A COMPARATIVE STUDY OF HEAVY METAL ION REMOVAL FROM WASTEWATER USING COMMONLY USED NATURAL ADSORBENTS: A REVIEW

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Abstract: Water pollution caused by heavy metal ions became a major problem for the environment and has become cause of concern for engineers. The damages caused to the environment is due to industrial and domestic waste water and it adversely affecting the human health. Different heavy metal ions have very adverse effect on human and aquatic life. Chromium is one of the most important heavy metal ion to concern, it is carcinogenic in nature and also contaminates soil and groundwater. Various different natural adsorbents are being investigated and are found to be very effective for Chromium removal. Adsorbents like sawdust, groundnut hull, agriculture waste, coffee husk and neem leaves found to be very effective against chromium. The review article presents the effect of the above mentioned adsorbent on hexavalent chromium under the parameters of Effect of pH, Effect of contact time and Effect of adsorbent dosage under batch scale study.

Keywords: Adsorbents; Sawdust; Groundnut shell; Neem leaves; Agriculture waste; Coffee husk; Chromium; Adsorption isotherms.

I. INTRODUCTION

Water is basis of all life on earth, as it is necessary for survival. Water pollutants such as heavy metal ion are a major concern to environment. Heavy metal ion contaminates surface water such as sea, lake, reservoirs etc., addition to this it also contaminates underground water by leaking in trace amount. A number of metal ions which are significantly toxic to human beings and ecological environments, they include chromium (Cr), copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg), zinc (Zn), manganese(Mn) nickel (Ni), etc. Heavy metal ion is available in nature in various forms as they are present in compound having different oxidation states. Chromium is one of the heavy metals used by modern industries like plastic, pigment, wood preservative, electroplating, leather tanning, cement, mining, dyeing and fertilizer. Among them, chrome tanning industry contributes more chromium pollution in water and land environment. Chromium occurs in nature in different oxidation states ranging from divalent to hexavalent state. Hexavalent chromium is well thought out to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties. It is included in the priority list of hazardous substances since it affects both; human and aquatic life. The toxicity level of the chromium ranges between 50-150 µg/kg. Removal of toxic level of the chromium content from the water and wastewater is a complicated process and the cost of this process is very high. Conventional treatment methods such as chemical precipitation, coagulation and flocculation, ion exchange, electrolytic recovery, membrane filtration, floatation and adsorption have been used to remove chromium from wastewater. Removal of chromium has also been investigated using phytoextraction, RO, UF, nanofiltration, membrane and biological process. To reduce the heavy metal ion concentration to an environmentally acceptable level, a cost-effective and efficient separation method is to be developed. Ion exchange, Adsorption and Precipitation are the most efficient methods used to remove the heavy metals from the wastewater. In adsorption method use of activated carbon adsorbent is very effective for chromium removal but cost of this adsorbent is very high. Adsorption using activated carbon is most effective because it has a high capacity for adsorption, but its use is limited because of its high cost. In recent years the low-cost materials are used as an adsorbent has been encouraged. low cost sorbents were especially investigated and their technical feasibility for heavy metal removals from the contaminated streams has been reviewed for adsorption method.

II. MATERIAL AND METHODS

2.1 Adsorbate preparation: stock solution of Cr(VI) metal ion is prepared by dissolving required quantity of analytical grade $K_2Cr_2O_7$ in 1L of distilled demineralized water. [5,6,12,18]

2.2 Adsorbent preparation:

1. **Sawdust:** After collection it was washed thoroughly with double distilled water to remove impurities of dirt and dust, then it is washed with 0.1N NaOH and 0.1N H_2SO_4 to remove lignin based color materials. Finally, it was washed again with distilled demineralized water several times and dried in an oven at 100°C for a period of 6 hours and sieved to get desired particle size of 30 mesh screen. [7,15,22]
2. **Groundnut hull:** Washed the hulls severally with clean water, and then boiled for 6 hours in order to remove dirt and colored compounds. On cooling, the shells rinse with distilled water. The washing continued until the filtrate become colorless. The resulting material then dried in the oven maintained at 80 °C for 24 hours and thereafter grounded to get powder of desired particle size of 30 mesh screen. [11,22]

3. **Neem leaves:** Collected neem leaves from local area and then washed thrice to remove soluble impurities. After the removal of impurities allowed it to dry in an oven until the leaves become crisp. Then crushed using domestic mixture. Screen analyzed it by using a set of sieves in a sieve shaker to get desired particle size of 30 mesh screen. [16,22]
4. **Agricultural waste:** Rice husk ash adsorbent were prepared by collecting the sample from local rice mill. It is then washed thoroughly with double distilled water to remove the impurities present in the husk then kept in furnace at 500°C for 4 hours. The ash was then cooled and ground to pass through 30 mesh screen. [1,6,15]
5. **Coffee husk:** The coffee husk was washed with water and dried. Then it is crushed and impregnated with 40% H_3PO_4 for 2 hours. Then the activated coffee husk powder was subjected to carbonization at 500°C with a constant heating rate of 5°C/min in a tubular furnace for 1 hour. After completing the carbonization process it was cooled overnight in a tubular furnace. Then it is ground to the particle size of 30 mesh screen. [14]

Fig. 1 - Products containing different forms of Cr(VI).

Products	Type of hexavalent chromium chemicals
Pigments, inks and plastics	Lead chromate, zinc chromate, barium chromate, calcium chromate, potassium dichromate and sodium chromate
Anti-corrosion coating	Chromic trioxide (chromic acid), zinc chromate, barium chromate, calcium chromate, sodium chromate
Stainless steel and other Cr alloys	Hexavalent chromium (when cast, welded, or torch cut)
Textile dyes	Ammonium dichromate, potassium chromate, potassium dichromate and sodium chromate
Wood preservations	Chromium trioxide
Leather tanning	Ammonium dichromate

2.3 ADSORPTION STUDIES

After the preparation of adsorbate and adsorbent the experiments were carried out. Parameters used for experiment were

1. pH
2. Contact time
3. Adsorbate concentration.

The amount of hexavalent chromium adsorbed per gm of the adsorbent was estimated using the formula:

$$Qe = \frac{(Co-Ce)V}{W}$$

Where Co and Ce are the initial and equilibrium liquid phase concentrations of the Cr(VI) ions, V is the volume of the solution and W is the amount of adsorbent used in g. [7]

2.3.1 Adsorption isotherms: The adsorption isotherm is the equilibrium relationship between the concentration of adsorbent held on the surface of solid and the concentration or partial pressure of the adsorbate in the fluid phase at given temperature. The adsorption isotherm may be represented in the form of an equation or a curve. The equilibrium adsorption data can be fitted to some empirical relation called the adsorption isotherm. the common types of adsorption isotherms are Freundlich adsorption isotherm and Langmuir adsorption isotherm.

2.3.2 Freundlich adsorption isotherm: The Freundlich adsorption isotherm is mathematically expressed as

$$\frac{x}{m} = Kp^{\frac{1}{n}}$$

x = mass of adsorbate

m = mass of adsorbent

p = equilibrium pressure of the gaseous adsorbate in case of experiments made in the gas phase (gas/solid interaction with gaseous species/adsorbed species)

III. EFFECTS OF VARIOUS NATURAL ADSORBENTS

3.1 pH: Chromium exist in various oxidation states although trivalent and hexavalent form is mostly observed as chromium is very stable in those forms. pH of the system defines the stability of chromium. In hexavalent chromium at higher pH HCrO4 predominates. When pH is steadily increased decrease in adsorption were observed. This caused due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent which reduced the adsorption capacity. Increase in pH results in decrease in net positive surface potential of the adsorbent which decreases its adsorption capacity.

Sawdust: 1gm dose of sawdust for 5ppm Cr(VI) solution for contact time of 45 min at 1 pH found to have 70% removal efficiency. [15,22]

Rice husk ash: Under same parameters rice husk ash found to have nearly 50% removal efficiently. [1,6,15]

Groundnut hull: groundnut hull maximum removal efficiency of 80% observed at pH 2 under parameters of 60 min contact time and 13 ppm conk of Cr(VI). [11,22].

Neem leaves powder: 1.6 gm dosage of NLP adsorbent on 17ppm Cr(VI) solution with contact time of 180 min gave maximum removal of 82% at pH of 4 which is decreased beyond pH of 6. [22,24]

Coffee husk: coffee husk adsorbent 1gm of adsorbent dose on 100 ppm Cr(VI) solution gave maximum removal efficiency at pH 2 till pH 6 (approx. 90 to 95%). [24]

3.2 Contact time: The effect of contact time on removal efficiency of Cr(VI) from water was studied under different initial concentration and different adsorption dosages. It is observed that increase in contact time also increased the adsorption efficiency but after a point it becomes constant. Rapid adsorption at initial stages gives very slow approach to equilibrium. Adsorbent's nature and its active available pore sites also affects the adsorption.

Sawdust: at 3 pH, 5ppm Cr(VI) solution and 1gm of adsorbent dosage gave maximum efficiency of 60% on contact time of 300 min. [7,15,22]

Rice husk ash: Under same parameter for rice husk ash it gave removal efficiency upto 65%. [1,6,15]

Groundnut hull: at parameters of 2 pH, 2g of adsorbent dosage and 13ppm conc of Cr(VI) gave maximum efficiency at contact time of 80 min. After that it attained equilibrium after which the amount of Cr(VI) ions adsorbed from solutions remains unchanged. [11,22]

Neem leaves powder: The neem leaves adsorbent at 1gm dosage on 100ml solution of Cr(VI) having 200 ppm conc gave 82.66% percentage removal on contact time of 120 min. [16,22]

Coffee husk: adsorbent 80% of removal efficiency achieved on 150 min of contact time at constant pH of 2 and adsorbent dosage of 3gm. [14]

3.3 Adsorbent dosage: With increase in the adsorbent dosage the percentage adsorbance increased so that increased in the percentage removal of Cr(VI). This is due to the increased in the surface area and more active pore site available for adsorption. After a particular absorbent dosage, the percentage adsorption does not increase and due to decrease in number of active pore sites available for adsorption.

Sawdust: at pH of 3, Cr(VI) conc of 5ppm and contact time of 45 min the percentage adsorption increased from 15% to 60% when adsorption dosages are increased from 0.2 gm to 1.1 gm. [7,15,22]

Rice husk ash: Under the same parameters for rice husk ash percentage adsorption increased from merely 8% to upto 45% when adsorption dosage increased from 0.2 gm to 1.1 gm. [1,6,15]

Groundnut hull: When adsorbent dosage increased from 5 to 40 mg the percentage adsorption increased from 50 to 80% under parameters of 2pH, 60 min contact time and 13ppm initial concentration of Cr(VI) solution. [11]

Neem leaves powder: For 100ml solution of 200ppm concentric Cr(VI) adsorbent dosage of 0.25 gm to 0.75 gm increased the percentages adsorption from 13.73% to 65.43%. further increase in dosage the removal efficiency becomes constant. [16,22,24]

Coffee husk: adsorbent at 2 pH on 100 ppm Cr(VI) solution almost complete efficiency achieved with 1gm of dosage. Further Increase in dosage removal efficiency remained constant. [14].

IV. CONCLUSION:

Wastewater mainly contains soluble salts, radioactive isotopes, micro and macro nutrients, bacteria, viruses, chemicals from soap detergents and heavy metals. Chromium is one of the heavy metal ions having a very adverse effect on human and aquatic life. Thus various methods for chromium removal from wastewater are studied. In all the method adsorption is found to be a very useful method when economic and environmental impact of methods are studied. It has advantages of minimum sludge formation, low cost, high efficiency and possibility of regeneration of catalyst. Many different adsorbents which can be made from natural material with low cost are studied. Sawdust, Neem leaves, Groundnut hull, Agriculture waste and coffee husk found to be very useful as natural adsorbents. This adsorbent particularly sawdust due to its organic nature and high amount of carbon content showed the chromium removal efficiency upto 95% under certain parameters of pH, concentration, contact time and dosage. The chemicals found in neem leaves such as niacin, tyrosine, glutamic acid, glutamine and aspartic acid have the strong presence of amino, carboxyl and hydroxyl group which are polar and electronegative in nature thus contribute towards negative surface change. Rice husk powder and coffee husk powder also founded very effective. Thus it can be concluded that chromium removal from wastewater largely depends upon the above mentioned parameters. While studying chromium removal it showed that nearly all the adsorbents work excellently when the pH of wastewater is acidic and gradually decreased towards the basic.

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