International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064

Performance of Low-Cost Bio Adsorbents for the Removal of Metal Ions – A Review

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Abstract: ***Adsorption is widely used to remove various pollutants from wastewater. The adsorption process by using the activated carbon is expensive and uneconomical from the operational cost aspect. So, the alternative adsorbents include agricultural waste, industrial solid waste, sludge from treatment plants, soils, marine waste, etc are used . The various parameters which affect the adsorption process in batch and column studies are being optimized. The results obtained are used to fit in the available adsorption isotherms for verifying their feasibility. This review article presents the information about the application of alternative bio adsorbents along with conventional activated carbon for the removal or reduction of metal ions from the water and wastewater.***

Keywords: Activated carbon, adsorption, adsorbent, agricultural waste, bio-adsorbent, isotherm

1. Introduction

The increasing demand for high quality water has prompted the researchers to pay considerable attention to recover and reuse wastewater. These metals are of special concern because of their persistency. Industrial wastes are the major sources of various kinds of metal pollution for the natural water bodies. These heavy metals enter into the natural water bodies through the wastewater discharge from electroplating, leather tanning, foundry, chemical manufacturing, jewelry works, dye manufacturing, mining, industries of Cd-Ni batteries, phosphate fertilizer, pigments, etc [1]. Environmental constraints have forced the metal plating industry to reduce their emissions to water bodies, otherwise mass usage of metals could cause severe environmental problems and disasters. Hence it is a challenging task for the industrialists and environmentalists for the safe & effective disposal of waste containing heavy metals.

Various treatment methods used to remove the heavy metals from the industrial wastewater include chemical coagulation, membrane filtration, electro dialysis, reverse osmosis, ion exchange, etc [2]. But these methods are costlier due to operation, maintenance and sludge disposal aspects with certain limitations. The need of safe and economical methods for the removal of heavy metal ions from contaminated water has developed interest towards the adsorption process with low cost adsorbents.

In this review paper, articles published recently on adsorption of metal ions are studied and the key issues presented.

2. Adsorption

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as liquid - liquid, gas - liquid, gas - solid, or liquid - solid interface. The substance being adsorbed is the "adsorbate" and the adsorbing material is termed the "adsorbent". The driving forces for adsorption process are surface affinity, chemical reactivity, pH, surface area for adsorption per unit volume and reduction in surface tension. Adsorption is a separation process in which certain components of the fluid phase are transferred to the surface of the solid adsorbents.

2.1 Adsorbents

B.C.Lowitz established the first use of charcoal for the removal of bad tastes and odours from water on an experimental basis in 1789-90. The credit of developing commercial activated carbon however, goes to Raphael Von Ostrejko whose inventions were patented in 1900 and 1901. Wetonabe & Ogawa first presented the use of activated carbon for the adsorption of heavy metals [3]. Commercial activated carbon available either in powdered or granular form is commonly used as an adsorbent.

Activated carbon is costlier and its practical applications are limited. Hence, various investigators focused their attention on the use of alternative locally available low cost adsorbent materials and their technical feasibility by modifying the adsorbent chemically. Some low-cost adsorbent materials include fly ash, bark, peat, saw dust, paper pulp, bagasse & bagasse fly ash, lignite coal, rice husk carbon, coconut fibre, coconut shell carbon, blast furnace flue dust, blast furnace slag, bituminous coal, fertilizer waste, human hair, straw, wool, bone char, seaweed, algae, chitosan, egg shell, seed shell, sand & soils, red mud, etc [4,5].

2.2 Types of Adsorption

Due to the attractive interaction between the surface of the adsorbent and the species being adsorbed.

2.2.1 Physical adsorption

It is a result of intermolecular forces of attraction between molecules of the adsorbent and adsorbate. When the intermolecular attractive forces between molecules of a solid and the gas are greater than those between molecules of the gas itself is defined as physical adsorption. It occurs at lower or closer to the critical temperature of the adsorbate. Commercial adsorbents rely on physical adsorption.

2.2.2 Chemisorption

It is a result of chemical interaction between the solid and the adsorbed substance. Chemisorption is also called activated adsorption. Catalysis is the example of chemisorption. It occurs only as a monolayer and substances chemisorbed on solid surface are hardly removed because of stronger forces.

2.3 Adsorption Dynamics

It consists of the following consecutive steps

(i) Transportation of adsorbate from the bulk solution to external surface of the adsorbent by diffusion through the liquid boundary layer.
(ii) Internal (interphase) mass transfer by pore diffusion from the outer surface of the adsorbent to the inner surface of the porous structure.
(iii) Surface diffusion along the porous surface.
(iv) Adsorption of the adsorbate on the internal surface of the pores of the active sites.

The last step of the adsorption is usually very rapid in comparing with the other steps. The overall adsorption rate is controlled by either by film or intra particle diffusion or a combination of both [6].

2.4 Types of Adsorption Processes:

Adsorption processes can be operated either in batch mode or in continuous flow system. Further, continuous flow adsorption processes are classified into three types:

- Fixed bed adsorption system
- Fluidized bed or Expanded bed adsorption system.
- Moving bed adsorption system

Based on the direction of flow, they are:

(a) Up flow system
(b) Down flow system

2.5 Advantages of Adsorption Process: [7]

- ✓ **Cheap:** The cost of adsorbent is low since they are often made from locally, abundantly and easily available materials.
- ✓ **Metal Selective:** The metal sorbing performance of different types of bio-mass can be more or less selective on different metals.
- ✓ **Regenerative:** Sorbent material can be possible to reuse after regeneration
- ✓ **No Sludge Generation:** Unlike the problems in other techniques (ex: precipitation), there is no issue of sludge generation in adsorption process.
- ✓ **Metal Recovery:** If sorbate is a metal ion, it is possible to recover the metal ion after being desorbed from the adsorbent materials.
- ✓ **Competitive Performance:** Performance of adsorption process in terms of efficiency and cost is comparable with the other methods available.

3. Literature Review

Ajmal Mohammed et.al (2008) used teak leaves (Tectonagrandis) for the removal of Pb(II) ions from aqueous solution. Maximum adsorption occurred at pH5.0. The adsorption of lead was found endothermic in nature. The breakthrough capacity of the adsorbent reported that 30mg of lead with 1gm of adsorbent. The investigators concluded that the advantages of the adsorbent lied in its regeneration property, which made the process more economical.

Benavente Marthe (2008) studied adsorption of metallic ions onto chitosan. The studies were conducted for the adsorption of Cu(II), Zn(II), Hg(II) and As(V) using chitosan as a adsorbent. The investigators have reported that As(V) removal was effective at pH 3.0 whereas Cu(II), Zn(II) and Hg(II) between pH 4.0and 6.0. It was also reported that the adsorption capacity of the metal ions onto chitosan is in the order of Hg>Cu>Zn>As. During the column studies, the investigator observed that the breakthrough for Cu(II) and Zn(II) reached in about 60 and 30 bed volumes, respectively. It was also reported that the adsorbed metallic ions could be removed from chitosan with $(NH_4)_2SO_4$, NaCl and NaOH solutions. The investigators concluded that 97% and 71% removal of Cu(II) and Zn(II) respectively from the mining effluents with chitosan [8].

Removal of Cr(VI) was studied by Shivamani and Prince (2008) using Crude Pongamia Leaf Powder (CPLP) and nitric acid treated Pongamia Leaf Powder (APLP) as adsorbents through batch studies. The authors reported that both adsorbents were efficient for the uptake of Cr(VI) at pH 2.0 and contact time 165 minutes. APLP was found to be more efficient than CPLP with an initial Cr(VI) concentration of 5mg/l. The authors also reported that the data was found to follow both Langmuir and Freundlich isotherms; however it was well fit in Freundlich isotherm [9].

Removal of Cadmium and Zinc from metal finishing industrial effluents with low cost adsorbents was studied by Basava Rao, etal (2007). The investigators used Powdered Activated Carbon (PAC), Granular Activated Carbon (GAC size- 1.3mm) and Fly Ash (FA) and observed the effect of pH, contact time, adsorbent dose and initial metal ion concentration to remove Zn^{2+} and Cd^{2+} ions from the synthetic solutions using batch studies. Authors reported that the optimum pH for PAC and FA 5.0 and 2.0 respectively. The contact time for all the three adsorbents was between 2.5 and 3.0 hours with a adsorbent dose of 20 g/l. [10].

The effect of some parameters such as the flow rate, initial solute concentration and column bed depth on fluoride removal was studied by Bhargava and Killedar (2009) using fishbone charcoal. The study was conducted using the fixed bed column with continuous flow operation. The useful treated effluent volume (effluent concentration of 1mg/l) of fluoride is a function of flow rate, column bed depth and initial fluoride concentration. An empirical relationship was established to predict the useful effluent volume for any value of initial fluoride concentration (range 2.5 to 20.0 mg/l), flow rate (3.06 to 15.3 ml/min/cm^2) and column bed depth (20-65 cm). The authors concluded from the relationship the higher co-efficient of correlation between the projected and the observed values [11].

Adsorption studies on Cr(VI) and Pb(II) removal from aqueous solutions using areca nut shell (agricultural solid waste by product) was conducted by Geetha et.al (2009). The maximum removal of Cr(VI) and Pb(II) was found at pH 4.0 and 5.0 respectively. The investigators achieved 100 & 86% removal of Cr(VI) and Pb(II) respectively at initial metal ions concentration of 20 mg/l. Maximum desorption of 88% for Cr(VI) and 91% for Pb(II) were achieved. The authors reported that Areca nut shell can be used to remove the heavy metals from the waste water [12].

Jeyanthi and Shanthi (2007) studied the removal of Pb(II) from electroplating industrial effluent using sago waste. The studies were conducted under batch adsorption. The investigators concluded that the coarse sago waste is a good adsorbent for Pb(II) removal from electroplating industrial effluent. The optimal conditions for the effective removal of Pb(II) by coarse sago waste were found to be pH 5.0, contact time 3 hours, temperature 30^0C and adsorbent dose 4.0gm/l [13].

Mise and Shivarajappa (2010) investigated the adsorption of Cr(VI) using activated carbon of date palm seeds (Phoenix Dactylifera). The investigators conducted batch studies and used Freundlich and Langmuir isotherms to understand the adsorption mechanism. It was reported that maximum adsorption took place at pH 2.0 and the data followed Langmuir isotherm. It was further stated that chemically activated $CaCl_2$ carbon with impregnation ratio (I.R) 0.75 and H_2SO_4 carbon with IR 0.75 adsorbed more Cr(VI) ions compared to other physically and chemically activated carbons having IR-0.25 and 0.50 [14].

Removal of Cr(VI) and Ni(II) with bagasse, fly ash (FA) and Powered Activated Carbon(PAC) was studied by Rao et.al (2003). The investigators conducted batch studies and reported that Cr(VI) removal was higher at pH 2.0 with PAC, whereas Cr(VI) and Ni(II) were effectively removed between pH 6 and 8 (which are nearer to neutral pH). To understand the mechanism of kinetics, the results obtained in laboratory studies were used to fit into Helfferich model. The authors introduced a new constant, which was not available in the original form of Helfferich equation earlier in their study for its better fit. The order of removal efficiency was PAC > bagasse > FA for Cr(VI) removal and PAC > FA> bagasse for Ni(II) removal at optimum conditions [15].

Khuzaimah Noor et.al (2011) studied Ni(II) removal from aqueous solution using Rambai Stem (Baccaureamotleyana) adsorbent. The highest adsorption capacity was obtained at low pH (ie4-5) with adsorbent dose 0.1 mg and initial metal ions concentration of 30 ppm. The percentage removal of nickel from the solution was observed 51%. The experimental data was fitted well in Freundlich isotherm. The adsorption of Ni(II) by Rambai stem (Baccaureamolteyana) was followed by heterogeneous surface phenomena [16].

Removal of Cu(II) and Zn(II) from electroplating industrial waste water using activated Topioca peel waste biomass was investigated by Kanimozhi (2008-2009). Topioca peel powder biosorbent was activated by using nitric acid. The maximum percentage of removal of Cu(II) was occurred at pH 3.0 and zinc at pH 4.0, contact time 4 hours for both Cu(II) and Zn(II), adsorbent dose 400 mg for both Cu(II) and Zn(II). The maximum removal efficiency was 82% for Cu(II) and 84% for Zn(II) at optimal conditions [17].

Gowda Rudure et.al (2011) investigated the removal of Ni(II) from the industrial wastewater using coconut leaves as adsorbent. By conducting batch adsorption studies at room temperature (25-32°C), the maximum removal of Ni(II) was 93.2% with 1.0gm/50ml of coconut leaves at pH 8.0, contact time 3 hours and initial Ni(II) concentration 26.81mg/l. Langmuir and Freundlich adsorption isotherm models were applied to evaluate the adsorption data. The adsorption of Ni(II) ions followed the Freundlich isotherm and pseudo-second order adsorption kinetics. The authors concluded that the adsorbent used in this work was most effective [18].

4. Conclusions

The paper briefly highlighted the theory behind adsorption process and its advantages. Also the review of various papers publishes in recent journal on removal of metal ions from industrial wastewater by adsorption using various low cost adsorbents instead of expensive activated carbon. The efficiency of adsorbents in the removal of metal ions depends on dose of adsorbate, characteristics of adsorbent, hydrogen ion concentration, temperature, contact time, speed of agitation, etc. Their reports reveal that these low cost adsorbents also comparable with activated carbon to remove the organic matter. Hence, these low cost adsorbents may be used effectively and efficiently to treat the wastewater. The exhausted adsorbents may be reused after the regeneration with simple alkali / acid treatment. However, still, there is a strong need to conduct extensive research on the disposal of the spent adsorbents in an eco friendly way.

Acknowledgements

The author is grateful to Dr. Y. R. M. Rao, Principal, Dr. Pauls Engineering College, Villupuram district for guidance and encouragement and also to my colleagues Mr. K. Stalin and Mr. K. Kaviyarasan for their whole hearted cooperation.

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Author Profile

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