Ain shams University
Faculty of Science
Chemistry Department

"Treatment of Waste Solutions Using Various Sorbents via modifications of Some Solid Wastes"

Thesis Presented By

Mohamed Refaat Hassan
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Chemistry Department, Faculty of Science Ain shams University For the Degree of Ph.D. of Science in Chemistry
Supervised By

Prof .Dr.
Mostafa Mohamed Hassan Khalil
Prof. of Inorg. Chem.,
Faculty of Science
Ain shams Universit

Prof .Dr.
Mourad Aziz Hanna
Prof. of Rad. Chem.,
Nuclear Research Center
Atomic Energy Authority

Prof .Dr.
Hoda Ahmed Omar
Prof. of Rad. Chem.,
Nuclear Research Center
Atomic Energy Authority

Dr.
Hamdi Mohamed Hassan Gad
Ass. Prof. of Appl. and Phys. Chem.,
Hot Labs. Center
Atomic Energy Authority

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1. INTRODUCTION

1.1. Overview

Massive industrial, research pollution and uncontrolled population growth in the world is a serious threat to the environment in one or the other way **[Tornero and Ribera, (2014) & Amirez et al., (2007)]**. The aqueous bodies viz., rivers, streams, ponds are rich with toxic metal ions such as (mercury, lead, cobalt, cadmium, zinc,……. etc) and organic pollutants such as (dyes, humic and fulvic acids,……. etc) above the prescribed limits, thus leading to various health hazards and environmental degradation. Pollution can also generate from laboratories, chemotherapy, radiotherapy, electric power generation stations and nuclear research which contain many pollutants.

The removal of the above mentioned waste contaminants from aqueous solution is currently one of the most important environmental issues being investigated. Environmentalists are primarily concerned with the presence of wastes due to their high toxicity, carcinogenic or mutagenic effects, bioaccumulation and subsequent magnification making them unavoidable even at very low concentrations **[Zhang et al., (2013) & Barros et al.,(2007) & Preetha and Viruthagiri , (2007)].**

1.2. Sources of Metals in the Environment.

Metals in the aquatic environment may exist in dissolved or particulate forms. They may be dissolved as free hydrated ions or as complex ions chelated with inorganic ligands such as OH^-, Cl^- or CO_3^{2-} or they may be complexed with organic ligands such as amines, humic or fulvic acids and proteins **[Ryan et al., (2012)]**. Knowledge about metal speciation i.e. the different physical or chemical forms in which a metal occurs is widely regarded as crucial to the understanding and prediction of metal behavior and impact in any environmental system **[Amigo et al., (2012) & Cornelis et al., (2005)]**. The chemical speciation of a metal depends upon its oxidation state and its interactions with other components in the system as well as on other parameters including pH, redox potential, ionic strength, salinity, alkalinity and concentration of metal ions in aqueous solution **[Adekunle et al., (2014)]**. Changes in these variables can result in transformation of the metal's chemical form and can alter its availability and toxicity.

Modern industry, mining and scientific research are, to a large degree, responsible for contamination of the environment. Among the toxic substances reaching hazardous levels are heavy metals. Adsorption-desorption of heavy metals from waste water is becoming increasingly important as society realizes the environmental impact of these persistent and toxic contaminants as well as the necessity for recycling and conservation of essential metals. Increasingly stricter discharge limits on heavy metals have also accelerated the search for highly efficient yet economically attractive treatment methods for their recovery **[Visa and Chelaru, (2014) & Hashim and Chu, (2004)]**. When assessing pollution, a distinction must be made between natural sources of metals and those 'unearthed' and released into the environment through human activity (anthropogenic source).

Metals in minerals and rocks are generally harmless, becoming potentially toxic only when they dissolve in water. They can enter the environment through natural weathering of rocks, leaching of soils and vegetation and through volcanic activity. Most of the metal load is transported by water in a dissolved or particulate state, and reaches the ocean via rivers or land runoff.

Humans, on the other hand, contribute metals to the environment during a variety of activities including mining and ore processing activities, burning fossil fuels (e.g. coal-fired power generation) and disposing of industrial and research waste (e.g. leather, tanning , dyeing, printing, mining and metallurgical engineering, electroplating, semiconductor, aerospace, battery manufacturing processes, etc.) **[Gad et al., (2014) & Bradl , (2005)]**.

1.2.1. Impact of Metals on the Environment.

Depending on the angle of interest and the environmental impacts, metals can be divided into four major categories: (1) Toxic heavy metals, (2) strategic metals, (3) precious metals, and (4) radionuclides **[Wang and Chen, (2006)]**.

In terms of environmental threat it is mainly categories 1 and 4 that are of interest for removal from the environment. According to **Duffus (2001)**, the term “heavy metal” is often used in the literature as a group name for metals and semi-metals (metalloids) that have been associated with contamination and potential toxicity. However, the term has never been defined by any authoritative body such as IUPAC and research shows that the term “heavy metals” has been used inconsistently. Some authors define it in relation to density or specific gravity **[Scott and Mercer, (1996)]**, others define it in terms of atomic mass **[Rand et al., (1995)]** or atomic number **[Lyman, (1996)]** while some definitions have no clear basis except toxicity **[Crompton, (1997)]**. This term is misleading because they are not all “heavy” in terms of atomic weight, density, or atomic number and some are not even entirely metallic in character e.g. arsenic (metalloid).

1.3. Sources of Organic Pollutants in the Environment.

Organic pollution is the term used when large quantities of organic compounds are release to the environment. It originates from domestic sewage, urban run-off, industrial effluents and agriculture wastewater, sewage treatment plants and industry including food processing, pulp and paper making, agriculture and aquaculture. During the decomposition process of organic pollutants the dissolved oxygen in the receiving water may be consumed at a greater rate than it can be replenished, causing oxygen depletion and having severe consequences for the stream biota. Wastewater with organic pollutants contains large quantities of suspended solids which reduce the light available to photosynthetic organisms and, on settling out, alter the characteristics of the river bed, rendering it an unsuitable habitat for many invertebrates. Organic pollutants include pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals, proteins and carbohydrates [**Sharma et al., (2014)**].

Toxic organic pollutants cause several environmental problems to our environment. The most common organic pollutants named persistent organic pollutants (POPs). POPs are compounds of great concern due to their toxicity, persistence, long-range transport ability [**Putraa et al., (2009)**] and bioaccumulation in animals **[Burkhard and Lukazewycz, (2008)]**, travel long distances and persist in living organisms. POPs are carbon-based chemical compounds and mixtures (twelve pollutants) that include industrial chemicals such as phenols, pesticides, herbicides, aliphatic and aromatic hydrocarbons, and their halogen derivatives, dyes, surfactants, organic sulfur compounds, ethers, amines, and nitro compounds. More than 1500 different organic compounds are suspected to be present in drinking waters. Many of these compounds have been or continue to be used in large quantities and due to their environmental persistence, have the ability to bioaccumulate and biomagnify [**Kurniawan and Lo, (2009)**].

1.4. Removal of Contaminants from Wastes.

As previously mentioned , the removal of heavy metal ions or radionuclide from wastes before release to the environment is extremely important. Industrial and research wastewaters containing heavy metals and organic pollutants require efficient and cost effective treatment **[Manzoor et al., (2013)]** to remove these contaminants.

The discharged effluents are loaded with numerous pollutants like toxic metals, dyes suspended solids, microbial pathogens and parasites, biodegradable, volatile and recalcitrant organic compounds **[Patel and Vashi, (2010)]**. The effluents from industry and research change the biological life of rivers and lakes **[Visa and Duta, (2013a)]**. Wastewaters with a load like this cause damages to the environment by creating problems to the groundwater resources **[Visa et al., (2011)]**. These wastewaters are highly colored, have a fluctuating pH, high temperature and chemical oxygen demand, large amounts of suspended oils.

The main problem related to the organic pollutants (which are stable to light and are not biodegradable) **[Sljivic et al., (2009)]** in wastewater is the color which decreases the light permeability thus causing a negative effect on photosynthesis [**Visa and Duta, (2013b)**]. Decreasing permeability of light, the amount of oxygen decomposed lead to extinction of some living beings and to restriction of the reuse of water. The heavy metals from the organic pollutants structure represent also a problem. Metals are present in organic pollutants because they are used as catalysts during the manufacture of some organic compounds and can be present as impurities or exist into dye molecule, forming an integral structural element **[Visa, (2012)]**.

The presence of heavy metals in wastewater is unwanted due to their solubility in water thus can be absorbed by living organisms and like this they enter in the food chain and start to accumulate in the human body. Ingestion of heavy metals beyond the permitted concentration can cause serious health disorders **[Martens et al., (2011) & Ling et al., (2011)].**

Conventional methods of heavy metal and organic pollutants removal include chemical precipitation, electrochemical techniques, reverse osmosis, evaporation, oxidation, biodegradation and ion-exchange **[Ahluwalia and Goyal, (2007)]**. However, these processes may be ineffective or extremely expensive especially when the pollutants in wastes solution are present in the range of 1–100 mg/l **[Lodeiro et al., (2006)]**. These techniques may also cause secondary environmental problems due to the creation of metal-bearing sludges which are extremely difficult to dispose of. For these reasons, alternative technologies that are practical, efficient and cost effective at low pollutants concentrations are being investigated.

Table (1.1) summarizes the merits and demerits of the different technologies have been used till date to remove pollutants from aqueous wastes. The long list of demerits against each process leads to the search for new low cost and effective technology. Recently biosorption process has been emerging as the most prominent alternative technology.

Table (1.1): Merits and demerits of different treatment technologies for the biosorption of heavy metals and organic pollutants from aqueous systems.

Technology	Merits	Demerits	Reference
Membrane Filtration	Low solid waste generation Low chemical consumption Small space requirement Metal selective method	Valid at room temperature. At elevated temperature membrane deterioration can be rapid Various types of polyamide TFM exhibit significant differences in stability at low pH High initial capital cost High maintenance and operation costs Membrane fouling and limited flow rates	**[Barakat and Schmidt, (2010)]**
Electrochemical Treatment	Applicable for the treatment of very toxic wastes. Valid at room temperature and atmospheric pressure. Run by electricity and easy to operate.	High initial capital, maintenance and operation cost Needs continuous supply of electricity	**[Bilal et al., (2013)]**
Flotation	Metal selective Low retention times Removal of small particles	High initial capital, maintenance and operation cost	**[Sudilovskiy et al.,(2008)]**
Coagulation–Flocculation	Bacterial inactivation capability Good sludge settling and dewatering characteristics	Much chemical consumption Large volume sludge	**[Kurniawan et al., (2006)]**
Chemical Precipitation	Process simplicity Applicable to different metals Low capital cost	Large volume sludge formation High sludge disposal and maintenance cost	**[Fu and Wang , (2011)]**
Ion exchange	Metal selective Limited pH tolerance High regeneration capacity	High initial capital and maintenance cost	**[Alyüz and Veli.,(2009)]**
Adsorption	Wide variety of target pollutants High capacity and fast kinetics Possibly selective depending on adsorbent.	Performance depends on type of adsorbent Needs chemical modification to improve its sorption capacity	**[Banerjee et al., (2012)]**

The most widely used method for removing pollutants is coagulation and precipitation. Heavy metals, for example, can be precipitated as insoluble hydroxide at high pH or sometimes as sulfides. A major problem with this type of treatment is the disposal of the precipitated waste. Another weak point is that in most time the precipitation itself cannot reduce the contaminant far enough to meet current water-quality standards. Ion exchange treatment is the second most widely used method for metal removal. This method does not present a sludge disposal problem and has the advantage of reclamation of metals. It can reduce the metal ion concentration to a very low level. However, ion exchange does not appear to be practicable to waste water treatment from a cost stand point **[Bilal et al., (2013)]**. Adsorption with activated carbon can also be highly efficient for the removal of numerous trace elements from water, but the high cost of commercial activated carbon inhibits its large-scale use as adsorbent **[Banerjee et al., (2012)]**. Then, the need for effective and economical removal of unwanted materials resulted in a research for unconventional methods and materials that might be useful in this field.

The trace elements and organic pollutants in water are so numerous that only a combination of various treatment processes can provide the effluent quality desired and only a non-specific process such as adsorption appears appropriate for their removal **[Nguyen et al, (2013)]**. Scientists have, therefore, centered their interest on adsorbents research in recent years. The utilization of agricultural by product materials is increasingly becoming of vital concern because these materials represent unused resources and, in many cases, present serious disposal problems. During the past decade, a great deal of attention has been given to methods of converting these materials into useful products. Agricultural by–products is one of the most appealing materials for removing pollutants, such as, dyes, salts and heavy metals, etc. from water and waste water [**Sharma et al., (2014)**].

1.5. Adsorption Technique.

Adsorption is a separation process in which certain components of the fluid phase are transferred to the surface of the solid adsorbents. When a solid surface is exposed to a fluid phase, the molecules of organic pollutants or metal ions, from the bulk of the fluid phase, have tendency to accumulate or concentrate at the surface of a solid. The phenomenon of the enrichment of chemical substances at the surface of a solid is called ‘adsorption’. All adsorption performance processes depend on solid-liquid equilibrium and on mass transfer rates **[Hui et al., 2009]**. If the mass transfer is in opposite direction then it is called as ‘Desorption’. Most adsorbents are highly porous materials, and adsorption takes place primarily on the walls of the pores or at the specific sites inside the particle. Separation occurs because differences in molecular weight, shape, or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules or hydrated ions. The overall rate of adsorption is controlled by the rate of diffusion of solute within the capillary pores of the adsorbent and varies with square root of the contact time with the adsorbent. The adsorption operation can be batch, semi-batch and continuous.

1.5.1. Types of Adsorption:

At molecular or ions level, adsorption is due to attractive interactions between a surface and the species being adsorbed. attractive interactions may be due to physical or chemical force .

1.5.1.1. Physical Adsorption.

It is a result of intermolecular forces of attraction between molecules of the adsorbate and the adsorbent. In this case the molecular attractive forces that retain the adsorbate on the surface are purely physical are called Vander Walls forces. This is a readily reversible phenomenon. The energy of interaction between the adsorbate and adsorbent has the same order of magnitudes as, but is usually greater than the energy of condensation of the adsorptive. Therefore, no activation energy is needed.

1.5.1.2. Chemical Adsorption.

It is a result of chemical interaction between the solid and the adsorbed substance. It is also called activated adsorption. It is irreversible. It is particularly important in catalysis. Therefore, the energy of chemisorptions considered like chemical reaction. It may be exothermic or endothermic processes ranging from very small to very large magnitudes. The elementary step in chemisoption often involves large activation energy (Activated adsorption).

1.5.2. Biosorption.

Biosorption is a relatively new process that has proven very promising in the treatment of contaminants from aqueous effluents using low-cost adsorbents derived from agricultural materials **[Gad et al., (2013) & Park et al., (2006) & Shin and Rowell, (2005) & Pagnanelli et al., (2003)]**. The major advantages of biosorption compared with conventional treatment methods are: local available adsorbent, renewable, low cost, high efficiency and minimization of chemical and/or biological sludge, regeneration of biosorbent, no additional nutrient requirement, and possibility of metal recovery. Agricultural residues are lignocellulosic substances which contain three main structural components: hemicelluloses, cellulose and lignin **[Ahmed et al., (2014) & Guo et al., (2009)]**.

1.5.3. Factors Affecting Adsorption Process:

Many factors influence the rate at which adsorption reactions occur and the extent to which a particular material can be adsorbed. Some of the more important factors will be discussed blow.

1.5.3.1. Effect of Agitation Rate.

The adsorption capacity of metals on adsorbent depends on the agitation rate. Adsorption increases, although not in direct proportion, by increasing the agitation speed. It may be thought that as the speed increases the particle of adsorbent spreads through the solution and resistance to mass transfer from bulk to the adsorbent phase decreases, resulting in increased adsorption rate. **Pimentel et al., (2008)** noted that by increasing the agitation speed the percent adsorption increases for all of the solutes but at different extents. They attributed that due to the difference in molecular size.

1.5.3.2. Effect of Particle Size.

The adsorption capacity of adsorbent very much depends on the surface activities, in other words the specific surface area available for solute surface interaction, which is accessible to the solute. This phenomenon is expected, as the size of the particle decreases, surface area of the adsorbent increases, thereby the number of active sites on the adsorbent are better exposed to the adsorbate **[Yadla et al. , (2012)]**.

1.5.3.3. Effect of Interfering Ions.

1.5.3.3.1. Presence of Cations.

Other sorbable ions in the solution may compete with the metal ion or organic compound of interest for sorption sites. The binding of this metal ion is then decreased. The amount of inhibition depends on the binding strength of the respective ions to the biomass **[Naja et al., (2010)]**.

1.5.3.3.2. Presence of Anions.

Theoretically, the presence of ligands (at levels which do not cause precipitation) can lead to **[Chiban et al., (2012)]**:

(1) formation of complexes that have a higher affinity than the free metal ions to the sorbent, i.e. an enhancement of sorption; (2) formation of complexes that have a lower affinity than the free metal ions to the sorbent, i.e. a reduction of sorption; (3) interaction of anions with the biomass, changing the state of the active sites such that the binding is either enhanced or reduced.

1.5.3.4. Effect of Contact Time and Initial Concentration.

Adsorption of metals or organic pollutants on adsorbent depends on both the initial concentration of metal ions or organic pollutants and the contact time. It was reported that the initial concentration of adsorbate has a strong effect on the adsorption capacity of adsorbent. Generally adsorption capacity increases with increasing initial concentration of the solute **[Manas, (2011) & Ofomaja et al., (2010)]**.

The effect of contact time on the removal of adsorbate to reach equilibrium varies depending on the type of solute. As the time increases, more amounts of adsorbate gets adsorbs onto the surface of the adsorbent and surface area available decreases. The adsorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the capacity of the adsorbent is exhausted **[Yadla et al., (2012)]**.

1.5.3.5. Effect of pH.

Adsorption of metal ions or organic pollutants from waste water is influenced by the pH of solution. pH influences the surface charge of the adsorbent, the degree of ionization and the species of adsorbate . So pH is an important factor controlling the process of adsorption **[Yadla et al., (2012)]**. It is commonly agreed that the sorption of metal cations (e.g. Cd, Cu, Zn, Pb, Ni, Mn, Al, Co) increases with increasing pH (blow the precipitate limits) **[Huang et al., (2014a) & Chong et al., (2013) & Kılıc et al., (2013)]**. Only those metal ions which can occur as negatively charged complexes or that have a strong character (i.e. tendency to form strong covalent bonds) such as Ag, Hg or Au (e.g. as tetrachloroaureate), may show either a decrease in binding with increasing pH or may have no significant pH effect at all

The pH of a medium will control the magnitude of electrostatic charges which are impacted by the ionized organic molecules. As a result the rate of adsorption will vary with the pH of an aqueous medium [**Chowdhury et al., (2011a)**]. The effect of pH solution on the adsorption process can be studied by preparation of adsorbent–adsorbate solution with fixed adsorbent dose and organic molecules concentration but with different pH by adding NaOH (0.1N) or HCl (0.1N) solutions and then shaken until equilibrium. Generally, at low pH solution, the percentage of organic molecules removal will decrease for cationic organic molecules adsorption, while for anionic organic molecules the percentage of organic molecules removal will increase.

In contrast, at a high pH solution the percentage of organic molecules removal will increase for cationic organic molecules adsorption and decrease for anionic organic molecules adsorption. At high pH solution, the positive charge at the solution interface decreases and the adsorbent surface appears negatively charged **[Özcan et al., (2007)]**. As a result, the cationic organic molecules adsorption increases and anionic organic molecules adsorption shows a decrease. In contrast, at a low pH solution, the positive charge on the solution interface will increase and the adsorbent surface appears positive charged, which results in an increase in anionic organic molecules adsorption and a decrease in cationic organic molecules adsorption.

Point of zero charge (pH_{pzc}) is an important factor that determines the linear range of pH sensitivity and then indicates the type of surface active centers and the adsorption ability of the surface [**Yagub et al., (2012)]**. Many researchers studied the pH_{pzc} of adsorbents that prepared from agricultural solid wastes in order to better understand of adsorption mechanism. Cationic organic molecules adsorption is favored at $pH > pH_{pzc}$, due to presence of functional groups such as OH^{-}, COO^{-} groups. Anionic organic molecules adsorption is favored at $pH < pH_{pzc}$ where the surface becomes positively charged [**Yagub et al., (2014)]**.

1.5.3.7. Effect of Temperature.

Effect of temperature is another significant physico-chemical process parameter because temperature will change the adsorption capacity of the adsorbent [**Yagub et al., (2014)]**. If the amount of adsorption increases with increasing temperature then the adsorption is an endothermic process. This may be due to increasing mobility of the adsorbate and an increase in the number of active sites for the adsorption with increasing temperature. Whereas the decrease of adsorption capacity with increasing temperature indicates that the adsorption is an exothermic process. This may be due to increasing temperature decrease the adsorptive forces between the adsorbate and the active sites on the adsorbent surface as a result of decreasing the amount of adsorption **[Salleh et al., (2011) & Kumar et al, (2012)]**.

1.6. Raw Materials.

Several raw materials are considered as precursors for activated carbon. The quality of the resulting activated carbon is considerably influenced by characteristics of the raw material. Although the activation procedure employed mainly determines the chemical nature of the surface functional groups and the surface area of the resultant product, the structure of the pores and the pore size distributions are largely predetermined by the nature of the starting material. Any carbonaceous cheap substance with a high carbon and low ash content can be used as a raw material for the production of activated carbon, In recent years many author used for this purpose agricultural by–products, such as rice husk **[Cope et al., (2014) & Lin et al., (2013)]**, sawdust **[Shaaban et al., (2014) & Božić et al., (2013)],** fruit stone **[Abbas et al., (2014)]**, hazelnut **[Guney et al., (2013)]**, peanut shell **[Ugwekar and Lakhawat, (2012) & Oliveira et al., (2010)]**, pine bark **[Khokhotva and Waara (2010)]**, wheat straw **[Zhao et al., (2014)]** and rice waste **[Gad et al., (2009)]**. Since the manufacturing process involves the removal of volatile matter, the economic relationship between price, availability and quality of raw materials on one side and volatile content on the other side, is an important one.

1.6.1. Sawdust.

Many studies present a brief review on the role of sawdust in the removal of unwanted materials from waters. Application and comparison of different methods and affecting factors on adsorption are discussed in the literature. Not only sawdust is abundant, but also it is actually an efficient adsorbent that is effective to many types of pollutants, such as, dyes, oil, salts, heavy metals, etc. Many agricultural by products are little or no economic value, and some, such as sawdust, which are available in large quantities in lumber mills, are often present a disposal problem. The use of sawdust for removing pollutants would benefit both the environment and wood agriculture: contaminated streams would be cleaned, and a new market would be opened for the sawdust **[Gad et al., (2013)]**.

Based on the behavior of heavy metal adsorption on sawdust, scientists have speculated that ion exchange and hydrogen bounding may be the principal mechanism for the removal of heavy metals **[Kaczala et al., (2009)]**. There are a great deal of facts to support this speculation, including the components and complexing properties of the sawdust, the properties of heavy metals and the adsorption behavior, such as the effect of pH of the aqueous media. It has long been recognized that heavy metal cations are readily form complexes with O-, N-, S-, or P-containing functional groups in polymer materials **[Shukla et al., (2002)]**. Although a detailed characterization of the nature of the binding sites on different sawdust materials was not conducted. The cell walls of sawdust mainly consist of cellulose and lignin, and many hydroxyl groups, such as tannins or other phenolic compounds **[Pietrzak., (2010)]**. All those components are active ion exchange compounds. Lignin, the third major component of the wood cell wall, is a polymer material. Lignin molecule is built up from the phenylpropane nucleus, i.e. an aromatic ring with a three-carbon side chain. Vanillin and syringaldehyde are the two of other basic structural units of lignin molecule **[Kaczala et al., (2009)]**. The lignin content of hardwoods is usually in the range of 18–25%, whereas that of softwoods varies between 25 and 35% **[Djilali et al., (2012)]**. However, tropical hardwoods can exceed the lignin content of many types of softwood. Tannins are complex polyhydric phenols which are soluble in water and have the property of precipitating protein (e.g. gelatin) from solution and converting hides into leather. They occur chiefly in hardwoods, and are also present in many barks, including softwoods barks, as well as in the leaves and fruits of some trees.

The heavy metal cations are completely released under circumstances of extreme acidic conditions **[Hashim et al., (2011)]**. In most cases, the percentage of adsorption of metal ions increased with an increase in pH up to a certain value and then decreased with further increase of pH. Due to different properties of various heavy metal ions and different sawdust materials, the maximum adsorption took place in a slightly different pH range for different metals. In a certain pH range, for one specific divalent heavy metal there may be a number of species present in solution, such as M, MOH^+, $M(OH)_2$, etc. At low pH, the