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Adsorption for Cadmium Removal from Effluent- A Review

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Abstract— **Removal of heavy metals from the effluent is very important part of the research carried out in environmental field. Various methods tried by the researchers include adsorption, biological methods, electro coagulation, electro dialysis and various membrane separation techniques among others. Adsorption by using various low cost adsorbents was found be very effective method with the percentage removal upto 99 percent while the biological methods were also effective with the removal percent more than 90 percent. In this review paper an attempt is done to summarize the research work on adsorption by using various low cost materials, in order to study their effectiveness and the findings. Various low cost materials such as flyash, peanut shells, activated carbon, rice husk, rice husk ash, barley hull and barley hull ash, coconut shells activated carbon, cashew nuts activated carbon, tamarind seeds activated carbon, calcite, Leca, nettle ash have been tried by various researchers with good results. Also some researchers have carried out the studies on regeneration of the adsorbents. Effective regeneration can be very important factor in choosing the adsorbent. There is potential for research in adopting new low cost adsorbents and using them in fixed, fluidized, moving beds to study the adsorption process in terms of mass transfer and regeneration of the adsorbent effectively.**

Index Terms— **heavy metals, cadmium, adsorbents, removal**

I. INTRODUCTION

The sources of heavy metal in water bodies are electroplating, pigment, alloy, fertilizer and chemical industries . The pollution of water bodies because of heavy metals is a cause of concern for the mankind and hence important area of research. Cadmium is one of the important water pollutants, emitted from the sources such as smelting, metal plating, cadmium-nickel batteries, phosphate fertilizers, pigments, stabilizers, alloy industries. The cadmium concentration in these wastewater ranges from 0.01 to 3.2 mg/l. Most important source of cadmium is electroplating industry which constitutes fifty percent of the cadmium emitted to water bodies. It is observed that the intake of cadmium by the crops increase the concentration in the food and subsequently in human bodies. Cadmium presence in human bodies above certain level may cause liver damage, renal damage, hyper tension and anemia. In india the maximum permissible limit for cadmium concentration in drinking water is 0.01 mg/l.

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II. ADSORPTION FOR HEAVY METAL REMOVAL

The ability of certain solids to preferentially concentrate specific substances on their surfaces is the basis for adsorption. In this manner, the component of either gases or liquid solutions can be separated from each other. Adsorption is a low cost and important physical process for the treatment and renovation of wastewater. Activated carbon is a highly effective low cost adsorbent and shows 10 – 15 % carbon loss during regeneration. Various non-conventional adsorbents, like saw dust, baggase pith, rice husk ash, activated coconut shell powder controlled burnt wood charcoal , flyash, peat, wood , jute fibers , have been tried for heavy metal removal.In this review, the research on adsorption of cadmium on various low cost adsorbent by various researchers is summarized with their findings.

III. ADSORBENTS FOR CADMIUM REMOVAL

Various low cost adsorbents discussed with respect to research include sugarcane bagasse, bagasse flyash, peanut shells activated carbon, rice husk, rice husk activated carbon, waste wood activated carbon,barley hull, barley hull ash, coconut shell activated carbon, cashew nut shell activated carbon, carboxylated chitosan, tamarind seeds activated carbon, nano zerovalent iron particles and calcite. Following section contains discussion about research on adsoption of cadmium by these materials.

A. Bagasse Flyash

Garg et.al. have carried out research on removal of cadmium (II) by using various wastes as adsorbents[1]. They used sugarcane bagasse (SCB), maize corncob (MCC) and Jatropha oil cake (JOC) as adsorbents. They studied the effect of the parameters like initial metal ion concentration, pH, and adsorbent dose on the removal efficiency. The isotherm studies indicated that the adsorption of cadmium was a monolayer one and both the isotherms fitted reasonably well for the uptake of cadmium. For the adsorbent dose of 20g/l of the solution the contact time of 60 minutes was observed to be optimum. At the optimum conditions the percentage removal for Jatropha oil cake, maize corncob (MCC) and sugarcane bagasse (SCB) was observed to be 99.5%, 99% and 85% respectively. Gupta et.al. have observed that about 90 percent cadmium and nickel removal can be obtained by using bagasse flyash as an adsorbent in 60 and 80 minutes contact time respectively [2]. According to their research the at initial concentration of a4 and 12 mg/l for cadmium and nickel, the percentage removal was maximum. They also observed that the optimum pH values were 6 and 6.5 for these two metals. The adsorbent dose of 10 g/l was sufficient for the optimal removal of these metal ions. With increase in temperature, the adsorption was found to increase. Also the adsorption data followed Langmuir model better than the Freundlich model. El-Sherif and Fathy tried to modify the adsorption properties of the bagasse flyash (BFA) in order to increase the adsorption capacity[3]. The studied the influences of the parameters like solution pH, contact time, initial metal concentration, adsorbent dosage, and temperature on the adsorption performance of Cd (II) onto natural and modified BFA adsorbents. They carried out chemical modification of bagasse flyash using hydrochloric and nitric acid. It resulted in increasing sorption efficiency more than twofold. The adsorption followed Langmuir isotherm and it was observed to be pseudo first order operation. Studies on temperature dependence indicated that it was endothermic and spontaneous process

The review on cadmium removal carried out by Rao et.al.[4] Indicates that bagasse flyash is very good adsorbent for cadmium removal. The study also revealed that many agricultural waste materials and biosorbents have been tried effectively by various researchers for cadmium removal. Mohan and Singh have derived activated carbon from bagasse flyash[5]. They used this activated carbon for removal of cadmium and zinc from the wastewater. The cadmium uptake follows Freudlich and Langmuir isotherms. The data are better fitted by Freundlich isotherm than the Langmuir. Competitive adsorption of nickel and cadmium onto bagasse flyash was carried out by Shrivastava et.al[6]. They also obtained equilibrium data for this. They observed that the single ion adsorption data fitted in Langmuir, Freundlich and Redlich–Peterson (R–P) isotherm models. They also analyzed the isotherms for competitive adsorption of these two metals. The Freundlich isotherm fitted better for the competitive adsorption. They also carried out desorption studies, in which they concluded that hydrochloric acid was the best solvent for this. The maximum elution was about 65% for Cd (II) and about 42% for Ni (II). The study on cadmium removal by using fly ash was carried out by Visa and Duta[7]. They studied the kinetics and thermodynamics of the process. They modified the surface characteristics of the fly ash by contacting it with alkaline solutions and the complexion agents for long time. Also they discussed the immobilization efficiency in connection with contact time, wastewater volume, adsorbent mass ratio and ions concentration. They also observed that the adsorption process follows the Langmuir and Freundlich mechanisms and pseudo second order kinetics. According to their experimental observations, moderate NaOH concentrations (2N) are enough for developing a substrate that, in optimized conditions brings about 97 % removal for cadmium and nickel ions in a large concentration range.

B. *Rice Husks*

The removal of cadmium and zinc from binary aqueous solution was tried by Shrivastava et.al.[8]. They used rice husk ash from rice husk fired furnaces as an adsorbent. They observed that the pH value of 6 was the optimum pH value for the adsorption. They studied competitive adsorption of these metals. They observed that equilibrium metal removal decreased with increase in the other metal ion concentration. Mahvi et.al. have carried out cadmium removal from the wastewater by using rice husk and its ash[9]. According to their research the cadmium removal efficiency increased with increase in the pH value.The maximum adsorption was observed to be 97.2 and 99.2 percent for rice husk and rice husk ash. The optimum values for initial concentration, pH and contact time were observed to be 20 mg/l, 6 and 180 minutes respectively.They concluded that rice husk ash was a better adsorbent than rice husk. . Biosorptive removal of cadmium in different experimental conditions by rice husk was carried out by Shafiei and Ghadaksaz[10]. They conducted several batch experiments at various values of parameters like pH, temperature, contact time, sorbent concentration and size, and rotation speed. Their research also emphasizes the importance of these parameters in the adsorption operation. Preatreated rice husk was used for the cadmium removal by Kumar and Bandopadhyay[11]. They observed some simple and low cost chemical modifications increased the capacity by 25-40 percent. Chemisorption of the cadmium was observed to be rate limiting step. They studied the effect of pH, sorption kinetics and isotherms in batch experiments. The equilibrium data were betted fitted in the Langmuir isotherm than Freudlich isotherm.

Kayal et.al. have carried out the research on use of chemically modified rice husk[12]. It has been observed that rate of adsorption is dependent on the nature of the adsorbent, adsorbent dose, particle size of the adsorbent, concentration, pH, contact time, temperature. They observed that the chemically modified rice husk was more capable of removing heavy metals than untreated rice husk and rice husk ash. Chemically modified rice husk was observed to be very good adsorbent with removal capacity of 99.8% Pb, 95% Cd and 97% Zn. A review on use of rice husk as an adsorbent for removal oh heavy metal was carried out by Raju and Naidu[13]. They highlighted various properties of rice husk and various methods used to modify the rice husk in order to increase the adsorption efficiency. The activated carbon prepared from rice hulls was used by Teker et. al for adsorption of cadmium and copper[14]. They used chemical activation and high temperature heating for activation of the adsorbent. They used $ZnCl_2$ and HCl for the chemical activation. In case of cadmium, the equilibrium was attained in 80 minutes while for copper It was attained in 60 minutes. In case of the initial concentration, the adsorption of Cu (II) and Cd (II) on the adsorbent decreased from 98.00 %and 77.62 % to 48.33 % and 19.36 % by increasing the Cu (II) and Cd (II) concentrations from 5 ppm to 100 ppm respectively.. They observed that the adsorption percentage of Cu (II) and Cd (II) almost the same, in the pH range 5-8..It increased sharply before and after these values of pH. Adsorption studies of cadmium (ii) using novel composites of polyaniline with rice husk and saw dust of eucalyptus camaldulensis were carried out by Kanwal et.al[15]. They prepared the polyaniline/ ricehusk (PANI/R.H) compositeTheir observations recommended that there is no molecular structural difference occurred in polyaniline during composite synthesis. . In case of polyaniline/saw dust (PANI/S.D) composite, the maximum percentage removal of 93 percent was obtained for iptimum contact time of 20 minutes.The corresponding contact time waswhile 30 minutes for polyaniline (PANI) and polyaniline/rice husk (PANI/R.H) composite. For the maximum adsorption speed of 100 rpm, the maximum % age removal of Cd (II) was 94.45 % using polyaniline/rice husk (PANI/R.H) composite, 89.53 % employing polyaniline/saw dust (PANI/S.D) composite and 75.96 % in case of simple polyaniline (PANI).

Goodhead and Dagde have carried out research on adsorption of acetic acid, cadmium ions, lead ions and Iodine using activated carbon from waste wood and rice husks[16]. The results showed that RH 600°C, Was having the highest adsorptive capacity, and hence the most developed surface area. They also observed that the adsorptive capacities of the samples increased with increase in initial concentration of acetic acid. Their study indicated that saw dust activated at 800°C showed better adsorption of lead than saw dust at 600°C. They also concluded that It that the yields of the two different raw materials at the respective temperatures fell within the same range with rice husk samples having the higher yield. Kumar et. al have carried out investigation on thermodynamics and kinetics of cadmium adsorption on rice husk[17]. They studied the adsorption behavior of rice husk for cadmium ions from aqueous solutions as a function of appropriate equilibrium time, adsorbent dose, temperature, adsorbate concentrations and pH in a batch system. They observed that the maximum removal of 98.65 percent was observed for the pH value of 6, contact time of 60 minutes and initial concentration of 25 mg/l. The adsorption preocess was spontaneous in nature and exothermic as well. They also infered that the adorption process was pseudo first order in its nature hence chemisorptions was predominant.

C. Peanut Shells Activated Carbon

Long and Dang modified the peanut shells by using potassium permanganate for removal of cadmium in the fixed bed[18]. They studied the effect of influencing the adsorption such as bed height, initial concentration and influent flow rate. They observed that the with increase in the bed height the height of mass transfer zone remained unchanged whereas it increased with initial concentration and influent flow rates. The breakthrough time decreased with initial concentration and influent flow rate. Zhengjun et.al. have investigated the cadmium removal by using peanut shells[19]. The studied the effect of pH and cadmium concentration. The adsorption capacity of peanut shells was observed to be 87.72 mg/g. Wilson et.al. have carried out research on metal adsorption by using activated carbon prepared from peanut shells[20]. They carried out pyrolysis, steam activation and oxidation for preparation of granular activated carbon from the peanut shells. For the activated carbon prepared from peanut shells, the yield values were lower for non crushed samples. For the crushed samples, the yield was highest for for the 2 hour steam activation and lowest for the 4 h steam activation. According to their studies the peanut shell-based carbons which were steam activated for 4 h and not crushed (8-4-4-N) or crushed (8-4-4-C), showed significantly higher adsorption for all five metal ions (copper, lead, nickel, zinc,and cadmium) than all of the other peanut shell-based carbons.

D. Barley Hull And Barley Hull Ash

Adsorption of cadmium on Barley Hull and Barley Hull Ash was tried by Maleki et al.[21]. They screened the barley hull to various screen sized washed with distilled water and heated to 100 °C. The barley hull ash was obtained by burning barley hull electrically in the oven at 600 °C. Sharp increase in the percentage removal was obtained when pH was increased from 2 to 9, . The increase in the removal was more than three fold for both the adsorbents. High dose of adsorbent also gave high percentage removal for both the adsorbents. The optimum mesh size was 40 mesh. Their study revealed that with the increase in initial cadmium concentration from 10-50 mg L/l, on barley hull and barley hull ash, the loading capacity increased from 1.98-8.00 mg/g of barley hull and from 1.99-9.50 mg/g of barley hull ash. He adsorption followed Freundich adsorption isotherm, indicating chemisorptions.The research on cadmium uptake by barley was carried out by Singh and Myhr[22]. They carried out investigation to determine the effect of cadmium source and pH on the uptake. They applied Cadmium was as NPK fertilizers at three rates. The concentration of Cd in barley tended to increase with increased Cd applied through CdCl2 in the last two years. Also they observed that other sources of Cd not showed any consistent effect on Cd concentration in barley. Cadmium concentration in barley increased from the first to the fourth year in all the treatments. Their results suggested that the concentration of Cd in barley grain was not affected significantly by the Cd applied through different sources in any of the years under study.

E. Coconut Shell Activated Carbon

Coconut shell activated carbon was used for the removal of cadmium from the effluent by Olowoyo and Garuba[23]. They carbonized the coconut shells, and chemically activated them using phosphoric acid, potassium hydroxide, calcium carbonate and zinc chloride solutions as activating reagents. According to their studies, the rate of adsorption increased rapidly in first 10-20 minutes for 50 ml of effluent taken in 100 ml flasks. With further increase in the contact time, there was no significant increase in the uptake of metal. They observed that the adsorption of cadmium ions increased at a steady rate as the pH increased most especially in CaCO3 and KOH activating agent. At pH higher than 9, the precipitation of cadmium reduces the uptake of metal. They also observed that the influence of activating agents and pH could either affect the adsorption capacities of the activated coconut shell positively or negatively depending on the nature of the activating agents and the range of the pH.

F. Cashew Nut Shells Activated Carbon

Tangjuank et.al. carried out research on adsorption of lead(ii) and cadmium(ii) ions from aqueous solutions by adsorption on activated carbon prepared from cashew nut shells[24]. They observed that an increase of activation time decreases the yield of activated carbons. For the activated carbons of group with KOH/char ratio equal to 4, the yield decreased from 82-64% with the increase of the activation time from 20–150 minutes. They observed that it was possible to prepare the activated carbon of high BET area using cashew nut shells by KOH oxidation and CO_2

gasification. Kumar et.al. have tried cashew nut shells activated carbon for removal of cadmium from waste water[25]. They studied the effect of various parameters such as solution pH, cashew nut shell concentration, contact time, initial cadmium(II) concentration and temperature. Acidic conditions favored the removal and the equilibrium was achieved in 30 minutes. Their results suggested that the adsorption of cadmium (II) could be described by the pseudo-second order equation.

G. Tamarind Seeds Activated Carbon

Suganthi has carried out investigation on removal of metal ions such as cadmium and copper on tamarind seeds activated carbon in a fixed bed[26]. They assessed the effect of the effect of pH, flow rate and bed height on the adsorption of metal ions from aqueous solutions. They also analyzed the regeneration capacity of the activated carbon by repeated adsorption and desorption processes. Most of the cadmium removal was observed in the pH range of 4 to 7. They also used the commercial activated carbon in order to compare the results. He concluded that metal ion uptake was higher in phosphorylated tamrind seed activated carbon than commercial activated carbon. It was also observed that copper was more readily adsorbed on the phosphorylated tamrind seed activated carbon than cadmium whereas commercial activated carbon showed equal percentage removal for both the adsorbents. Suganthi and Shrinivasan carried adsorption of cadmium on phosphorylated tamrind seed activated carbon[27].They prepared activated carbon from phosphoric acid treatment of Tamarind nuts (seeds). They chose the carbon granules in the size range of 300 to 800 µm for the studies. According to their study, The mechanism of adsorption for cadmium on PTNC was found to follow ion exchange process predominantly The cadmium removal and the surface modification are also confirmed by SEM studies.

H. Carboxylated Chitosan

LV et al. prepared Carboxylated chitosan (CKCTS) for the removal of Cd(II), Pb(II), and Cu(II) from aqueous solutions[28]. They investigated the effect of pH value, initial concentration, contact time and temperature on the adsorption. They observed that with, increase in pH, the adsorption capacity increases.Also the data fitted well in the Langmuir equation, suggesting monolayer adsorption.

I. Nano Zerovalent Iron Particles

Boparai et al. have tried the adsorption of cadmium ions on the nano zerovalent iron particles[29]. They also studied thermodynamic and kinetic aspects of this process. They conducted the studies in the concentration range of 25-480 mg/l. They found that the adsorption in this case increases with the increase in temperature as with endothermic reactions. The adsorption process was observed to be second order. In this case the Freundlich and Temkin isotherms fitted the adsorption process. The adsorption on the surface was the rate determining step.

J. Compost, Cellulose Pulp Waste And Anaerobic Sludge

Ulmanu et al. have used low cost waste materials such as activated carbon, kaolin, bentonite, diatomite and waste materials such as compost, cellulose pulp waste and anaerobic sludge[30]. According to the studies, the bentonite was found to be best adsorbent compared to others, showing 99 percentage removal of cadmium even in presence of copper. The equilibrium data fitted in the Freundlich and Langmuir isotherms for all the adsorbents.

K. Calcite

Yavuz et al. have used calcite for removal of cadmium and lead from aqueous solution[31]. They carried out batch experiments at room temperature. They used centrifugal separator for separation of calcite. It was observed that the adsorption followed Langmuir isotherm reasonably well. Natural calcite showed considerable removal of cadmium and hence can be used as low cost adsorbent for the removal of cadmium.

L. Nettle Ash

Mousavi and Seyedi have carried out research on nickel and cadmium removal by using nettle ash as an adsorbent[32]. They observed that the optimum pH required was 6. Also the the experimental data well fitted in the Langmuir isotherm equation with the monolayer adsorption capacity of 142.8 mg/g. The adsorption kinetics was found to follow pseudo second order kinetics.

IV. CONCLUSION

Adsorption for removal of heavy metal is widely studied area of research.. Various agricultural wastes have been effectively used for the heavy metal removal by investigators. Most of the adsorbents have shown the cadmium removal efficiency above 90 percent except few exceptions. The key to the effectiveness of this method for removal of heavy metals, and hence cadmium is the effective method of regeneration. The research is also being carried out to recover the heavy metals from the adsorbents. This will make the operation more economical and attractive alternative for cadmium treatment.

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