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Treatability Study of Low Cost Adsorbents for Heavy Metal Removal from Electro Plating Industrial Effluent: A Review

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1. Abstract: Electroplating Industrial Wastewater contains heavy metals, causes serious environmental problems. Adsorption process is one of the promising method for the treatment of the industrial effluent. This paper deals with the fundamental principles of adsorption and its application in treatment of industrial effluent. The feasibility of adsorption process mainly depends upon the type of adsorbents used. Number of adsorbents with their treatability studies are found in literature still the choice of low cost adsorbents is an important parameter for application of adsorption process in industry.

Keywords: *Adsorption, Heavy metals, Electroplating wastewater, Heavy metal Removal, Low Cost adsorbent.*

2. Introduction

The production of heavy metals increased rapidly since the industrial revolution took place in the present era. Heavy metals cause direct toxicity to humans and other living beings due to their presence in aquatic environment beyond the permissible limits. The industry of metal finishing and electroplating units are one of the major sources of pollutants which contribute greatly to the pollution load of the receiving water bodies and therefore increases the environmental risks.

A major challenge for the electroplating industry is finding solutions that equate to positive environmental and economic aspects regarding the treatment of their effluent. Due to the discharge of large amounts of metal-contaminated wastewater, industries bearing heavy metals, such as Cd, Cr, Cu, Ni, As, Pb, and Zn, are the most hazardous among the chemical-intensive industries. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. The heavy metals even at relatively low concentrations are toxic to biological processes and thus prevent the effective degradation of organic wastes.

Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment. Heavy metals removal from electroplating industrial effluent can be achieved by Adsorption. Adsorption is one of the promising processes for the removal of heavy metals from waste water. Adsorption is suitable even when the metal ions are present in concentration as low as 1mg/l [1].The adsorbents may be of mineral, organic or biological origin, zeolites, industrial by-products, agricultural wastes, biomass, and polymeric materials. This article present an overview of various Adsorption treatments for removal of heavy metals from wastewater of Electroplating industrial effluent.

3. Adsorption of single and multi-metal ions

The study of the time dependence of adsorption on solid surface (adsorption kinetic) helps in predicting the progress of adsorption in industrial application, however the determination of the adsorption mechanism is also important for design purposes. In a solid-liquid adsorption process, the transfer of the adsorbate is controlled by either boundary layer diffusion (external mass transfer) or intra-particle diffusion (mass transfer through the pores), or by the both [2].

It is generally accepted that the adsorption dynamics consists of three consecutive steps:

- Transport of adsorbate from the bulk solution to the external surface of the adsorbent

  by diffusion through the liquid boundary layer.

- Diffusion of the adsorbate from the external surface and into the pores of the adsorbent.

- Adsorption of the adsorbate on the active sites on the internal surface of the pores.

The last step, adsorption, is usually very rapid in comparison to the first two steps. Therefore, the overall rate of adsorption is controlled by either film or intra-particle diffusion, or a combination of both. Many studies have shown that the boundary layer diffusion is the rate controlling step in systems characterized by dilute concentrations of adsorbate, poor mixing, and small particle size of adsorbent [3].

Adsorption is an important process that describes the interaction between adsorbent and metal ion to develop design model for wastewater industrial treatment. The applicability of relationship between the experimental adsorption capacities and the metal ions concentrations (adsorption isotherm) have been widely used by the Langmuir and Freundlich models.

3.1 Langmuir model

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed metal. The Langmuir adsorption isotherm model is successfully used to explain the metal ions adsorption from aqueous solutions [4]. The expression of the Langmuir model is given by Eq. (1),

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$$q_e = \frac{q_{max} * K_L * C_e}{1 + K_L C_e} \qquad (1)$$

and the linearized Lagmuir isotherm equation can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{\max} + \left(\frac{1}{q_{\max} K_L}\right)\left(\frac{1}{C_e}\right)} \qquad (2)$$

3.2 Freundlich model

The Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption (heterogeneous surface). This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption and is given by Freundlich, (1906). The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as:

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

and linearized Freundlich isotherm equation can be expressed as:

$$\log q_e = log K_F + \frac{1}{n \log C_e} \qquad (4)$$

4. Adsorbent

There are many types of adsorbents; Earth's forests and plants, ocean and freshwater plankton, algae and fish, all living creatures, that including animals are all "biomass adsorbents". There are various types of Adsorbents are used in Electroplating Industry for removal of heavy metals according to requirement and availability.

4.1 Inorganic adsorbents:

They may be natural minerals, ores, clay and waste materials from various industries like fly ash, metallurgical solid wastes like bauxite red muds etc. Minerals like Montmorillonite have been used to remove Pb(II) and Cd(II)[5], Kaolinite was used to accumulate Zn(II)[6], Illite to remove Pb(II)[7], Bentonite was used to adsorb Cr(VI)[8], Activated red mud was used to trap Ni(II) and Cr(II)[9].

4.2 Organic adsorbents:

A large number of waste materials of organic origin like dead leaves of trees, bark, roots, seed shells, oil cakes and saw dust from various plants in the form of powder have been utilized for the removal of heavy metals and their adsorption properties have been explored. In addition to these adsorbents wool, albumin, feathers, waste rubber, hair, used tea leaves, bagasse, rice husk etc. have also been used as organic non-conventional adsorbents [10]. Exhausted coffee was used to remove Cd(II) and Cr(VI)[11], Formaldehyde-polymerized peanut skin was used to remove Cd(II) and Pb(II) removal[12], Untreated sawdust was used to remove Cr(VI) from tannery effluents[13], Leaf mould was used to remove Cr (VI)[14]. Activated carbon from hazelnut shells was used for the adsorption of Co (II) from aqueous solution [15]. Activated carbon from coconut coir pith was used for the removal for Cd(II) from aqueous solution [16].

4.3 Biosorption

Biosorption has advantages compared to the conventional techniques [17]. Some of them are Cheap; the cost of the biosorbent is low since they often are made from abundant or waste material.

They included biomass of algae fungi, and peat moss etc. The advantages of biosorption are low cost, high efficiency of heavy metal removal from dilute solutions, regeneration and possible metal recovery. Filamentous fungi have been found to possess a high potential of accumulating Cu, Ni, Co and uranium in aqueous solutions [18]. It has been reported that the biomass of brown algae of the sargassum family possesses a metal binding capacity superior to other organic and inorganic sorbents [19, 20]. Several researchers have concluded that the major mechanism of heavy metal uptake by algae [21]. However, direct application of living fungal cells as biosorbents for heavy metals is unfavourable due to the resistance of living cells to metal ions. Sargassum seaweed was used to accumulate Cd and Cu [22], C. Vulgaris was used for the removal of Cd(II)[23], Sphagnum moss peat was used to remove Cu(II) and Ni(II) from aq. Medium [24, 25].

Bark and other tannin – rich materials

Timber industry generates bark as a by-product that is effective because of its high tannin content. The polyhydroxy polyphenol groups of tannin are thought the active species in the adsorption process. Ion exchange takes place as metal cations displace adjacent phenolic hydroxyl groups, forming a chelate [26, 27].

Chitosan

Among various biosorbents, chitin is the second most abundant natural biopolymers after cellulose. However, more important than chitin is chitosan, which has a molecular structure similar to cellulose. Presently, chitosan is attracting an increasing amount of research interest, as it is an effective scavenger for heavy metals. Chitosan is produced by alkaline N-deacetylation of chitin, which is widely found in the exoskeleton of shellfish and crustaceans. It was estimated that chitosan could be produced from fish and crustaceans [28].

Zeolites

Basically zeolites are naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms. During 1970s, natural zeolites gained a significant interest, due to their ion-exchange capability to preferentially remove unwanted heavy metals such as strontium and cesium [29].

Clay

It is widely known that there are three basic species of clay: smectites (such as montmorillonite), kaolinite, and micas; out of which montmorillonite has the highest cation exchange capacity and its current market price is considered to be 20 times cheaper than that of activated carbon [30].

Peat moss

Peat moss, a complex soil material containing lignin and cellulose as major constituents, is a natural substance widely available and abundant, not only in Europe (British and Ireland), but also in the US. Peat moss has a large surface area (>200 40 m2/g) and is highly porous so that it can be used to bind heavy metals. Peat moss is a relatively inexpensive material and commercially sold at US$ 0.023/kg in the US [31].

4.4 Low cost adsorbents

The disadvantages of using microorganisms can be overcome by using low cost adsorbents. In general, a sorbent can be assumed to be “low cost” if it requires little processing and is abundant in nature, or is a byproduct or waste material from another industry, which has lost its economic or further processing values.

The idea of using various agricultural products and byproducts for the removal of heavy metals from solution has been investigated by number of authors. Friedman and Waiss, (1972), Randall et al. (1974) and Henderson et al. (1977) have investigated the efficiency of number of different organic waste materials as sorbents for heavy metals [32].

Various low cost adsorbents have been studied for the removal and recovery of toxic metals like Cr, Ni, Cu, Cd, Zn, Pb etc.

Phosphate treated saw dust showed remarkable increase in sorption capacity of Cr (VI) as compared to untreated sawdust. The adsorption process was found to be pH dependent. Total (100%) adsorption of Cr (VI) was observed in the pH range < 2 for the initial Cr (VI) Concentration of 8-50 mg/l. The effect of various adsorbent doses at pH 2 confirmed Langmuir adsorption isotherms. 100% removal of Cr (VI) from synthetic waste as well as electroplating waste containing 50 mg/1 Cr (VI) was achieved by batch as well as by column processes. The adsorbed Cr (VI) on phosphate treated saw dust was also recovered (87%) using 0.01 M sodium hydroxide. The results obtained from column as well as by batch processes were found to be almost identical [33].

Mangifera indica (Mango) seed and seed shell powders were studied for their possible application in the removal of Cu (II) from wastewater. The adsorption of Cu (II) on the powder of Mango seeds and seed shell was found maximum at pH 6 and followed Freundlich type adsorption Isotherm The overall process was spontaneous and exothermic in nature. The total adsorption on each adsorbent increased with the increase in temperature between 30-50 ^{0}C and then decreased up to 60 ^{0}C. More over, it was found that the seed shell of *Mangifera indica* had higher sorption capacity than that of the seed powder for Cu (II). The presence of Ca (II), Mg (II), and K (I) decreased the percent adsorption of Cu (II) on these adsorbents [34].

Sawdust, an inexpensive material, has been utilized as an adsorbent for the removal of Cu (II) from wastewater. The effect of contact time, pH concentration, temperature, dose and particle size of the adsorbent and salinity on the removal of Cu (II) has been studied. The equilibrium nature of copper (II) adsorption at different temperatures (30-50 ^{0}C) has been described by the Freundlich and Langmuir isotherms and a tentative mechanism has also been proposed. The thermodynamic parameters such as free energy, entropy and enthalpy changes for the adsorption of Cu (II) have also been computed and discussed. The Kinetics and the factors controlling the adsorption process have also been studied. In order to widen the applicability of the removal technique, the optimized method was applied for the removal of Cu (II) from Ganga river water. The removal efficiency was found to be 63%. In the river water sample, the adsorption capacity was slightly decreased, probably due to the presence of other major cations like calcium and magnesium. The process was found to be economically feasible and easy to carry out [35].

The fruit peel of orange (Citrus reticulate) is a low cost adsorbent, which is abundantly available in India as waste material. The ability of fruit peels of orange to remove Zn(II), Ni(II), Cu(II), and Pb(II) and studied. The adsorption was found in the order Ni(II)>Cu(II)>Pb(II)>Zn(II). The extent of removal of Ni(II) was found to be dependent on sorbent dose, initial concentration, pH and temperature. The adsorption followed first order Kinetics. The process was found to be endothermic showing monolayer adsorption of Ni (II) with a maximum adsorption of 96% at 50^0C for an initial concentration of 50 mg/l at pH 6. Thermodynamic parameters were also computed. Desorption was possible with 0.05 M HCl and was found to be 95.83% in Column and 76% in Batch process respectively. The spent adsorbent was regenerated and recycled thrice. The removal and recovery was also done in wastewater and found to be 89% and 93% respectively [36].

Adsorption behaviour of Ni(II), Zn(II), Cd(II) and Cr(VI) on untreated and phosphate treated ***rice husk (PRH)*** showed that adsorption of Ni(II) and Cd(II) was greater when phosphate treated rice husk was used. The thermodynamic parameters indicate that process is endothermic and spontaneous. The maximum adsorption occurs at pH 6.

The adsorption behavior of various heavy metals on ***mustard oil cake*** (MOC) was studied. The maximum adsorption of Cu (II) was observed followed by Zn(II), Cr(VI), Mn(II), Cd(II), Ni(II) and Pb(II). The adsorption of Cu (II) was found to be dependent on initial concentration of solution, pH, adsorbent dose, temperature and contact time.

5. Conclusion

This aspect needs to be investigated further in order to promote large-scale use of non-conventional adsorbents. Most of the adsorption processes were modeled by Langmuir and Freundlich isotherms. If low-cost adsorbents perform well in removing heavy metals at low cost, they can be adopted and widely used in industries not only to minimize cost inefficiency, but also improve profitability. In addition, if the alternative adsorbents mentioned previously are found highly efficient for heavy metal removal, not only the industries, but the living organisms and the surrounding environment will be also benefited from the decrease or elimination of potential toxicity due to the heavy metals. Thus, the use of low-cost adsorbents may contribute to the sustainability of the surrounding environment. Undoubtedly low-cost adsorbents offer a lot of promising benefits for commercial purpose in the future.

List of Notations and Abbreviations

q = Amount of adsorbate adsorbed at equilibrium time t (mg of adsorbate / gram of adsorbent)

q_e = Amount of adsorbate adsorbed at equilibrium time (mg of adsorbate / gram of adsorbent)

q_{max} = Langmuir constant (adsorption capacity) (mg/g)

b = Langmuir constant (energy of adsorption) (L/mg)

RL= Equilibrium parameter

kf = Freundlich constant

n = Freundlich constant

C_{eq} = Adsorbate concentration in solution at equilibrium (mg/L)

k_{ad} = Lagergren adsorption rate constant (l/min)

BGH = Bengal gram husk

MCL = Maximum Contamination Limit in mg

TDH=Tur dal husk

TH =Tamarind husk

CH = Coffee husk

FG = Fast green

MB = Methylene blue

RB = Rhodamine B

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