detergents and heat, which may increase the amount of metal uptake (Jaya Mishra et. al, 2021).

Methods of Adsorption

In most of the studies only two method of adsorption are used to experiment viz. Fixed Bed method and Batch Experiment. The cyclic-batch operating mode using fixed bed is widely used with both gas and liquid feeds (Bashir A. Dar et. al, 2012). Separation in a fixed bed is, in virtually all practical cases, an unsteady state rate-controlled process. This means that conditions at any particular point within the fixed bed vary with time (Jaya Mishra et. al, 2021). Adsorption only occurs in a particular region of the bed, known as the mass transfer zone (MTZ), which moves through the bed. Applications of fixed bed adsorption, also called percolation, include the removal of dissolved organic compounds from water. The factors which determine the number and arrangement of fixed beds include total feed flow rate, allowable pressure drop, energy demands, length of the MTZ, method of adsorbent

regeneration, and the capital investment (Veena Bobade et. al, 2015). Batch experiments, also known as static systems, are carried out by adding certain amount of solid into solution containing specific concentration of contaminants with a specific solid/liquid (S/L) ratio. These mixtures are vigorously stirred or shaken during the entire reaction time (Veena Bobade et. al, 2015). Batch adsorption is often used to adsorb solutes from liquid solutions when the quantities treated are small in amount, as in the pharmaceutical or other industries (Patiha et. al, 2016). As with many other processes, an equilibrium relation such as the Freundlich or Langmuir isotherm and a material balance are needed (Deepshikha Sareen et. al, 2014).

Removal of Heavy Metal Using Various Adsorbent

Removal of Heavy metals using Agricultural Waste: According to Renu et. al, (2016), the study on chemically modified agricultural plant for heavy metal removal has attracted the attention of many researchers. Mostly acid and bases were used for modification of agricultural wastes. After chemical modification the adsorption capacity of adsorbents has been increased due to increases in number of active binding sites, better ion-exchange

properties and formation of new functional groups and it favors metal uptake. Although, after chemical modification adsorption capacity has been increased but cost of chemicals used and method of modification must have to be taken into consideration in order to produce 'low cost' adsorbent.

Study of Heavy Metal Removal using Adsorption: According to Jaya Mishra et.al, (2021); and Veena Bobade et. al, (2015), the heavy metals removal based on the performance of various adsorbents such as natural materials, industrial byproduct, agricultural and biological waste, biopolymers and hydrogels. The objective of this study is to contribute in the search for low cost adsorbents and investigate the parameters that influence the adsorption of heavy metals on adsorbents.

Removal of Heavy metals using Tea waste: According to Lokendra Singh Thakur et. al, (2013), tea is one of the most popular beverages and about 3.5 million tons of tea was consumed annually in the world and in India yearly production of tea is approximately 857000 tones which is 27.4% of total world production. The adsorption ability of tea waste was investigated for the removal of Cu (II) and

Cd (II) from single (non-competitive) and binary (competitive) aqueous systems. Experiment results showed that maximum removal of Nickel ion by tea waste at optimum condition (5 pH, 120 min. contact time, 0.5g/100ml adsorbent dose and 20ppm concentration) is 94% and for Copper & Zinc ion are 89% & 91% respectively at optimum condition (5 pH, 120 min. contact time and 0.5g/100ml adsorbent dose, 10ppm concentration).

Heavy metal removal using Chitosan-g-poly composite: According to Shyam R. Khairkar et. al, (2014), a natural bio polymer "Chitosan" was grafted onto Acrylic acid and Acrylamide and adsorption of some heavy metal studied by batch method. Synthesis of grafted chitosan supersorbent was synthesized by radical polymerization method.

The adsorption of heavy metal cations, Cu (II), Cd (II), Ni (II), and Pb (II) from aqueous solution by newly-synthesized superabsorbent composite of chitosan-g-poly (acrylic acid-co-acrylamide) was investigated. The superabsorbent gel was characterized on the basis of FTIR, X-ray diffraction, Scanning electron Microscopy and thermal properties. The percentage adsorptions of metal ions on adsorbent were determined by batch methods using

atomic absorption spectrophotometry (AAS). The effect of experimental parameters, such as pH, treatment time, temperature, adsorbent dose, initial metal ion concentration on the removal of metal ions was also studied.

Palm dates as adsorbent for removal of heavy metals: According to Arshad I. Esmael et. al, (2014), Palm date pits are considered a low cost source of activated carbon.

Heavy metals adsorption was studied for individual elements, and for industrial wastewater samples collected from a tannery and an electroplating factory. The kinetic studies showed that Cu, Cr+6, and Fe were adsorbed very rapidly within the first 30 minutes, while equilibrium was attained within 90 min.

The adsorption capacity and removal efficiency for individual elements reached 89.17% for Cu, 71.30% for Cr+6, and 85.17% for Fe respectively. As for the removal of heavy metals from industrial wastewater collected from the tannery, removal efficiency reached 85.17% for Cu, 65.42% for Cr+6, and 87.03% for Fe and for the electroplating factory effluent: 82.857% for Cu, 61.65% for Cr+6, and 89% for Fe.

Heavy metal pollution removal from water using a cost-effective bio-

Adsorbent: According to Shaymaa I. Saeed, et. al, (2017), in the study the adsorbent was prepared by washing the Westland Irish peat moss using an acidic bath for half an hour with a continuous shaken process, then the mixture was centrifuged to separate the peat moss particles, which was washed using deionized water and dried using an oven. The dried sample was ground and sieved at 80 mesh screen before it was used as an adsorbent. The experiments were accomplished in a batch system as a function of initial solution pH, contact time as well as peat moss dosage. The maximum copper removal, 94.8%, was obtained at a pH of 6, optimum adsorption-equilibrium time of 80 minutes, and peat moss dosage of 7.5 g/L.

Adsorption of Heavy Metal using Waste Biomass: According to Shraddha Rani Singh et. l, (2017), the biomass waste from a pharmaceutical industry can be effectively used as an adsorbent material for the removal of heavy metals from aqueous media over a wide range of concentration. Zn and Cr metal ions adsorb strongly on the surface of biomass and can be removed up to 90 % and above. The experimental data fits well with the

Langmuir and Freundlich adsorption isotherm models. The adsorbent used is cost effective and easily available so it can be employed conveniently for the treatment of industrial waste waters.

Removal of Heavy Metals by Adsorption on Azadirachta Indica Activated Carbon:

According to N. Yuvaraja et. al, (2019), this adsorbent incorporates materials of a regular cause like zeolites, mud, peat greenery and chitin are observed to be a compelling operator for the expulsion of dangerous overwhelming metals like Pb, Cd, Zn, Cu, Ni, Hg, Cr and so forth. Aside from these different rural squanders like rice husk, neem bark, dark gram, squander tea; Turkish espresso, walnut shell and so forth were additionally settled as an intense adsorbent for overwhelming metal expulsion. Effects like fly fiery remains, impact heater slime, squander slurry, lignin, iron hydroxide, and red mud, husks, tea manufacturing plant squander, sugar beet mash, battery industry squander, ocean knob buildup and grape stalk squanders have been investigated for their specialized attainability to expel lethal overwhelming metals from sullied water.

Removal of Cadmium from waste water using Natural Adsorbents: According to

Vinaykumar S N et. al, (2019), commercially activated carbon is widely used as an adsorbent for removal of heavy metal ions from industrial wastes though its cost is a restricting factor. The present study explores the effectiveness of activated carbon obtained from sources other than wood, such as groundnut shell, Indian beech and Onion skin for removal of cadmium ions from aqueous waste.

Adsorption studies were carried out for removal of cadmium ions on activated carbon obtained. Adsorption studies were carried out at various pH values and for a range of initial concentrations of cadmium. Utilization of groundnut shell, Indian beech and Onion skin serves dual purpose of simultaneous waste eradication as well as cost effective pollution treatment process.

Removal of Heavy Metals from Tannery Waste Water by Using Natural Absorbents: According to Saravanan M et. al, (2020), the tannery industry releases harmful Heavy metals 20 to 40 then the standard values. Heavy metal is one of major cyclic pollutant which affects the human health as well as fertility of the soils. The recycling of tannery waste water with bark canker, chlorophyll dead and neem leafs as a mixing absorbent. Bark

canker, coffee husk, dried watermelon peel, charcoal as a filtration bed along with slow sand filter. The reduction of chromium, cadmium, lead and nickel metals are up to 90%.

Removal of Cd (II) ion by adsorption onto polyaniline coated on sawdust: According to M.S. Mansour et. al, (2011), the ability of Polyaniline coated on saw dust as synthetic adsorbent was investigated for adsorptive removal of Cd (II) ions from aqueous solutions by batch operation. It was found that polyaniline coated on saw dust (PANI/SD) is very easy and simple to prepare and can be used as an effective adsorbent for removal of Cd (II) ions from aqueous solutions. Various physico-chemical parameters such as pH, initial metal ion concentration, and adsorbent dosage level and equilibrium contact time were studied. The adsorption of Cd (II) ions increased with an increase in pH. The optimum solution pH for adsorption of Cd (II) from aqueous solutions was found to be 6. Adsorption was rapid and occurred within 20 min for a cadmium concentration range of 10: 40 mg L⁻¹. The kinetic process of Cd (II) adsorption onto PANI/SD was found to fit the pseudo-second-order rate equation. The equilibrium adsorption data for Cd (II)

were better fitted to the Freundlich adsorption isotherm model.

Removal of Chromium (VI) using alternative adsorbents: According to Sunil H et. al, (2014), alternative adsorbents like Activated charcoal, modified activated charcoal, wheat bran, activated neem leaf powder and groundnut shell powder were used as adsorbents for effective removal of Cr (VI) ions and thus a comparative study between the adsorbents are presented. Waste water containing Cr (VI) ions was treated with all adsorbents for a calculated amount of time. Further, filtration was carried out and was analyzed for Cr (VI) metal ions using Spectrophotometric method.

Removal of Cr (VI) using Root of Neem Tree: According to Aparna Bhawnani and S. K. Gupta (2017), a novel adsorbent was prepared by using root of Neem Tree. The powder produced was characterized on the basis of surface morphology and specific surface area (854.52m²/g). Batch experiments were carried out to study the removal of Cr (VI) from synthetically produced chromium solution in laboratory.

Three parameters were varied i.e. adsorbent dose, contact time and initial metal concentration. The data fitted well in

Langmuir Isotherm with monolayer capacity of 20.36. The maximum removal efficiency was at lower concentrations. 5g/L of adsorbent dose was found optimum. Kinetics of removal was fast as equilibrium was reached in 60 min. Thus Neem Root adsorbent proves to be efficient and low cost for the removal of hexavalent chromium.

Removal of Fe (II) using Prosopis Juliflora Leaf Powder by Adsorption: According to Sureshkumar Halnor and Milind Ubale (2013), Prosopis Juliflora Leaf Powder (PJLP) was treated with nitric acid and used as a low cost, easily available adsorbent for the removal of Fe (II) from aqueous solution and industrial waste water. Batch experiments were conducted to determine the effects of contact time, pH, and initial concentration of adsorbate, temperature and adsorbent dose. The adsorption of Fe (II) was found maximum (86.27 %) at 50 min contact time, (93.99 %) at 7 pH. (92.28 %) at 1 ppm metal ion concentration, (89.06 %) at 313 K and (86.26 %) at 1 g dose.

Equilibrium data were well represented by the Freundlich isotherm model for all tested adsorption systems. The thermodynamic study has showed that the Fe (II) adsorption onto PJLP was favorable

and spontaneous. The kinetics study showed that Fe (II) adsorption follows the second order kinetics.

Removal of Heavy Metal using Fly Ash Briquette: According to Deepshikha Sareen et.al, (2014), the utilization of economic, reused waste and ecofriendly adsorbent has been researched as an option process for substitution of presently unreasonable methodology for expelling dyes from waste water. Paper fly ash has been used as an adsorbent. Batch experiments have been done to observe the best adsorption by varying various parameters varying initial dye concentration, varying flow rate and varying the bed height.

Removal of Heavy Metal using Fungal Biomass: According to Shipra Jha et. al, (2014), a selective biosorption of Cu ions by micro-organism from industrial wastewater were investigated. Micro-organism was isolated and in the study a micro-organism which was identified as *A. lentulus* was used. In this study, the effects of dilution and nutrient supplementation for efficient Cu(II) removal from effluents and initial concentration of metal ion on the biosorption capacity were investigated. Under supplementations, comparatively faster Cu(II) removal by *Aspergillus*

lentulus was observed resulting in 97-99.8% removal in 120 h.

Adsorption Isotherms

The term “isotherm” is used for the equilibrium curves in the case of adsorption. This isotherm is characteristics for a specific system at a particular temperature (Mohammed Matouq et. al, 2015). The amount of biosorption was calculated from the following equation:

$$qe = \frac{C_0 - C_e}{mV}$$

This relationships depend on the type of adsorption that occurs; multilayer, chemical or physical adsorption. Were, qe : sorption capacity at equilibrium (mg of ions/g of Moringa), C_0 : initial concentration of metal ions in solution (mg/L), C_e : equilibrium concentration of metal ions in solution (mg/L), m : dry weight adsorbent (g), V : volume of aqueous solution (L).

Langmuir Isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. This model is presented by the following equation (Sureshkumar Halnor et. al, 2013):

$$q_e = \frac{q_m b_0 C_e}{1 + b_0 C_e}$$

Where, qm : maximum adsorption capacity (mg of ions/g of Moringa), bo : Langmuir isotherm constant (L/mg), Ce : equilibrium concentration of metal ions in solution (mg/L) The linear form of the Langmuir isotherm is described as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b_0} + \frac{C_e}{q_m}$$

Values of Langmuir parameters qm and bo is calculated from the slope and intercept of the linear

plot C_e versus C

(Sureshkumar Halnor et. al, 2013).

$$\text{plot } \frac{C_e}{q_e} \text{ versus } C_e$$

Freundlich Isotherm

Freundlich isotherm model describes the relationship between non-ideal and reversible adsorption. This model is applied to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules. The application of the Freundlich equation also suggests that sorption energy exponentially decreases upon the completion of the sorption centers of the adsorbent (Mohammed Matouq et. al, 2015). The discussed

isotherm is an empirical equation as follow:

$$q_e = K_f c_e^{1/n}$$

Where, K_f : Freundlich constant related to the bonding energy (mg/ g) (L/g)^{1/n}, n : heterogeneity factor (Bashir A. Dar et. al, 2012).

Freundlich equilibrium constants could be determined from the linear plot of $\ln q_e$ and $\ln C_e$ as the following equation provides:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Freundlich isotherm is widely applied in heterogeneous systems especially organic compounds or highly interactive species on activated carbon and molecular sieves. The slope (value of $1/n$) ranges between 0 and 1 and is a measure of adsorption intensity or surface heterogeneity.

As the value of the slope approaches zero, the more heterogeneous of the process, whereas a value below unity implies chemisorption's process (adsorption is chemical process). A slope above the value of one indicates a cooperative adsorption (adsorption is physical process) (Ajay K. Agarwal et. al, 2014).

TEMKIN ISOTHERM

The Temkin model assumes that the heat of sorption decreases with the coverage as a result of adsorbate–adsorbent interaction (Mohammed Matouq et. al, 2015). The generalized and linearized forms of the model are given by the following:

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$$

Where, KT : Temkin isotherm constant (L/g), R : ideal gas constant (8.314 J/mol K), T : temperature (K), b : constant related to the heat of sorption (J/mol) (Mohammed Matouq et. al, 2015).

A plot q_e versus $\ln (C_e)$ gives a straight line from which KT and b can be evaluated from the slope and intercept (Mohammed Matouq et. al, 2015).

Bet Isotherm

Brunauer, Emmett and Teller (BET)(Mohammed Matouq et. al, 2015) derived the first isotherm for multilayer adsorption. It assumes a random distribution of sites that are empty or that are covered with by one monolayer, two layers and so on, as illustrated alongside (Patiha et. al, 2016). The main equation of this model is:

$$\frac{[A]}{S_o} = \frac{c_B x_B}{(1 - x_B)[1 + (c_B - 1)x_B]}$$

Where,

$$x_B = p_A K_m$$

$$c_B = \frac{K_1}{K_m}$$

And $[A]$ is the total concentration of molecules on the surface, given by:

$$[A] = \sum_{i=1}^{\infty} i [A]_i = \sum_{i=1}^{\infty} i K_1 K_m^{i-1} p_A^i [A]_0$$

Where,

$$K_i = \frac{[A]_i}{p_A [A]_{i-1}}$$

In which $[A]_0$ is the number of bare sites, and $[A]_i$ is the number of surface sites covered by i molecules (Patiha et. al, 2016).

Dubinin–Radushkevich Isotherm

This isotherm model is more general than Langmuir isotherm because it does not assume a homogenous surface or constant adsorption potential. It is used to evaluate the nature of sorption process as chemical or physical and evaluate the mean energy of sorption. The Dubinin– Radushkevich isotherm equation is expressed as:

$$q_e = q_m \exp\left(-K \left[RT \ln \left(1 + \frac{1}{C_e}\right)\right]^2\right)$$

Where, K : Dubinin–Radushkevich constant related to mean free energy of adsorption (Bashir A. Dar et. al, 2012).

ADSORPTION ISOTHERM STUDIES

Study of Langmuir Adsorption Isotherm:

According to Patiha et. al, (2016), Langmuir adsorption isotherm equation is generally derived using the kinetics approach and based on some assumptions. These assumptions are usually not accompanied by an adequate explanation related with the mechanisms and the determination techniques of its adsorption constants. This study presents a simple technique on the determination of the isotherm equation based on the main assumption so called the monolayer assumption. Furthermore, a more precise technique for determining the adsorption constants is also described. This theoretical study is supported with statistical analysis on the experimental data adapted from the literature. Two theories based on adsorption mechanism and based on rate were introduced. Regardless of its limitations, the results show that the technique for the determination is valid.

Study of Adsorption Isotherms for Zinc ions onto coal fly ash:

According to Ajay K. Agarwal et. al, (2014), the possibility of the utilization of coal fly ash as a low cost adsorbent. Batch experiments were conducted to evaluate the removal of heavy metals from aqueous

solutions by fly ash under various conditions of initial metal concentration, pH and fly ash dosage and contact time.

The adsorption data was described by the Langmuir, Freundlich and BET adsorption Isotherm model. The best fit among the isotherm models was assessed by the linear coefficient of determination (R^2) and non-linear Chi-square. In this study, the Chi-square tests were performed for all the isotherm models. The test results indicated that fly ash could be used as a cheap adsorbent for the removal of Zinc ions from aqueous solution.

Study of Adsorption Isotherms for copper on powder of shed pods of Acacia nilotica:

According to Bashir A. Dar et. al, (2012), the adsorption effectiveness of Acacia nilotica pod powder in removing Cu^{2+} ions in order to consider its application in wastewater purification. The batch method has been employed, using metal concentrations in solution and the percentage adsorption was determined for the adsorption system as a function of adsorbate concentration. Effects of the temperature of the Cu^{2+} ion solution, pH, contact time, metal concentration, and adsorbent loading weight on the removal process were also investigated.

Langmuir, Freundlich isotherms were applied to experimental data and the goodness of their fit for adsorption was compared. Thermodynamic parameters, like enthalpy (ΔH) and the entropy (ΔS) were also calculated. A. nilotica pod powder proves to be a good adsorbent for Cu^{2+} ion removal from wastewater.

Study of Adsorption Kinetics using Moringa Pods:

According to Mohammed Matouq et.al, (2015), the investigation of the effectiveness of the removal of copper, nickel, chromium and zinc ions from synthetic waste water by using Moringa aptera Gaertn (MAG) was studied. The effect of biosorption experimental parameters such as initial metal concentration, contact time, temperature and adsorbent dose has been presented and discussed in details. The equilibrium data for biosorption were analysed by using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models to define the best correlation for each metal. Among the four isotherm models, both Freundlich and Temkin models were fitted with the equilibrium isotherm for copper, while Temkin and Dubinin–Radushkevich models best correlated for nickel and Langmuir isotherm model best

describe the experimental data for chromium.

CONCLUDING REMARKS

Based on the literature reviewed from various sources following conclusions appears to be justified:

- Heavy metal gives lots of dangerous health problem of human beings as well as aquatic organism. So, it is very necessary to illuminate that heavy metals (Pb^{2+} , Cd^{2+} , Hg^{2+} , Mn^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+}) from the aqueous solution and make river, lake, sea pollution free.
- In recent years study of new adsorbents, biosorbents and low cost adsorbents is done most frequently for the treatment of the heavy metal-contaminated wastewater; but in general, if we compare the all types of adsorbents except modified natural adsorbents no adsorbents have been used industrially for the removal of heavy metals.
- It is seen that use of low-cost adsorbents is the keen interest of research for heavy metals removal, more study is required to focus on reducing the cost of pretreatment, regeneration and disposal.
- Here we can see that a lot of low-cost adsorbent variety present like agriculture waste, industrial waste and animal waste in the removing of toxic metal ions from waste water effluent. Mostly all the adsorbent possess the phenol group, carboxyl group, hydroxyl group on the surface of the adsorbent, which we simply called functional group , it activates the adsorbing capacity of adsorbent. Also the lignin in Agrowaste plays as an inhabitant for the process.
- Finally, technical applicability, plant simplicity and cost effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent for the process. All the factors mentioned above should be taken into consideration in selecting the most effective adsorbent/biosorbent for the heavy metal's removal process most efficiently and effectively.
- Further studies will be conducted by extracting the laboratory data required for the study from a Dissertation Report of a Senior P.G. Student having similar topic to fit the collected data in various adsorption isotherm and analyze the result as well as behavior

of adsorption isotherm for finding the best fit isotherm.

ACKNOWLEDGMENT

The authors are very much thankful to Principal Dr. A. P. Bodkhe and Dr. P. S. Pajgade, Head, Department of Civil Engineering, PRMIT&R, Badnera, Amravati for their fullest cooperation. The authors are also thankful to Prof. Sachin Dharpal for timely guidance. Lastly thanking the college librarian to permit us for collecting the Research papers online as well as manually.

REFERENCES

1. Agarwal Ajay K., Kadu Mahendra S., Pandhurnekar Chandrashekhar P., Muthreja Ishwardas L. (2014) "Langmuir, Freundlich and BET Adsorption Isotherm Studies for Zinc ions onto coal fly ash" International Journal of Application or Innovation in Engineering & Management (IIAIEM), Volume 3, Issue 1
2. Agarwal Madhu, Singh Kailash, Renu (2016) "A Survey of Modified Agricultural Wastes for Heavy Metal Removal from Wastewater" International Journal of Engineering Sciences & Research Technology, Vol. 5, Issue 12
3. Bhawnani Aparna, Gupta S.K (2017) "Removal Of Cr (Vi) From Waste Water Using Root Of Neem Tree" International Journal of Chemical & Petrochemical Technology (IJCPT), Vol. 7, Issue 2
4. Bobade Veena, Eshtiagi Nicky (2015) "Heavy Metals Removal from Wastewater by Adsorption Process: A Review" APCChE 2015 Congress incorporating Chemeca 2015, Melbourne, Victoria
5. Dar Bashir A., Taher Abdo, Wani Abubakkar, Farooqui Mazahar (2012) "Isotherms and thermodynamic studies on adsorption of copper on powder of shed pods of Acacia nilotica" Journal of Environmental Chemistry and Ecotoxicology, Vol. 5(2)
6. Esmael Arshad I., Matta Minerva E., Halim Hisham A., Azziz Farouk M. Abdel (2014) "Adsorption of Heavy Metals from Industrial Wastewater using Palm Date Pits as Low Cost Adsorbent" International Journal of Engineering and Advanced

- Technology (IJEAT), Volume-3, Issue-
7. Halnor Sureshkumar, Ubale Milind (2013) "Removal of Fe (II) from Aqueous Solution and Waste Water by Prosopis Juliflora Leaf Powder by Adsorption" Chemical Science Review and Letters
 8. Patiha, E Heraldy, Y Hidayat, M Firdaus (2016) "The langmuir isotherm adsorption equation: The monolayer approach" 10th Joint Conference on Chemistry, IOP Conf. Series: Materials Science and Engineering 107 (2016) 012067
 9. H Sunil, V Karthik K., N Pradeep H, Shetty Mahesh Kumar (2014) "Removal of Chromium (VI) metal ions from waste water using alternative adsorbents - A comparative study" International Journal of Scientific and Research Publications, Volume 4, Issue 1
 10. Jha Shipra, Chauhan Ritu, Dikshit S. N. (2014) "Fungal Biomass as Biosorbent for Removal of Heavy Metal from Industrial Wastewater Effluent" Asian Journal of Plant Science, Vol. 1, Issue 2
 11. Khairkar Shyam R., Raut Arun R. (2014) "Adsorption studies for the removal heavy metal by chitosan-g-poly (acrylicacid-co- acrylamide) composite" Science Journal of Analytical Chemistry, Vol. 2, Issue 6
 12. M Saravanan, M Keasavan, N Rajeshwari, R Karthick, K Karan (2020) "Removal of Heavy Metals from Tannery Waste Water by using Natural Absorbents International Research Journal of Engineering and Technology (IRJET), Vol. 7 Issue 4
 13. Mansour M.S., Ossman M.E., Farag H.A. (2011) "Removal of Cd (II) ion from waste water by adsorption onto polyaniline coated on sawdust" Desalination 272 (2011) 301–305
 14. Matouq Mohammed, Jildeh Nina, Qtaishat Mohammed, Hindiye Muna, Al Syouf Maha Q. (2015) "The adsorption kinetics and modeling for heavy metals removal from wastewater by Moringa pods" Journal of Environmental Chemical Engineering, Vol. 3
 15. Mishra Jaya, Saini R, Singh D (2021) "Review Paper on Removal of Heavy Metal Ions from Waste Water Using Adsorption Process" International Research Journal of Engineering and Technology (IRJET), Vol. 8 Issue 5

16. S N Vinaykumar, Chandrashekar Reddy Basavaraj, Sah A Brahma Prakash (2019) "Removal of Cadmium from Electroplating Industrial Waste Water using Natural Adsorbents" International Research Journal of Engineering and Technology (IRJET), Vol. 6 Issue 5
17. Saeed Shaymaa I., Ahmed Rasha Z. T., Grmasha Ruqayah Ali, Alenezi Soltan M., Salman Jasim M., Al-Sareji Osamah J., Mubarak Hayfaa A., AlKhayyat Ahmed (2017) "Heavy metal pollution removal from water using a cost-effective bio-adsorbent" STEPS 2020, IOP Conf. Series: Materials Science and Engineering
18. Sareen Deepshikha, Dr. Garg Rajeev, Dr. Grover Neelkanth (2014) "A Study on Removal of Methylene Blue Dye from Waste Water by Adsorption Technique Using Fly Ash Briquette" International Journal of Engineering Research & Technology (IJERT), Vol. 3 Issue 7
19. Singh Shraddha Rani, Dr. Singh A. P. (2017) "Adsorption of Heavy Metals from Waste Waters using Waste Biomass" International Journal of Engineering Research & Technology (IJERT), Vol. 6 Issue 01
20. Thakur Lokendra Singh, Parmar Mukesh (2013) "Adsorption of Heavy Metal (Cu²⁺, Ni²⁺ and Zn²⁺) from Synthetic Waste Water by Tea Waste Adsorbent" International Journal of Chemical and Physical Sciences, IJCPS Vol. 2, No. 6
21. Yuvaraja N., Sathya T. (2019) "Removal of Heavy Metals from Industrial Effluents by Natural Adsorption on Azadirachta Indica Activated Carbon" International Journal of Engineering Research & Technology (IJERT), ICONEEEE - 2k19 Conference Proceedings