International Journal of Research in Advent Technology, Vol.5, No.7, July 2017
E-ISSN: 2321-9637
Available online at www.ijrat.org

Removal of Metal from industrial effluent water by using Natural Adsorbent

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Abstract- Heavy metal such as Cu is major toxic pollutants with severe health effects on humans. Hence their removal is important. Conventional treatment methods of metal removal are often limited by their cost and ineffectiveness at low concentrations. Hence, this study chose Adsorption as the method for removal of Cu. The Cu (II) adsorption by adsorbents of pistachio shell were evaluated in batches. The purpose of the presented study was to evaluate the ability of agro-waste, pistachio shells to remove copper compounds from wastewater. The batch studies revealed that adsorption rate was influenced by factors like initial concentration of stock, adsorbent dosage and agitation effect. The choice of pistachio shell over other waste raw materials is due to its availability all year round and it is agro-waste, and its possession of advantageous properties such as carbon content, low ash content. The studies revealed that pistachio shells can be used as an economic adsorbent and ensures copper removal up-to approximately 70%.

Index Terms- Adsorption, copper metal, pistachio shell, batch adsorption.

1. INTRODUCTION

Mass transfer is the net movement of mass from one location, usually meaning stream, phase, fraction or component, to another. The heavy metals, having hazardous effects on health and environment, can be treated from wastewater by using various physiochemical methods. Adsorption, ion exchange, precipitation, ultrafiltration, reverse osmosis and electro dialysis are the most frequently preferred methods. Among them, adsorption receives considerable interest with the high efficiency in heavy metal removal.

The heavy metals, having hazardous effects on health and environment, can be treated from wastewater by using various physicochemical methods [1]. Adsorption, ion exchange, precipitation, ultrafiltration, reverse osmosis, and electro dialysis are the most frequently preferred methods [2]. Among them, adsorption receives considerable interest with the high efficiency in heavy metal removal. Adsorption has demonstrated its efficiency and economic feasibility as a wastewater treatment process compared to the other Purification and separation methods, and has gained importance in industrial applications. Activated carbon is the most commonly used adsorbent in the adsorption processes due to its high adsorption capacity, high surface area, and high degree of surface reactivity, whereas, it has a relatively high price, high operation costs, and problems with regeneration for the industrial scale applications [3]. This led to a search directed to developing low-cost and locally available adsorbent materials with maximum adsorption capacity [6], [8]. A wide variety of materials such as bark/tannin-rich materials, lignin, chitin, chitosan, dead biomass, sawdust, peat moss, Pistachio shells, modified wool, modified cotton, banana pith, rice husk, and leaves are being used as low cost alternatives to expensive adsorbents.

1.1 Industrial Wastewater and Heavy Metals

Heavy metals are commonly released in the wastewater from various industries. Electroplating and surface treatment practices leads to creation of considerable quantities of wastewaters containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver and titanium). Apart from this wastewater from leather, tannery, textile, pigment & dyes, paint, wood processing, petroleum refining industries and photographic film production contains significant amount of heavy metals [5]. These heavy metal ions are toxic to both human beings and animals. The toxic metals cause physical discomfort and sometimes life threatening illness and irreversible damage to vital body system. The metals get bio accumulated in the aquatic environment and tend to biomagnified along the food chain.

Thus, the organisms at higher trophic level are more susceptible to be affected by their toxicity. There are 20 metals which are almost persistent and cannot be degraded or destroyed. Mercury (Hg), lead (Pb), cadmium (Cd), chromium (Cr [VI]), Zinc (Zn), Arsenic (As), Nickel (Ni) etc., are toxic heavy metals from ecotoxicoligal point of view. The table below shows Maximum Contaminant Level (MCL) standards for some heavy metals established by USEPA [4]. These heavy metals can lead to serious effects such as stunted growth, damage to vital organs, damage to brain, cancer and in some cases death also. Health hazard related to heavy metal toxicity are not new. Human diseases like minamata, itai, fluorosis, Arsenicosis etc. are due to heavy metal ingestion above permissible levels.

Table 1: The MCL standards for the most hazardous heavy metals [4]

4Heavy metal	Toxicity	MCL (mg/L)
Arsenic (As)	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium (Cd)	Kidney damage, renal disorder, human carcinogen	0.01
Chromium (Cr)	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper (Cu)	Liver damage, Wilson disease, Insomnia	0.25
Nickel (Ni)	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc (Zn)	Depression, lethargy, neurological signs and increased thirst	0.80
Lead (Pb)	Damage the fetal brain, diseases of kidney, circulatory system and nervous system	0.006
Mercury (Hg)	Rheumatoid arthritis and disease of kidneys.	0.00003

1.2 Adsorption

As discussed earlier, adsorption has emerged out as effective, economical and ecofriendly treatment technique. It is a process potent enough to fulfill water reuse obligation and high effluent standards in the industries. Adsorption is basically a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions [4]. It is a partition process in which few components of the liquid phase are relocated to the surface of the solid adsorbents. All adsorption methods are reliant on solid-liquid equilibrium and on mass transfer rates. The adsorption procedure can be batch, semi-batch and continuous. At molecular level, adsorption is mainly due to attractive interfaces between a surface and the group being absorbed. Depending upon the types of intermolecular attractive forces adsorption could be of following types:

1.2.1 Physical adsorption

It is a general incident and occurs in any solid/liquid or solid/gas system. Physical adsorption is a process in which binding of adsorbate on the adsorbent surface is caused by van der Waals forces of attraction [9], [10]. The electronic structure of the atom or molecule is hardly disturbed upon physical adsorption. Van der Waals forces originate from the interactions between induced, permanent or transient electric dipoles. Physical adsorption can only be observed in the environment of low temperature and under appropriate conditions, gas phase molecules can form multilayer adsorption. Commercial adsorbents utilize physical adsorption for its surface binding.

1.2.2 Chemical adsorption

It is a kind of adsorption which involves a chemical reaction between the adsorbent and the adsorbate. The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds (Covalent, Ionic). Chemical adsorption is also referred as activated adsorption [11]**.** The adsorbate can form a monolayer. It is utilized in catalytic operations.
In general, the main steps involved in adsorption of pollutants on solid adsorbent are:
Transport of the pollutant from bulk solution to external surface of the adsorbent.
Internal mass transfer by pore diffusion from outer surface of adsorbent to the inner surface of porous structure.
Adsorption of adsorbate on the active sites of the pores of adsorbent.
The overall rate of adsorption is decided by either film formation or intra particle diffusion or both as the last step of adsorption are rapid as compared to the remaining two steps
.

1.3 Low Cost Adsorbents

The removal of heavy metals by using low cost adsorbent is found to be more encouraging in extended terms as there are several materials existing locally and profusely such as natural materials, agricultural wastes or industrial by-products which can be utilized as low-cost adsorbents [15]. To be commercially viable, an adsorbent should have high selectivity to facilitate quick separations, favorable transport and kinetic characteristics, thermal and chemical stability, and mechanical strength, resistance to fouling, regeneration capacity and low solubility in the liquid in contact. Adsorption process has several advantages over the conventional methods of heavy metal removal. Some of the gains of adsorption process are:

(I) Economical,
(II) Metal selectivity,
(III) Regenerative,
(IV) Absence of toxic sludge generation,
(V) Metal recovery and most importantly

Various low cost adsorbent derived from various natural as well as anthropogenic sources have been implemented for treatment of waste water contaminated with heavy metals.

2. MATERIALS AND METHOD

2.1. Instrumentation

Adsorbent utilization was carried out in the Laboratory of Physical Chemistry, and all the adsorption experiments were conducted in the Laboratory of Mass Transfer Operations for Chemical Engineering at Department of Chemical Engineering, Mumbai University. The instruments used for the adsorbent utilization and adsorption experiments were also available in the laboratories.

2.2. Adsorbent utilization

Pistachio shells are collected, washed with distilled water and dried under sunlight till moisture demolished, dried pistachio shells are then feeded to a crusher and sieved to get uniform size particle of size 0.151mm.

2.3 Stock solution of Cu (II)

The stock solution of Cu (II) of synthetic effluent was prepared from analytical grade by dissolving 4 g (±0.001) $CuSO_4.5H_2O$ (99% pure from Aldrich) in 1 L of distilled water in 1 L of Erlenmeyer flask.

2.4 Method of Estimation of Metal

Convectional titration method is used for estimation of Copper metal from effluent water. In which titration method involves:

1. Standardization of Sodium Thiosulphate
2. Estimation of Copper

2.5 Parameters Studied

- Agitation speed
  (Provided all other parameters like time of agitation, concentration of stock solution, adsorbent dosage are kept constant)
- Loading of adsorbent
  (Provided all other parameters like time of agitation, agitation speed, concentration of stock solution are kept constant)
- Concentration of stock solution
  (Provided all other parameters like time of agitation, agitation speed, adsorbent dosage are kept constant)

Percent removal of copper metal can be estimated by:

$$\% \text{ Removal} = \frac{(Ci-Cf)}{Ci}*100$$

C_i- Initial Concentration
C_f- Final Concentration

3. RESULT AND DISCUSSION

3.1 Effect of agitation speed

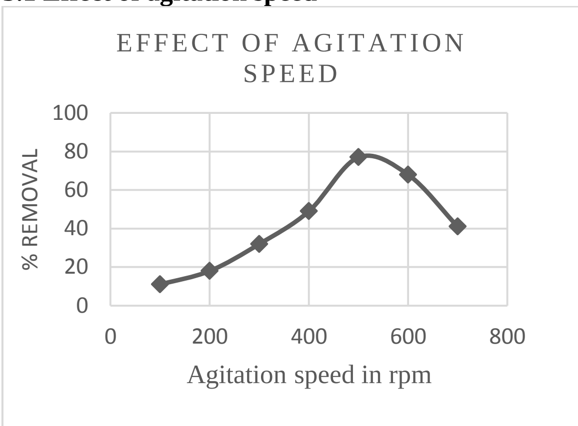

Fig 3.1 %Removal vs agitation speed in rpm (Effect of speed)

The effect of agitation speed on adsorption of copper was studied over the range of 0-700 rpm for 150 min with 50 ml of 50 mg/l copper and 1 g of pistachio shells. Fig.3.1 indicates that the percent adsorption increased with an increase of agitation speed and obtained a maximum 77% adsorption at near 500 rpm. At low and high speeds, the copper removal was lower than optimum. Low speed could not spread the particles properly in the water for providing active binding sites for adsorption of copper. It is resulted an accumulation of pistachio shell in the bottom of water and buried the active binding sites. On the other hand, the high speed vigorously spreading the particles of pistachio shell in the water and did not allow sufficient time to bind with copper ions.

3.2 Effect of adsorbent dosage

The result of adsorption experiments using different dosages i.e. 1, 2, 4, 6 and 8g of pistachio shell in 50 mg/l of copper metal stock solution were carried out. Fig. 3.2 shows the behavior of pistachio shell with increasing adsorbent dosage.

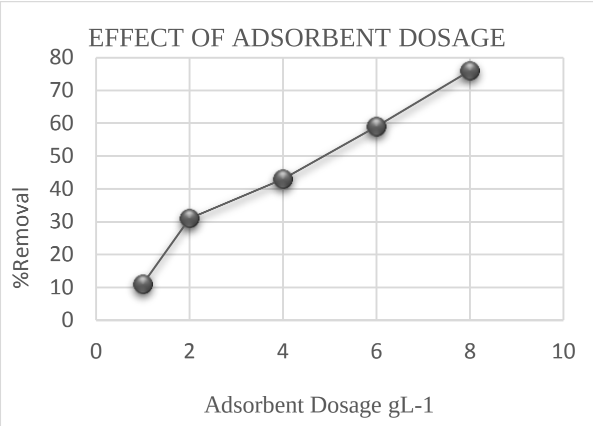

Fig 3.2 %removal vs adsorbent dosage gL^{-1} (Effect of adsorbent dosage)

It was observed that there is sharp increase in percentage removal with adsorbent dosage. It is apparent that the percentage removal of copper increases with increase in the dose of adsorbent due to the increased availability of the active sites/surface area for the adsorption of copper whereas at lower adsorbent dosage the number of copper molecules was relatively higher, compared to availability of adsorption sites/surface.

3.3 Effect of initial concentration:
The adsorption of copper ion on adsorbent depends on initial concentration. Copper ions have smaller hydrated radii (8.38 Å) and hence can enter into smaller pores on the surface of the adsorbent. Copper has high electro negativity (1.9) and standard reduction potential (0.341) which shows a trend with sorption capacity. At low concentrations, metal ions are easily adsorbed on vacant sites. As the metal ion concentration increases, the vacant sites are filled up and no further adsorption occurs due to saturation of vacant sites of adsorbent.

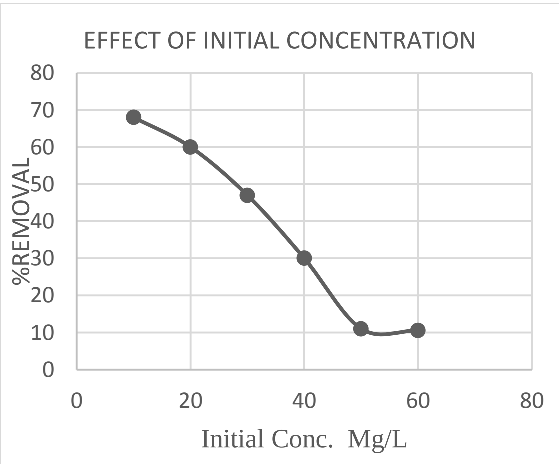

Fig 3.3 % Removal vs Initial concentration (effect of initial concentration)

Figure 3.3 shows the effect of metal ion concentration on percent removal of copper. As the metal ion concentration decreases, the percent removal increases.

4. CONCLUSION
The present study demonstrates that pistachio shell can be used as an effective and economical adsorbent for removal of copper ions from aqueous and industrial effluents. The adsorption process using this adsorbent can reduce the levels of toxic heavy metal ions from industrial effluents. Activation of the pistachio shell is not required hence, only drying and size reduction costs are considered.
The experimental studies shows that:

- Percentage removal of copper metal increases with decrease in initial conc. Of the solution.
- Percentage removal of copper metal increases with increase in adsorbent dosage.
- Percentage removal of copper metal increases with increase in agitation speed at first then after optimum agitation speed the percentage of removal of copper decreases with the further increase in agitation speed.

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