ADSORPTION OF CHROMIUM (VI) ON BIOMATERIAL

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ABSTRACT

Removal of toxic metals from industrial waste water is essential from the standard point of environmental pollution control. Among all toxic heavy metals mercury, lead, chromium and cadmium are in the lime light due to their major impact on environment. Chromium (VI) is one of them and its permissible limit in drinking water is 0.05mg/lit and when present above permissible limit it causes various types of acute and chronic disorder. The toxicity of Cr (VI) is greater than Cr(III).

Many physico-chemical waste water treatment process such as Oxidation- Reduction, Precipitation, Ion exchange and Liquid membrane are being used. However, all these processes have the limitation of technical and/or economic constriants. Adsorption is viable and attractive method for the removal of metal from the effluents due to its high efficiency, easy handling and less expensiveness. Keeping above in mind we utilized Adsorbents like rice polish, saw dust, tea powder and coconut coir, which are low cost biodegradable and poses no disposal problems.

These adsorbents are capable to remove as much as 50% of Cr (VI) next to 2.0 pH 300C. The effect of different parameters such as contact time, adsorbate concentration, pH of the medium have been studied. The applicability of Langmuir isotherm suggests the formation of monolayer coverage of adsorbate on the surface of the adsorbent. The thermodynamics of adsorbate-adsorbent system shows spontaneous and endothermic nature of the process.

Key words: mercury, lead, chromium and cadmium.

1. INTRODUCTION:

The present word deals with adsorption studies of Cr(VI) on different adsorbents at different concentrations and pH. The adsorption Cr(VI) ion in waste water is atypical heavy metal environment pollutant. The potential source of chromium in wastewater is industrial waste from textile, leather tanning, metal finishing, electroplating, ceramics, cooling tower effluents and animal glue manufacture. Maximum permissible limit of Cr(VI) by WHO, ICMR and other is 0.05mg/lit. Injection of Cr(VI) above its permissible limit cause pain, vomiting, nausea hemorrhage, acute diarrhea and abnormalities related to genetic cycle causing mutation. The toxicity of Cr(VI) is greater than that of Cr(III) however this is probably due to its relatively higher solubility as compare to Cr(III).

Various wastewater treatment processes viz. Oxidation-reduction, precipitation, Ion exchange and liquid membrane are being used. Adsorption is viable and attractive method for removal of metal from the effluents due to its high efficiency, easy handling and less expensiveness. For this many biosorbents viz. Teapowder, wood saw dust, coconut coir, rice polish etc. Were used but coconut coir appeared to be more efficient.

Many chemi-sorbents like activated carbon, carbon slurry etc. Are also used for the removal of heavy metals, which have very high dynamics and rate of intra-particle diffusion has been evaluated. The adsorption equilibrium investigation of suitability of adsorption isotherm model has also been studied.

TYPES OF ADSORPTION:

(i) Physical adsorption: Physical adsorption, or Vander Waals adsorption, a readily reversible phenomenon is the result of inter molecular forces of attraction between molecules of the solid and the substance adsorbed.

(ii) Chemisorption: Chemisorption, or activated adsorption, is the result of chemical interaction between the solid and the adsorbed substance. The strength of the chemical bond may vary considerably, and identifiable chemical compounds in the usual sense may not actually form, but the adhesive force is generally much greater than that found in physical adsorption.

NATURE OF ADSORBENTS:

- It should have a large internal surface area.
- The area should be accessible through force big enough to admit the molecule to be adsorbed. It is a bonus if the pores are also small enough to exclude molecule it is desired not to adsorb.
- The adsorbent should be capable of being regenerated easily.
- It should not age rapidly, that is lose its adsorptive capacity through continual recycling.
- It should be mechanical strong enough to with stand the bulk handling and vibration that are part of any industrial unit.

2. LITERATURE REVIEW

2.1. ADSORPTION:-

- The process of accumulation of any substance on the surface of another substance is termed adsorption.
- Adsorption is a surface phenomenon.
- The inter can be between the liquid and a gas, a solid (or) another liquid.

Adsorption process is usually thought of , as a polishing or tertiary treatment for water (or) waste water, which has received other normal treatments?

2.2. ADSORBENT:

- The material on the surface of which adsorption takes place is called adsorbent.
- The largest the surface area of the adsorbent, the more the adsorption.

Many solids are used as adsorbents to remove impurities from water and waste water. The efficiency of the process depends on the surface area of the adsorbent. Most of the surface of an adsorbent is provided by a network of pores inside the particle .

Examples of adsorbent:

1) Activated carbon
2) Activated alumina
3) Silica gel
4) Activated clay
5) Bagasse
6) Saw dust
7) Coconut coir
8) Tea powder
9) Banana pith
10) Fly ash

2.3. FACTORS EFFECTING ADSORPTION:

Many factors influence the rate at which adsorption reaction occur and the extent to which a particle material can be adsorbed. Several of the more important factors are

1) Surface area
2) Nature of the adsorbent
3) Hydrogen ion concentration pH of the solutions
4) Nature of the adsorbate
5) Temperature

2.4. SURFACE:

Adsorption is a surface phenomenon and as such the extent of adsorption is proportional to specific surface area. Specific surface area can be defined as the portion of the total surface area that is available for adsorption. Thus the amount of adsorption occurred per unit weight of a solid adsorbent is greater, if the solid is more finely divided and more porous.

For porous materials like activated carbons, the breaking up of large particles to form smaller ones in some instances serve to opentiny, sealed channels in the carbon which might then become available for adsorption. Hence the equilibrium capacity of an adsorbent is influenced by the particle size. However, it also has been observed that small activated carbon particles give increased resistance to flow particularly in packed beds operated in down flow mode.

Therefore the choice of particle size is often compromise between the desire to optimize adsorption rates and minimize resistance to flow.

2.5. NATURE OF ADSORBENT:

The physicochemical nature of the adsorbent can have profound effects on both rate and capacity for adsorption. Adsorption by activated carbon is a surface phenomenon and is affected by the following parameters.

1) Surface functional groups, and
2) Structural details

Significant amounts of carbonyl and carboxyl groups are present on activated carbon surface. The behaviour of activated carbon as an adsorbent as to be related to the surface functionally of this material, and the evidence for chemical interaction at the surface between carbonyl and carboxyl groups and adsorbents is convincing. The adsorption capacity of activated carbon may well be accomplished by increasing the concentration of the appropriate functional groups.

2.6. EFFECT OF pH:

The percentage removsl of Cr (VI) on Coconut coir is optimal at pH = 2 and there after there is abrupt decrease of the percentage removal with the increase of pH from 2.0 to 7.0 the adsorbent used here is rich in several metal oxides. These oxides when mixed with adsorbatesolution undergo surface hydroxylation's and form surface hydroxyl compounds which gives positively or negatively charged surface as a result of subsequent acid-base dissociation.

2.7. NATURE OF ADSORBATE:

The nature of adsorbate (molecular structure and solubility of the solute) is particularly important in dictating the degree of adsorption that can actually occur. A polar groups with high affinity for water usually diminish adsorption from aqueous solutions. The landelius rule states that an inverse relationship can be anticipated between the extents of adsorption of increase in solubility acts to oppose the attraction of the adsorbate to carbon. Thus, a solute and its solubility in the solvent from which adsorption occur. Adsorption increases with decreasing solubility of the solute in the solvent. The greater the solubility, the stronger the solute solvent bond and the smaller extent of adsorption.

2.8. TEMPERATURE:

Adsorption is usually greater at higher temperature. Temperature effect on adsorption equilibria are generally not significant over the range of temperature practically encountered in water and waste water. Thus small variations in temperature don't alter the adsorption process to any significant extent.

2.9. ADSORPTION ISOTHERMS:

A relationship between the mass of substances adsorbed at a given temperature and the mass of adsorbent.

Freundlich adsorption isotherm is of the form

$x/m = k*p^{1/n}$ for solids

(or)

$x/m = k*c^{1/n}$ for solutions

The adsorption isotherm is a functional expression for variation of adsorption with concentration of adsorbate in the bulk solution at constant temperature. Commonly, the amount of adsorbed material per unit weight of adsorbent increases with increasing concentration of the solute to be adsorbed but not in the direct proportion.

The adsorption capacity of adsorbent can be measured to a fair degree by determining the adsorption isotherm, experimentally in the system under consideration.

Several types of isothermal adsorption relations have been developed. The most common relation between 'x/m' and 'c' obtained, for systems in which adsorption from solution leads to the deposition of an apparent single layer of solute molecules on the surface of the solid. Equation that once often used to describe the experimental isotherm data were developed by

(1)Freundlich

(2)Langmuir, and

(3) Brunauer , Emmet, and Teller

Freundlich isotherm equation (or) Van Bemmeless Equation:-

It is widely used for many years for isothermal adsorption, Freundlich equation is mostly useful in dilute solutions over small concentration ranges.

The general form of Freundlich equation is

$$x/m = k*c^{1/n}$$

$$\log(x/m) = \log k + (1/n)\log C$$

If log(x/m) is plotted against log C, a straight line should be obtained. The slope of the line will give the value of '1/n' and the intercept on the Y-axis gives the value of logk.

Analysis of the graph shows that as 'p' increase x/m also increases and, thus the Freundlich's equation indicates no limit to this increases. But experimental values, when plotted show some deviations from linearly especially at low pressures. If we compare theoretical and experimental curves the two agree over a certain range of pressure only. Thus, freundlich equation has a limitation that it is valid over a certain range of pressure only.

Limitations of Freundlich's Equation:-

1) It is valid over a certain range of pressure only.
2) The constant k and n vary with temperature.
3) Freundlich's adsorption equation is a purely empirical formula without technical foundation.

Freundlich's adsorption isotherm holds good for a certain range of pressure only. To solve this difficulty Langmuir worked out an adsorption isotherm known as Langmuir's adsorption Isotherm.

3. EXPERIMENTAL PROCEDURE:

Pretreatment of Adsorbents

i. The adsorbent materials were washed well with distilled water to remove dirt particles.
ii. Tea powder, Saw dust, Coconut coir, were treated separately with 0.1N NaOH solution for a period of 10hours which cause delignification.
iii. The materials were washed 2 (or) 3 times with distilled water at an average room temperature.
iv. Adsorbents materials were treated again separately with 0.1 N H2SO4 solution for about 4 or 5 hours to remove the alkalinity from the adsorbents materials.
v. Then the adsorbents materials were washed well with distilled water till the wash water became colorless.
vi. These treated adsorbent materials were dried in sun light and stored.

3.1. PROCEDURE FOR PLOTING CALIBRATION CURVE:

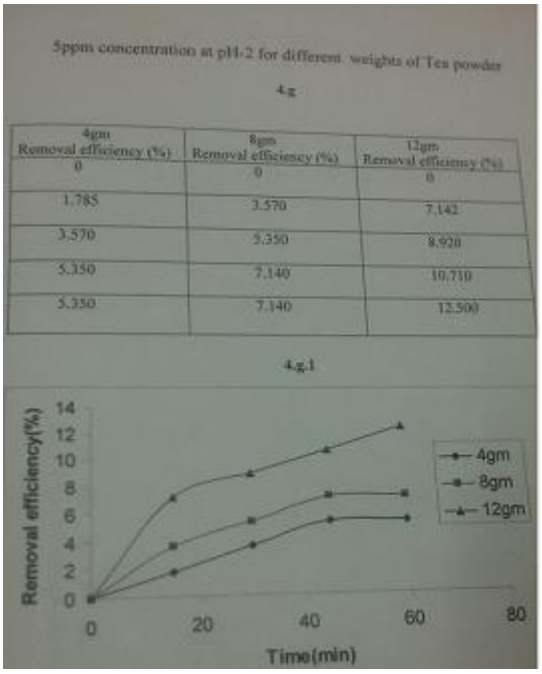
1. 22.6 mg of K2Cr2O7 is dissolved in 1000ml of distilled water to get 8ppm solution.
2. 500ml of 8ppm solution is pipette out and diluted to 1000ml to get 4ppm solution.
3. Similarly the same procedure is followed to get 2,1 ppm solutions.
4. From the prepared 8,4,2,1 ppm solutions 5ml of each sample is pippetted out and 1ml of Diphenyl Carbazide and 1ml of H2SO4 are added to the sample.
5. Each sample is placed in colorimeter to find absorbance.

3.1.1. Experimental Procedure:

1. 1000ml of 5,10,15 ppm solutions of K2Cr2O7 are prepared.
2. From the above solutions 200ml is taken and 4,8,12gm of adsorbents like tea powder, sawdust, coconut coir are added.
3. The above solutions are vigorously shaked for about 1hr.
4. At regular intervals of time(15min) 5ml of the sample is taken and to that 1ml of Diphenyl Carbazide and 1ml of H2SO4 are added.
5. Now, absorbance is found out for the above samples and the corresponding concentrations are determined from the standard plot.

6. The above procedure is carried out at different pH i.e., 2, 7.

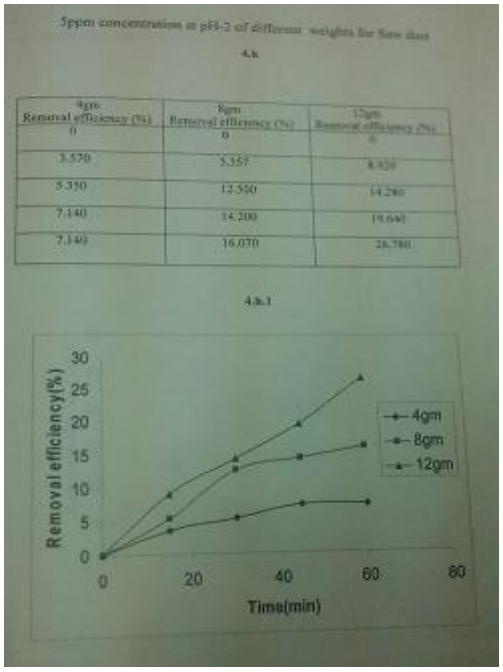
4. RESULTS AND DISCUSSION:


5ppm concentration at pH-2 for different weights of Tea powder

4.g

4gm Removal efficiency (%)	8gm Removal efficiency (%)	12gm Removal efficiency (%)
0	0	0
1.785	3.570	7.142
3.570	5.350	8.920
5.350	7.140	10.710
5.350	7.140	12.500

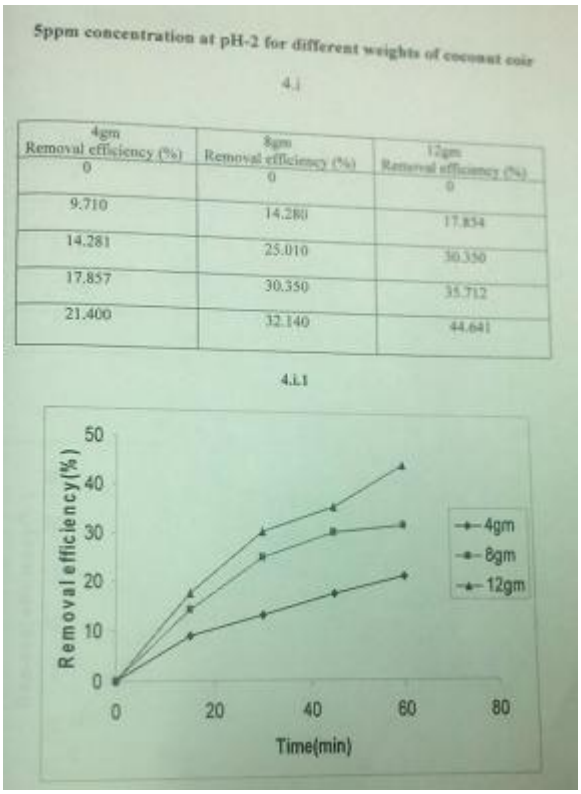
4.g.1


4.h

4gm Removal efficiency (%)	8gm Removal efficiency (%)	12gm Removal efficiency (%)
0	0	0
3.570	5.357	8.920
5.350	12.550	14.280
7.140	14.200	19.640
7.140	16.070	26.780

4.h.1

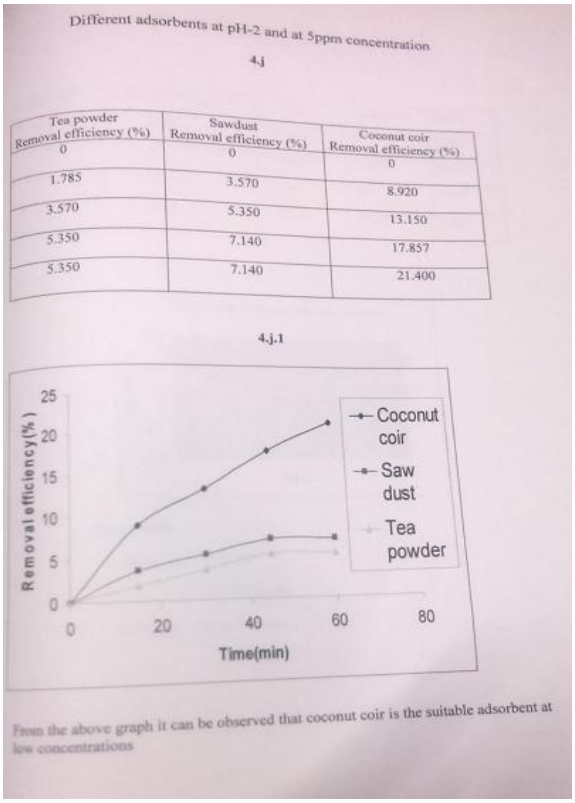
The coconut coir is effective adsorbent for the removal of Cr(VI) from waste water. The firness of Langmuir model shows the formation of monolayer coverage of adsorbate at the outer surface of the adsorbent and the process is endothermic in nature. The mechanism involves an initial rapid rate for the Cr(VI) removal due to surface adsorption followed by intra-particular diffusion, which is the only rate controlling step.


5ppm concentration at pH-2 for different weights of coconut coir

4.i

4gm Removal efficiency (%)	8gm Removal efficiency (%)	12gm Removal efficiency (%)
0	0	0
9.710	14.280	17.854
14.281	25.010	30.350
17.857	30.350	35.712
21.400	32.140	44.641

4.i.1


Different adsorbents at pH-2 and at 5ppm concentration

4.j

Tea powder Removal efficiency (%)	Sawdust Removal efficiency (%)	Coconut coir Removal efficiency (%)
0	0	0
1.785	3.570	8.920
3.570	5.350	13.150
5.350	7.140	17.857
5.350	7.140	21.400

4.j.1

From the above graph it can be observed that coconut coir is the suitable adsorbent at low concentrations

5. CONCLUSION

Biosorption is being demonstrated as useful alternative to conventional system for the removal of toxic metals from industrial effluents. The development of the biosorption process requires further investigation in the direction of modelling, of

regeneration of biosorbent material and of testing immobilized raw biomasses with industrial effluents. Due to the extensive research and significant economic benefits of biosorption, some new biosorbent materials are poised for commercial explotion.
The coconut coir is effective adsorbent for the removal of Cr(VI) from waste water. The firness of Langmuir model shows the formation of monolayer coverage of adsorbate at the outer surface of the adsorbent and the process is endothermic in nature. The mechanism involves an initial rapid rate for the Cr(VI) removal due to surface adsorption followed by intra-particular diffusion, which is the only rate controlling step.
Though this process has not given better efficiency for the removal of Cr but it can be used for the lower concentrations (5ppm).

6. REFERENCES:

1) G. Rich, K. Cherry, Hazardous Waste Treatment Technologies.
2) De, A.K. , 'Environmental Chemistry' Wiley Eastern Limited., New Delhi, India.
3) W.L.McCabe, J.C.Smith,Unit operations of Chemical Engineering(5^{th} edition)McGraw Hill Publisher.
4) B. Bhargavi, UDRI, Dept. of Chem. & Materials Engg. , UDRI Environmental Group, Univ. of Dayton, Dayton, Ohio.