The Removal of Heavy Metals from Waste Waters using Bioadsorbents

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Preface

Water pollution from industries is divesting the natural balance of aquatic ecosystems; also it indirectly affects the serenity and quality of all life forms in general. With the advent of industrialization the ill-effects of ever growing pollution levels cannot be ignored. Although there are number of methods available for extracting pollutants from effluent waters to match up the water quality standards within the permissible range, still each of the techniques available has some drawback associated. In general, each of the technique come with a cost, which is one of the major reasons of them being not used specially in developing countries.

Heavy metal pollution is of major concern cause of their non-biodegradable character. Developing countries face major of issues for the treatment of heavy metals from wastewaters. Many factors are to taken into consideration while selecting any specific method for the treatment process including desired water quality, set up and operating cost, accessibility of space for construction of the facility and way out for the waste disposal generated during treatment.
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# Table of Content

1. **INTRODUCTION** 6

1.1 WATER CONTAMINATION 6
1.2 LITERATURE REVIEW 7
   1.2.1 METHODS AVAILABLE FOR REMOVAL OF HEAVY METALS 7
   1.2.2 ADSORPTION ISOTHERM 10
   1.2.3 ADSORPTION KINETICS 11
   1.2.4 EVALUATION OF HEAVY METAL REMOVAL PROCESSES 11

**EXPERIMENTAL METHODS AND ANALYSIS** 16

3.1 SELECTION OF ADSORBENTS 16
CHARACTERIZATION OF BIOADSORBENTS 16
   3.5.1 INSTRUMENTAL ANALYSIS 16
   3.5.2 PHYSICOCHEMICAL CHARACTERIZATION 17
3.6 BATCH ADSORPTION EXPERIMENTS 19
3.7 ADSORPTION ISOTHERMS 19
   3.7.1 LANGMUIR ISOTHERM 20
   3.7.2 FREUNDLICH MODEL 20
   3.7.3 THE TEMKIN ISOTHERM 21
   3.7.4 THE DUBININ-RADUSHKEVICH ISOTHERM: 22
3.8 ADSORPTION KINETICS: 22
   3.8.1 PSEUDO FIRST ORDER KINETIC MODEL 23
   3.8.2 PSEUDO SECOND ORDER KINETIC MODEL 23
   3.8.3 INTRAPARTICLE DIFFUSION MODEL 24
   3.8.4 ELOVICH EQUATION 24
3.9 THERMODYNAMIC STUDIES 25

4. **CONCLUSION AND SCOPE FOR FUTURE WORK** 25

5. **REFERENCES** 26
1. INTRODUCTION

WATER CONTAMINATION

Water is one of the most imperative assets Mother Nature has given us. Rapid increase in population has lead to unplanned urbanization and industrialization, both of which have caused severe damage to the serenity of our ecological system specially water. Industrial effluents, toxic industrial wastes, runoff from farming fields and untreated sanitary waste are majorly at blame for the fresh water pollution. Effluents from Industries such as tannery, textile, fertilizer, leather, metallurgical, galvanizing, batteries, electroplating, paint, pigment and dyes industries, alloy industries, sewage sludge and other metal processing and refining operations contribute heavily in increased concentration of heavy metals in fresh waters. Elements with atomic density 5 are counted under the head of heavy metals. Heavy metals fall under the class of being non-biodegradable and hence are accumulated in living organisms by food chains (M. Dundar C. N., 2008). Some examples of heavy metals includes: Aluminum, Arsenic, Barium, Cadmium, Chromium, Copper, Gold, Lead, Lithium, Manganese, Mercury, Nickel, Platinum, Selenium, Silver, Tin and Zinc. The scope of metal recovery from industrial wastewater also needs attention. Metal accumulation in body may lead to serious physiological ailments. Because of their mobility and toxicity heavy metals are considered as major inorganic contaminants of the environment. Some of the major heavy metal pollutants their sources and effects on human health are listed in Table: 1 below (National Organization for Rare Disorders, 2005) (Standards, 2009):

<table>
<thead>
<tr>
<th>Metal</th>
<th>Acceptable Limit (mg/l)</th>
<th>Source</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.01</td>
<td>Pesticides, Insecticides</td>
<td>Headaches, drowsiness, confusion, seizures, brain damage, Skin problems, gastroenteritis, anemia, hypotension</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.003</td>
<td>Electroplating, storage batteries, e-waste</td>
<td>Fatigue, headaches, nausea, vomiting, abdominal cramps, diarrhea, fever, loss of lung function, pulmonary edema,</td>
</tr>
<tr>
<td>Substance</td>
<td>Concentration</td>
<td>Sources</td>
<td>Health Effects</td>
</tr>
<tr>
<td>-----------</td>
<td>---------------</td>
<td>---------</td>
<td>----------------</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.05</td>
<td>Cars, glass, pottery, textile</td>
<td>breathlessness, tachycardia, anemia, renal tubular dysfunction, proteinuria, osteomalacia</td>
</tr>
<tr>
<td>Lead</td>
<td>0.01</td>
<td>Battery, soldering, welding, galvanization, petroleum refining, printing and pigment industries, paints, paper and pulp chemical industries</td>
<td>Lung and respiratory tract cancer as well as kidney diseases, diarrhea and vomiting, often with blood, acidosis</td>
</tr>
<tr>
<td>Copper</td>
<td>0.05</td>
<td>Petroleum refinery, motor vehicle and aircraft plating and finishing, mining, electrical wires, alloys, paints, ceramics, industrial Wastes, pharmaceutical products and pesticides</td>
<td>Headaches, vomiting, abdominal pain, anorexia, constipation, slurred speech, changes in kidney function, anemia, brain damage, seizures, convulsions, swelling of the optic nerve, impaired consciousness, depression, anxiety, insomnia</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.02</td>
<td>Smelting operations, thermal power plants, production of stainless steel, metallurgy, chemical and food processing industries, as catalysts and pigments</td>
<td>Metal fume disease, lung cancer, Wilsons disease, coma, depression, hypertension, uremia, sporadic fever, mucosal irritation, capillary damage and gastrointestinal irritation</td>
</tr>
</tbody>
</table>

Data of Central Pollution Control Board show that Maharashtra, Gujarat and Andhra Pradesh contribute to around 80% of hazardous waste in India (Academy, 2011). In the present work adsorption a study involving Copper and nickel is carried out they being quite widely used in industry, pose as the most common pollutants in environment (M. Cempel, 2006) (C. A. Flemming, 1989).

**LITERATURE REVIEW**

**Methods Available for Removal of Heavy Metals**

Many treatment technologies exist with varying degree of sensitivity to remove heavy metals from wastewater. Some of them are chemical precipitation, ion exchange, membrane techniques like reverse osmosis and electrodialysis. However, in spite of the number of methods available,
Chemical Precipitation

Chemical precipitation involves adding a precipitation reagent to the wastewater, resulting in a chemical reaction that converts the dissolved metals into solid particles (K.G. Karthikeyan, 1996). The particles can then be aggregated by chemical coagulation and removed by filtration or sedimentation. Chemical precipitation is the most common method for removing dissolved heavy metals from wastewater (Y. Ku, 2001). However, it is not effective for treating wastewater with high acid content, and it produces a large quantity of toxic sludge that needs to be treated with chemical stabilization and disposed of properly. According to Malik et al, Lime is most commonly used in chemical precipitant (D. S. Malik, 2017) (S.A. Mirbagherp, 2004) (H.A. Aziz, 2008)

Ion exchange

Ion exchange is another method used for the removal of heavy metals from effluents. Though it is relatively expensive when compared to other methods, it has the ability to achieve parts per billion levels of clean up while handling a relatively large volume of effluents. The ion exchange method is based on the potential to exchange metals with cations in the wastewater (O.N Kononova, 2000) (M. Pagano, 2000). According to Malik et al, zeolites are most widely used in this process (Y. Fernandez, 2005) (D. S. Malik, 2017). Being highly sensitive to solution pH is a major shortfall of this process (D. S. Malik, 2017).

Membrane process

Different membranes are used to filter out suspended solids, oils, organic and inorganic materials and heavy metals (F. Fu, 2011). Depending on the size of the particles and wastewater different forms of this technique are used, such as ultrafiltration (UF), nanofiltration (NF), reverse osmosis (OS) and electrodialysis (ED) (D. S. Malik, 2017).

Ultrafiltration

In ultrafiltration contaminants are filtered as per their molecular size, where only lower molecular solutes can percolate through membranes (D. S. Malik, 2017). It can be been divided
Nanofiltration

“Nanofiltration is used in heavy metal separation from aqueous solutions” (D. S. Malik, 2017) (B. Al-Rashdi, 2011). Used for removing heavy metals such as nickel (Z.V.P Murthy, 2008), copper (A.L. Ahmad, 2010), chromium (M. Muthukrishnan, 2008) and arsenic (A. Figoli, 2010). In spite of promising perspectives it is associated with limitations of membrane fouling, limited lifetime of membranes and chemical resistance and insufficient rejection of pollutants in water treatment (B. Van der Bruggena, 2008).

Reverse osmosis

Reverse osmosis (RO) is a separation process utilizing a semi-permeable membrane that uses pressure to force a solution through membrane which retains solute on one side and allows pure solvent to pass through. It involves a diffusive mechanism, so that separation efficiency is dependent on solute concentration, pressure, and water flux rate (S.K. Gunatilake, 2015). The RO technique can be used to treat industrial effluents from tannery, chemical, textile, electrochemical, petrochemical, food and paper industries (D. S. Malik, 2017) (M. Mohsen-Nia, 2007). Membrane restoration and high power consumption are some of the drawbacks of Reverse osmosis.

Electrodialysis

“Electrodialysis (ED) is a separation process where dissolved ions are removed from one solution to another solution across a charged membrane under an electric field” (M. Sadrzadeh, 2008; D. S. Malik, 2017). Apart from wastewater treatment electrodialysis is also used in salt production, production of drinking water from seawater (M. Sadrzadeha, 2009). Corrosion and membrane emplacement are some limitation of this process.

Adsorption

The phenomenon of accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed as adsorption. The substance that adsorbs on the surface is called
Adsorbate, and the substance on which it adsorbs is called adsorbent (M.K. Toor, 2010). The term ‘adsorption’ was first used by H. Kayser in 1881 (V.K. Gupta A. R., 2008). In 1909 J. W. McBain introduced a similar term ‘sorption’. As per V. Inglezakis, in 1914 Freundlich gave an equation to explain adsorption isotherm, proposed actually by Bemmelen in 1888 but known as the Freundlich equation because Freundlich assigned great importance to it and popularized its use. Irving Langmuir was the first to introduce a clear concept of the monomolecular adsorption on energetically homogeneous surfaces in 1918 and derived a simple equation based on kinetic studies (V. Inglezakis, 2006) (P.S. Gayathri, 2009)

Types of adsorption

The unbalanced inward forces raised due to different properties of bulk and surface lead to attraction and retention the adsorbate molecules onto the surface (Q.U. Jiuhui, 2008). Based on the force holding onto the adsorbent on a surface two types of adsorption are possible. Physical adsorption or physisorption occurs if weak van der Waals forces are holding onto the adsorbent. This type of adsorption is characterized by low heat of adsorption about -20 to 40 kJ/mol (M.K. Toor, 2010). Physisorption is generally non specific and reversible in nature (E. R. Treybal, 1981). In physical adsorption the adsorbate molecules may form a monolayer or a multilayer depending upon the conditions of temperature and concentration. on the other hand chemisorption is a result of chemical bonding which may be either covalent or ionic in nature. The enthalpy of chemisorption is about 80 to 240 kJ/mol (S.Keleolu, 2007). Chemisorption is specific and irreversible in nature. In chemisorption, the adsorption layer is unimolecular.

Adsorption isotherm

The efficiency of an adsorbent can be accessed through adsorption isotherm curves, with the help of mathematical equations referred to as adsorption isotherm model equations, which are key to calculate the amount of adsorbate adsorbed per unit mass of adsorbent ($q_e$) at equilibrium. A number of isotherm equations were proposed by different investigators. Some of the frequently used isotherms are Freundlich adsorption isotherm, Langmuir adsorption isotherm, Dubinin–Radushkevich isotherm and Temkin adsorption isotherm.
Adsorption kinetics

The adsorption kinetics provides valuable insight into the reaction pathways and the mechanism of the reaction. Any adsorption process is normally controlled by three diffusive transport processes such as (i) transport of the adsorbate from bulk solution to the film surrounding the adsorbent (ii) movement of the adsorbate from the film to the adsorbent surface (iii) diffusion of the adsorbate from the surface to the internal sites followed by binding of the adsorbate onto the active sites (M.E. Argun, S.D., 2007). In kinetics modeling, all these three steps are grouped together and it is assumed that the difference between the average solid phase concentration and equilibrium concentration is the driving force for adsorption process (S.S. Baral, 2007) (A. Demirbas, 2004). Some frequently used models are Pseudo first order kinetic model, Pseudo second order kinetic model, Intraparticle diffusion model and Elovich equation. Since the precise mechanism of adsorption from solutions is very complex because physisorption, chemisorption or intraparticle diffusion may occur simultaneously.

Evaluation of Heavy Metal Removal Processes

Removal of heavy metals from the effluent is very important part of the research carried out in environmental field. Adsorption is one of the preferred physicochemical processes for heavy metals and dyes removal over conventional methods (M.K. Toor, 2010). Moreover, the adsorption capacity of the low-cost adsorbents can be easily worked on with simple and economically feasible methods (M.K. Toor, 2010) and the adsorbent can be easily recovered and reused (J. Crini, 2006). Major advantage of this process is no sludge generation (B.K. Nandi, 2009). Physico-chemical treatments offer various advantages such as rapid process, easy operation and control, various input loads etc. Whenever it is required, chemical plants can be modified also these treatment systems require a lower space and installation.

Adsorbents

The applicability of adsorption process is calibrated by adsorbents physical and chemical nature, selectivity, adsorption capacity, porous structure, cost, availability and equilibrium time (M.K. Toor, 2010) (G. Allen, 1980) (W.J. Masschelein, 1992). Wide varieties of such adsorbents are available and are being used in pollution control. The adsorbents can be divided into following three classes:
Oxygen-containing compounds – are generally hydrophilic and polar, including materials such as silica gel and zeolites.

Carbon-based compounds – are usually hydrophobic and non-polar, including materials such as activated carbon and graphite.

Polymer-based compounds - are polar or non-polar functional groups in a porous polymer matrix such as biomass.

A variety of adsorbents has been developed in recent years and applied for various applications. Some adsorbents are discussed below:

Activated carbon

Activated carbon (AC) is the principal adsorbent in wastewater treatment (A. Bhatnagar, 2006). Activated carbon is a processed form of carbon with porous nature and large dynamic surface area available for adsorption. Activated carbons are excellent and versatile adsorbents because of the high inter-particulate surface area, a high degree of micro porosity and surface chemical reactivity. Consequently, they are extensively used for purification, detoxification, decolourisation, dechlorination and deodorization of substances. Also, activated carbon has been extensively used as an adsorbent in a variety of industrial and environmental applications (S. Kurniawan, 2004). The type of precursor and the method employed for activation are the key factors that determine the quality of the activated carbon produced.

Carbonization

In carbonization the precursor is pyrolyzed at high temperature (300-900°C), in an inert atmosphere. The carbonization of the source raw material results in elimination of non carbon elements as volatile gaseous products while the residual elementary carbon atoms are grouped normally into stacks of irregular aromatic sheets cross-linked in a random fashion. This arrangement of irregular aromatic sheets leaves interstices which are called pores (C.A Toles, 1997).

Activation

Activation of carbon is usually carried out in two ways:
(a) **Physical activation:** In this process, the carbonized material is exposed to oxidizing atmospheres at around 300–1000 ºC, it produces highly porous adsorbent material (R. Parimalam, 2012).

(b) **Chemical activation:** Chemical activation involves impregnation of the raw or carbonized material with acids, bases and salts such as phosphoric acid, potassium hydroxide, sodium hydroxide, zinc chloride etc. (R. K. Nasrin, 2000) (M. Rodriguez-Reinoso, 2004). The combination of the chemical and physical activation processes leads to the production of activated carbon with specific surface properties. Activated carbon produced by chemical activation has large surface area and is highly porous in structure (R. Parimalam, 2012).

It has been observed that the activation of carbon by H$_3$PO$_4$ forms porous activated carbon (M. Molina-Sabio, 2004). Modified carbon surface has shown high adsorption capacity for a large variety of polar and non-polar organic compounds from water. Generally, H$_3$PO$_4$ is believed to function as a dehydrating catalyst, which can promote decomposition of the cellulosic precursor at a lower temperature (K.Y. Hameed, 2012). Moreover, the presence of H$_3$PO$_4$ in the interior of the precursor restricts the formation of tar as well as other liquids such as acetic acid and methanol by formation of cross-links, and inhibits the shrinkage of the precursor particle by occupying certain substantial volumes resulting in the lower weight loss and higher yield of the H$_3$PO$_4$ impregnated carbon (R. Yang, 2011); (R.C Bansal, 1978).

Cost being a major issue with activated carbon, low-cost adsorbents are finding their way out with extensive research especially in developing countries (C. Rivera-Utrilla, 2001). A wide variety of low-cost adsorbents have been prepared from different waste materials including biological, agricultural, industrial and municipal wastes.

*Silica gel*

The silica gel is considered an effective adsorbent and used in many industries for drying of gases and liquids, purification of hydrocarbons, etc (W.K. Backhaus, 2001). It is a chemically inert non-toxic, polar and stable amorphous form of SiO$_2$. Silica gel is prepared by the reaction between sodium silicates and H$_2$SO$_4$ followed by aging, pickling etc. recently many variants of
Fly ash
Fly ash is one of the residues generated in the combustion of coal. It consists of mainly SiO$_2$ and present in two forms: amorphous and crystalline. Fly ash is generally highly heterogeneous consisting of mixture of glassy particles with various crystalline phases such as quartz, mullite and various iron oxides. It is presently used in the synthesis of geopolymers and zeolites and also in waste water treatment (I.D. Mall, 2006).

Zeolites
Another class of selective adsorbent i.e. Zeolites are extremely versatile and their main applications include detergent manufacture, water softening resins and catalytic applications in the petroleum industry, separation processes and as adsorbents for water, carbon dioxide and hydrogen sulfide. Various zeolites have been employed for the removal of pollutants (B. Okolo, 2000) (A. Metes, 2004) (T. Motsi, 2009).

Biosorption
Biosorption as a new and attractive treatment technology is gaining its reputation for removal of heavy metals especially from dilute wastewaters (Gurel, 2017). Biosorption has received considerable focus for the designing clean and efficient technology for wastewater treatment (S. Musayev, 2017) (M. Dundar C. N., 2008).

During the past few decades the importance of designing low cost adsorbent material has been realized for them being more economic, eco-friendly and easily available. The potential of a number of plant materials, agricultural materials, industry and municipal waste has been tapped. The biodiversity of India has charmed many workers for exploring possibility of generating good alternatives for available options as adsorbent materials.

Plenty of agricultural waste are used as adsorbents as they have low ash content and reasonable hardness (M. Ahmedna, 2000), some of them include corn (W.T. Tsai, 2001), maize cob (M.M. Nassar, 2004), grape bagasse (N.V. Farinella, 2004), olive wastes (K. Nyazi, 2005), black

Low cost adsorbents are in focus as prime alternative for available activated carbon, easy availability, lesser cost and greener pathways. Many researchers have evaluated various industrial and agricultural by products and waste materials, for their adsorption characteristics some of which includes bagasse fly ash (V.K. Gupta I. A., 2000), Slag columns (S.V. Dimitrova, 2002), distillery sludge (K. Selvaraj, 2003), wine processing sludge (Y.S. Li, 2004), blast furnace slag (S.R. Kanel, 2006), Battery industry waste (A. Bhatnagar, 2006), leather industry solid waste (D.Q.L. Oliveira, 2008), steel making slag (D.H. Kim, 2008), pulp and paper waste (S. Sniannopkao, 2009), steel converter slag (A. Mendez, 2009), sewage sludge (M.J. Martin, 2003). Along with these some marine origin wastes have also been utilized like red mud (V.K. Gupta M. G., 2001) (M.K. Sahu, 2013), peat (J.M. Marquez-Reyes, 2013), (Z. Xiaoxi W. L., 2017)

**Bioadsorbents**

To have an adsorbent with high adsorption capacity, easy availability, geographic proximity and cost effectiveness is the only aim of the present study.

**EXPERIMENTAL METHODS AND ANALYSIS**

### 3.1 SELECTION OF ADSORBENTS

While selecting an adsorbent material it is a prime requisite that it must be non-toxic easily, locally and abundantly available, must cost less and should be easily process able and must have surface characteristics suited for an efficient and fast adsorption. Keeping in view all these factors a particular adsorbent material must be chosen.

**CHARACTERIZATION OF BIOADSORBENTS**

The biosorbents can be characterized as follows:

#### 3.5.1 Instrumental analysis

Specific functional group plays a significant role in imparting a specific character to the carbon. FT-IR produces superior spectra and can provides precise information concerning surface groups (B. Roopchand, 2005) Scanning Electron Microscopy can used to study the surface morphology of the biosorbent.
3.5.2 Physicochemical Characterization

3.5.2.1 Apparent density

A pre-weighed specific gravity bottle of 25 ml capacity is filled with the adsorbent and packed well by tapping with a rubber stopper. The weight of the adsorbent is determined. The weight (g) divided by the volume (ml) gives the apparent density of the adsorbent (A. Mohammed, 2012) (ASTMD-3172-89, 2001).

\[
\text{Apparent Density} = \frac{\text{Weight of Sample}}{\text{Weight of equal volume of water}}
\]  

(1)

3.5.2.2 Moisture content

A preheated, cooled, weighed silica crucible is used for moisture content determination. 1 g carbon sample was dried at 110°C for 1 h in a drying oven followed by cooling to room temperature. While cooling the dried sample is constantly reweighed at an interval of 10 min until constant weight is obtained. The ratio of the change in weight to the original weight expressed in percentage gives the moisture content (ASTMD-3172-89, 2001).

3.5.2.3 Volatile matter

A silica crucible is preheated at 990°C for 10 min in a muffle furnace and cooled in a desiccator. One gram of the carbon sample is taken in it, partially closed with a lid and heated at about 990°C for 10 min in the muffle furnace. The crucible containing biomaterial is retrieved and cooled in the desiccator. The loss in weight gives the volatile matter (ASTMD-3172-89, 2001).

3.5.2.4 Acid insoluble matter

500 mg of adsorbent is placed in an evaporating dish, mixed with distilled water to form thin slurry; 5-10 ml of concentrated HCl is added and digested by warming until sample is nearly dry. The digestion is repeated three times with 5 ml of the acid. Then it is diluted with 100 ml water, filtered using a previously weighed sintered crucible and the weight of the insoluble matter is calculated after drying for a constant weight at 110°C (ASTM D7348-13, 2013)
3.5.2.5 Water-soluble matter

1 g of adsorbent is mixed with 100 ml of distilled water and is shaken thoroughly for about 30 min and filtered. The residue i.e., adsorbent is dried, cooled and weighed. The loss in weight gives water soluble matter (Z. Hua, 2001).

3.5.2.6 Ash content

A silica crucible is preheated in the muffle furnace at 990°C for 1 h. It is then cooled in the desiccator and weighed. 1 g of each sample is placed in the crucible and heated at 990°C for 1 h with the lid on. The crucible and its content is then cooled in the desiccator and weighed. The weight of the incombustible residue accounts for ash content (ASTM D2866, 2006).

3.5.2.7 pH

The adsorbent material (0.1 gm) is mixed with 100 mL of water (pH 6.46) and equilibrated for 1 hr by agitating at 120 rpm. The supernatant is analyzed for pH, using Elico pH meter (ASTM D1293 - 12, 2005).

3.5.2.8 Point of zero charge (pH_{pzC})

Zero point charge is the pH at which the external surface charge is zero (H.Marsh, 2006). As per the method given by Ekpete and coworkers determination of the pH point of zero charge (pH_{pzC}) of the biomaterials can be carried out by using 50 ml of 0.01 M NaCl solution in an Erlenmeyer flask, whose pH is adjusted to a value between 3 and 10 by adding 0.1 N HCl or 0.1 N NaOH solution followed by addition of 0.1 g of prepared activated carbons. The flasks are sealed and placed on a shaker for 24 hrs after which the pH is measured. The pH_{pzC} occurs when there is no change in the pH after contact with adsorbent (O.A. Ekpete, 2011). The results are plotted with pH_{final} - pH_{initial} against pH_{final}. The point at which pH = 0 is known as pH_{zpc}.

3.5.2.9 Iodine number

To gain further knowledge of the porous structure of activated carbon, iodine adsorption from liquid phase is adopted (M.J. Martin, 2003). The adsorption of aqueous I$_2$ is considered a simple and quick test for evaluating the surface area of activated carbons associated with pores larger than 1 nm (A. Bacaoui, 2001). The iodine value can be measured according to the procedure established by the American Society for Testing and Materials (ASTM D4607 -14, 2003).
The concentration of iodine adsorbed by the activated carbon at room temperature is calculated using following equation (C.Gimba, 2007):

\[
\text{Iodine number: } = \frac{(B - S)}{B} \times \frac{V \cdot M}{W} \times 253.81 \quad (2)
\]

Where \( B \) is volume of thiosulphate solution required for blank and \( S \) is volume of thiosulphate solution required for sample titration. \( W \) is the mass of activated carbon sample, \( M \) is the concentration (mol) of the iodine solute, 253.81 is the atomic mass of iodine and \( V \) is 20 ml aliquot.

### 3.6 BATCH ADSORPTION EXPERIMENTS

Batch adsorption experiments needs carried out under optimized conditions as a function of adsorbent dose, agitation time, for a fixed period of time using a shaker, using Whatmann 42 filter paper for filtration. The concentration of metal ions in the filtrate is analyzed using the spectrophotometer. The values enabled the calculation of percentage removal of the metal ions and the amount of metal adsorbed on the surface of adsorbent, by using the following equations:

\[
\% \text{ Removal} = \left( \frac{C_0 - C_e}{C_e} \right) \times 100 \quad (3)
\]

\[
\text{Amount adsorbed (}q_0\text{)} = \frac{(C_0 - C_e)}{m} \times V \quad (4)
\]

Where, \( C_0 \) = initial concentration of metal solution in mg/l
\( C_e \) = equilibrium concentration of metal in mg/l
\( m \) = mass of the adsorbent in grams
\( V \) = volume of test solution in litres

Various parameters affecting the extent of adsorption needs calibrated in order to achieve a set of optimum conditions for the whole process.

### 3.7 ADSORPTION ISOTHERMS

The analysis of adsorption data is important to develop an equation which accurately represents the results and which could be used for design purposes. The most commonly applied isotherms, in solid/liquid system, are the theoretical equilibrium isotherm: the Freundlich, Langmuir, Temkin and Dubinin- Radushkevich
3.7.1 Langmuir isotherm

The theoretical Langmuir isotherm (Langmuir, 1916) is often used to describe sorption of a solute from a liquid solution as:

\[
q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e}
\]  

(5)

The constants \( q_{\text{max}} \) and \( K_L \) are characteristics of the Langmuir equation and can be determined from a linearized form of Equation 5, represented by

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} K_L} + \frac{C_e}{q_{\text{max}}}
\]

(6)

Alternatively,

\[
\frac{1}{q_e} = \left(\frac{1}{q_{\text{max}} K_L}\right) \frac{1}{C_e} + \frac{1}{q_{\text{max}}}
\]

(7)

When \( C_e/q_e \) is plotted against \( C_e \), a straight line is obtained (Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, 1918).

Where \( q_e \) is the solid phase adsorbate concentration in equilibrium (mg/g), \( q_{\text{max}} \) the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g), \( C_e \) is the concentration of adsorbate at equilibrium (mg/l) and \( K_L \) is the Langmuir constant (l/mg) (Wang, 2005). The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor (\( R_L \), also called equilibrium parameter) which is defined by the following Equation 8: (M. Ozacar, 2004) (G. Crini, 2007)

\[
R_L = \frac{1}{1 + K_L C_0}
\]

(8)

Where \( C_0 \) is the initial concentration (mg/l) and \( K_L \) is the Langmuir constant related to the energy of adsorption (l/mg). The value of \( R_L \) indicates the shape of the isotherms to be either unfavorable (\( R_L > 1 \)), linear (\( R_L = 1 \)), favorable (\( 0 < R_L < 1 \)) or irreversible (\( R_L = 0 \)).

3.7.2 Freundlich model

The Freundlich model is described by the following equation (Freundlich, 1906):

\[
q_e = K_F C_e^{1/n}
\]

(9)
Where $q_e$ is the solid phase adsorbate concentration in equilibrium (mg/g), $C_e$ the equilibrium liquid phase concentration (mg/l), $K_F$ the Freundlich constant (mg/g)(l/mg)$^{1/n}$ and $1/n$ is the heterogeneity factor. The value of $n$ indicates the degree of nonlinearity between the solution concentration and adsorption as follows: when $n = 1$, adsorption is linear; $n < 1$, adsorption is a chemical process; $n > 1$, adsorption is a physical process (G. McKay, 1981).

A linear form of the Freundlich expression can be obtained by taking logarithms of Equation 9:

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

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ enables the constant $K_F$ and exponent $1/n$ to be determined. The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of the monolayer.

### 3.7.3 The Temkin isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage (M.I. Tempkin, 1940) (C. Aharoni, 1977).

As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) carried out by plotting the quantity sorbed $q_e$ against $\ln C_e$ and the constants determined from the slope and intercept. The model is given by the following equation (M.I. Tempkin, 1940) (M. Ozacar, 2004)

$$
q_e = \frac{RT}{b} \ln(A C_e)
$$

A linearized Temkin isotherm equation is:

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

Where, $RT/b = B$ is the constant related to the heat of adsorption, $b$ is the heat of adsorption (J/mol), $R$ is the gas constant (8.314 J/mol.K), $T$ is the temperature (K) and $A$ is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. The adsorption data can
be analyzed according to Equation 12. Therefore, a plot of $q_e$ versus $lnC_e$ enables to determine the constants $A$ and $B$.

### 3.7.4 The Dubinin-Radushkevich isotherm:

The Dubinin-Radushkevich isotherm can be used to describe adsorption on both homogenous and heterogeneous surfaces. The Dubinin-Radushkevich equation has the following form:

$$q_e = q_m e^{-\varepsilon^2}$$  \hspace{1cm} (13)

A linear form of Dubinin-Radushkevich isotherm is:

$$lnq_e = lnq_m - \beta \varepsilon^2$$  \hspace{1cm} (14)

Where, $q_m$ is the Dubinin-Radushkevich monolayer capacity (mol/g), $\beta$ is a constant related to sorption energy, and $\varepsilon$ is the polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon = RT ln\left(1 + \frac{1}{C_e}\right)$$  \hspace{1cm} (15)

Where, $R$ is the gas constant (kJ/mol/K) and $T$ is the absolute temperature. The constant $\beta$ gives the mean free energy, $E$, of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship:

$$E = \frac{1}{\sqrt{2\beta}}$$  \hspace{1cm} (16)

The magnitude of $E$ is useful for estimating the mechanism of the adsorption reaction. In the case of $E < 8$ kJ/mol physical forces may affect the adsorption. If $E$ is in the range of 8-16 kJ/mol adsorption is governed by ion exchange mechanism, while for the values of $E > 16$ kJ/mol, adsorption may be dominated by particle (A. Ozcan, 2006).

### 3.8 ADSORPTION KINETICS:

Predicting the rate of adsorption is a very important part of adsorption studies (C. Chakrapani, 2009). The overall percentage removal and mechanism of adsorption is governed by the rate limiting step, therefore interpretation of data is a key in such studies. Four kinetic models namely pseudo first-order, pseudo second order, Elovich equation and Weber and Morris intra-particle
3.8.1 Pseudo First Order Kinetic Model

The Lagergren’s rate equation is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase (Lagergren, 1898) (W.J. Weber, 1963). The linear form of the model is:

\[
\frac{dq_t}{dt} = K_1(q_e - q_t)
\]  

(17)

After integration and applying boundary conditions, \(t = 0\) to \(t = t\) and \(q_t = 0\) to \(q_t = q_e\), the integrated form of Equation 17 becomes:

\[
q_t = q_e(1 - e^{-K_1t})
\]  

(18)

However, Equation 18 has a linear form:

\[
\log(q_e - q_t) = \log(q_e) - \frac{K_1t}{2.303}
\]  

(19)

Where, \(q_e\) and \(q_t\), are the amounts of metal adsorbed on adsorbent (mg g\(^{-1}\)) at equilibrium and at time \(t\) (min), respectively, and \(K_1\) is the rate constant of pseudo first-order kinetics (Ch.S. Babu, 2014).

3.8.2 Pseudo Second Order Kinetic Model

The adsorption process with chemisorption being the rate control follows pseudo second order kinetic model (M. K. Purkait, 2004) (G. Crini, 2007) (C. Gerente, 2007)

The sorption kinetics may be represented by pseudo-second-order model.

\[
\frac{dq_t}{dt} = K_2(q_e - q_t)^2
\]  

(20)

Rearranging and integrating within the boundary conditions \(t=0\) to \(t=t\) and \(q_t=0\) to \(q_t=q_e\), gives the linearized form as:

\[
\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2t
\]  

(21)

which is integrated rate law for a pseudo-second-order reaction. Rearranging Equation 21 reduces to (Ch.S. Babu, 2014).:
\[ q_t = \frac{1}{1 + \frac{t}{k_2q_e^2}} \quad (22) \]

This has a linear form:

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t \quad (23) \]

Where, \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the equilibrium rate constant. When pseudo second order kinetic equation applies, the plot of \( t/q \), against \( t \) of Equation 23 gives a linear relationship, and \( q_e \) and \( K_2 \) can then be determined from the slope and intercept of the plot (Ch.S. Babu, 2014).

### 3.8.3 Intraparticle Diffusion Model

The intra-particle diffusion model is expressed as (W.J. Weber, 1963):

\[ q_t = K_i t^{1/2} + C \quad (24) \]

Where, \( C \) can be correlated to the thickness of the boundary layer and \( K_i \) (mg g\(^{-1}\) min\(^{-0.5}\)) is the intraparticle diffusion rate constant. According to this model, if adsorption of a solute is controlled by the intraparticle diffusion process, a plot of \( q_t \) versus \( t^{1/2} \) gives a straight line.

### 3.8.4 Elovich equation

Although the Elovich equation was firstly used in the kinetics of chemisorption of gases on solids, it has been successfully applied for the adsorption of solutes from a liquid solution (C. Gerente, 2007) (Sengil, 2004). The Elovich equation is given as follows:

\[ \frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad (25) \]

The integration of the rate equation with the same boundary conditions as the pseudo first- and second-order equations becomes the Elovich equation.

\[ q_t = \frac{1}{\beta} ln(\alpha \beta) + \frac{1}{\beta} ln(t) \quad (26) \]

where \( \alpha \) (mg g\(^{-1}\) min\(^{-1}\)) is the initial sorption rate, and the parameter \( \beta \) (g mg\(^{-1}\)) is related to the extent of surface coverage and activation energy for chemisorption. Linear plots of \( q_t \), versus \( ln(t) \) are obtained if valued obtained follow Elovich equation (C. Chakrapani, 2009).
3.9 THERMODYNAMIC STUDIES

The thermodynamic parameters can be calculated from the following equations (P. S. Kumar, 2011):

\[
\Delta G^0 = -RT \ln K_c
\]

(27)

\[
\log K_c = \frac{\Delta S^0}{2.303 R} - \frac{\Delta H^0}{2.303 RT}
\]

(28)

Where, \( R \) is the gas constant (8.314 J/mol.K), \( K_c \) is the equilibrium constant obtained by multiplying the Langmuir constants \( q_m \) and \( K_L \) (D.H.K. Reddy D. R., 2011), and \( T \) is the temperature (K). The slope and intercept provide values of \( \Delta H^0 \) and \( \Delta S^0 \) from the plot of \( ln K_c \) versus \( 1/T \) (P. S. Kumar, 2011). Finally, the \( \Delta G^0 \) value is calculated by the following equation:

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]

(29)

4. Conclusion and Scope for Future Work

Bioadsorbents are potential alternative for application in minimization of water pollution. The potential of the selected biomaterials being promising adsorbent material can be depicted with the help of batch experiments. Different preparation techniques can be adapted to study the effect of variance in the chosen biomaterials, by means of physical and chemical activations. Prepared materials must be tested for their structural characteristics and adsorption behavior.

Further, the functional groups of the activated carbons present on the surface can be characterized by FT-IR spectroscopy and surface morphology by SEM method. Batch experiments must be carried out to determine the effective adsorbate dose.
The solution pH is other important parameters in the adsorption of metal ions from aqueous solutions. The pH value affects the surface charge of the adsorbent, the degree of ionization, and the speciation of adsorbate during the adsorption process. Experiments carried out at different initial pH exhibit the adsorption percentage of metal ions and their behavior can be explained using pH_{zpc} of the adsorbent. Negatively charged surface of adsorbent attract metal ions as the solution pH exceeded pH_{zpc}. Also, at low pH values, the H^+ ions occupy most of the adsorption sites on the adsorbent surface and only a small amount of metal ions could be adsorbed, because of electrostatic repulsion with H^+ ions on the adsorbent surface. With an increase in the pH value, the adsorbent surface becomes negatively charged, and hence, the adsorption of metal ions increases and then reaches the maximum. The decrease in the adsorption efficiency at higher pH is due to the formation of metal hydroxide in general.

The increase in percentage removal of metal ions with increase in the temperature is attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or the desolvation of the adsorbing species and the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature. Thermodynamic parameters such as Gibbs free energy \( \Delta G^0 \), enthalpy change \( \Delta H^0 \) and entropy change \( \Delta S^0 \) needs to be evaluated. The endothermic nature of adsorption is indicated by the positive values of \( \Delta H^0 \). The negative \( \Delta G^0 \) indicates the spontaneous nature of metal adsorption reaction with bioadsorbents.

In the Indian context, there are a lot of unexplored agricultural wastes available, which possess high enough adsorption capacity, and can be utilized for the treatment of different industrial wastewaters. These waste materials can be surface modified by physical or chemical methods to prepare more efficient adsorbents, which can serve as better alternatives to the commercial activate

5. References


Water is one of the most imperative assets Mother Nature has given us. Rapid increase in population has lead to unplanned urbanization and industrialization, both of which have caused severe damage to the serenity of our ecological system specially water.

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