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Experimental Study on Removal of Chromium by Cow Dung Ash and Eucalyptus Leaf Ash as Adsorbents

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Abstract: The presence and persistence of various heavy metals in the day to day environment have been ever increasing as a result of emerging industrial activities and advanced technological developments. These anthropogenic activities pose substantial threat to the environment and the public health due to its toxicity, bioaccumulation in the food chain and persistent nature. Industrial wastewater contains high levels of heavy metals that may pollute the water once it is discharged to the nature. These metals include arsenic, chromium, copper, zinc, aluminum, cadmium, lead, iron, nickel, mercury and silver. Among the above said heavy metals, Chromium (Cr) is one of the most toxic substances and is introduced into the environment through a variety of industrial activities. In order to remove the chromium from the contaminated water there are lot of methods available, even though they are not in natural way. In this study naturally availing materials like Cow dung ash and eucalyptus leaves ashes are used to remove the chromium by adsorbent method. Since the collected chromium contaminated waste water from the industry will have only a particular Cr+ concentration and pH value, an aqueous solution has been prepared with unique concentration and with different pH values. And activated ashes were added separately to the aqueous solution with different dosages and varying contact periods. From the careful investigation and interpretation of results it has been noted that the Cow dung ash has effectively removed the chromium content when it was added 6 g L^{-1} to the 1000 mL of aqueous solution. In the view of contact time of the adsorbent, 3 h of period been an ideal one and pH doesn't had a significant effect.

Key words: Chromium contamination, removal of heavy metal, activated carbon, cow dung ash as an adsorbent, Eucalyptus leaves ash as an adsorbent

INTRODUCTION

The presence and persistence of various heavy metals in the day to day environment have been ever increasing as a result of emerging industrial activities and advanced technological developments. These anthropogenic activities pose substantial threat to the environment and the public health due to its toxicity, bioaccumulation in the food chain and persistent nature (Gavrilescu, 2004). Among the various heavy metals, Chromium (Cr) is one of the most toxic substances and is introduced into the environment through a variety of industrial activities. Historically it has been used in a wide range of industrial applications including steel, pigments, wood preservatives, electroplating, metal finishing, dyes, leather tanning, textiles and chemical manufacture.

Chromium is widely used in alloys such as stainless steel, chrome plating and metal ceramics. Earlier, chromium plating was commonly used (Barnhart, 1997) to give steel a polished silvery mirror coating. Also, chromium is used in metallurgical industry to impart corrosion resistance and a shiny finish, in dye and paint industries, to produce synthetic rubies, as a catalyst in dyeing and in the tanning of leather, to make molds for the firing of bricks and Chromium Oxide (CrO_2) is used to manufacture magnetic tape. In specific, Hexavalent Chromium (Cr(VI)) is one of the world's most strategic and critical materials having a wide range of uses in the metal and chemical industries. The efficiency of activated carbons prepared by various chemical activations in the removal of hexavalent Chromium [Cr(VI)] was (Palmer and Wittbrodt, 1991) investigated in this study.

MATERIALS AND METHODS

Eucalyptus leaves:

- Eucalyptus leaf is legendary for its ability to clear respiratory and nasal passages of congestion and mucus, thus relieving colds, flu, sinusitis, influenza, croup, emphysema, pulmonary tuberculosis, chronic and acute bronchitis, sore throats, asthma and dry coughs

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- Eucalyptus leaf contains substances that have expectorant, antibacterial and antiseptic properties that are believed to help reduce inflammation and reduce fevers
- When inhaled, eucalyptus prompts the Eustachian tubes connecting the middle ear and the throat to open and when fluids drain from the ear as a result, earache pain and pressure is often relieved

Cowdung:

- In many parts of the developing world and in the past in mountain regions caked and dried cow dung is used as fuel
- Cow dung may also be collected and used to produce biogas to generate electricity and heat.
- The gas is rich in methane and is used in rural areas to provide a renewable and stable source of electricity
- In cold places, cow dung is used to line the walls of rustic houses as a cheap thermal insulator

Low cost adsorbent preparation

Activated eucalyptus leaves: The collected Eucalyptus leaves are washed repeatedly with distilled water and kept for drying at room temperature (Agarwal *et al*., 2006). The dried eucalyptus leaves are crushed and passed through 30 mesh BSS screens. Eucalyptus leaves are activated by treating 1 part of eucalyptus leaves with 1.8 parts by weight of concentrated HCL and kept in the oven for 24 h. The treated leaves are washed with distilled water to remove free acids and further dried for few hours. The Fig. 1 shows the raw leaves as collected and the final activated powder material ready to be used as absorbent.

Activated cow dung: The dried cow dung is treated with concentrated H_2SO_4 in the ratio of 1:1 and kept in the oven for 24 h. Then the activated cow dung is washed with the distilled water to remove the free acids and dried for few hours. Figure 2a, b shows the raw cow dung as collected and the final activated powder material ready to be used as absorbent.

Preparation of aqueous solution: In this research work, the aqueous solution is employed rather than the collected chromium contaminated waste water from the industry to study the influence of proposed activated cow dung and eucalyptus leaf. The reason for the use of aqueous solution for this research study is, the collected chromium contaminated waste water from the industry will

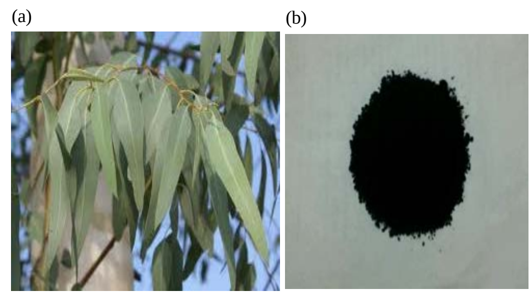

Fig. 1: a) Eucalyptus leaves as obtained; b) Activated eucalyptus leaves

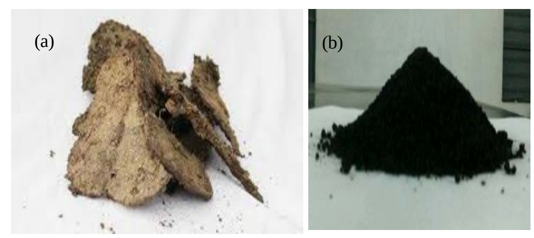

Fig. 2: a) Cow dung dried; b) Activatedcow dung

Fig. 3: Aqueous solution

have only a particular Cr+ concentration and pH value. A stock solution of Cr(VI) is prepared by dissolving 2.8287g of $k_2cr_2o_7$ in 1000 mL of water. The prepared solution is diluted as required to obtain standard solution. Initial concentration of prepared solution is 1000 ppm. The prepared aqueous solution is shown in Fig. 3.

To study the presence of chromium in the prepared solution a CONFIRMATORY TEST is carried out. In the 10 mL of prepared aqueous solution, we add 1 mL of Hydrogen Peroxide (H_2O_2) and add 2 mL of Sodium Hydroxide drop wise. Then heat solution in the boiling water bath for a several minutes. The presence of Chromium on the solution is confirmed through the change in solution as yellow colour (Cr_4^{2-}).

Experimental study

Preliminary tests: The use of absorbents should not significant alter the characteristics of the potable drinking water. For that, the preliminary studies such as evaluating p^H value (Muthukrishnan and Guha, 2008) and turbidity tests were carried out in prepared aqueous solution.

Test matrix: To the study the influence and effectiveness of the proposed low cost adsorbents, the following variability's were considered in the test matrix. The variability includes:

- Varying Contact time (1-3 h)
- Differing dose of adsorbents (4, 6, 8, 10 g)
- Water with different pH value (6, 7, 8 and 9.2)

The detailed test matrix is shown in Table 1. The test samples were prepared for various contact hours (1, 2 and 3 h contact time) with differing pH value e (6, 7, 8 and 9.2) and with varying chromium dosages from 4-10 g L^{-1}. For 1 h contact time, 7 pH, dosages were changed from 4-10 g. The test matrix includes total 96 samples to be tested with 48 no's each for Cow Dung and Eucalyptus Leaves.

- No. of samples for cow dung = 48
- No. of samples for Eucalyptus Leaves = 48
- Total no. of samples for all adsorbents = 96

The 80 mL of prepared aqueous solution, the different dosage values 4, 6, 8, 10 g with different pH values 6, 7, 8 and 9.2 at different contact hours 1, 2, 3 were prepared by stirring in a flocculator. At the end of each contact time, the mixture was filtered using filter paper and filtrate was stored in sample bottles to test the concentration of chromium in the test sample. The initial concentration present in the test samples can be evaluated as shown as:

- 2.287 g L^{-1} of $K_2Cr_2O_7$ = 1 g L^{-1} of chromium
- 1 g L^{-1} of Chromium = 1000 mg L^{-1} of chromium
- 1000 mg L^{-1} = 1000 ppm (Initial concentration of Chromium)

Absorbance (A): The spectrometer works by passing a light beam of the selected wavelength, through a cell containing the sample and compares the Intensity (I_t) of the transmitted light, with the Intensity (I_0) of the same light transmitted through a reference cell, without the sample. The output from the absorbance, A given by:

$$A = \log_{10}(I_0 / I_t)$$

The value of the absorbance for a given sample depends on the wavelength of the light beam. The standard absorbance value (A) for varying concentration for the spectrophotometer used in this experimental research work is shown in Table 2 and Fig. 4. In the Fig. 4, the slope in the standard graph, m = 0.1154 is used to calculate the final concentration of chromium in the test sample.

Batch experiment: The batch experiments are carried out in 1000 mL beaker by agitating a pre-weighted amount of the adsorbent with 100ml of the aqueous Cr (VI) solution for a predetermined period on a flocculator. The adsorbent is separated with filter paper.

Table 1: Test Matrix for the Cow Dung and Eucalyptus leaves

Concentration (C) in PPM	Absorbance (A)
0	0
2	0.2082
4	0.4658
6	0.6239
8	0.9125
10	1.2058

Table 2: Absorbance Value (A) for differing concentration

Contact time (h)	pH	------ Dosage (g L^{-1})-----				No. of samples
1	6.0	4	6	8	10	4
	7.0	4	6	8	10	4
	8.0	4	6	8	10	4
	9.2	4	6	8	10	4
2	6.0	4	6	8	10	4
	7.0	4	6	8	10	4
	8.0	4	6	8	10	4
	9.2	4	6	8	10	4
3	6.0	4	6	8	10	4
	7.0	4	6	8	10	4
	8.0	4	6	8	10	4
	9.2	4	6	8	10	4

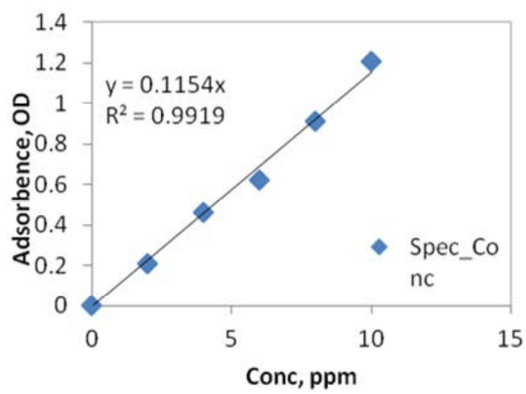

Fig. 4: Absorbance value (A) vs concentration

The amount of Cr (VI) adsorbed by the different adsorbents is calculated using the following equation:

$$Q = (C_0 - C_e)\, V/W$$

Where:

Q = Amount of Cr (VI) adsorbed by the adsorbent (m gL^{-1})
C_0 = Initial concentration of Cr (VI) (g L^{-1})
C_e = Concentration of Cr at equilibrium (g L^{-1})
V = Initial volume of Cr solution
W = Weight of the adsorbent (g)

The concentration of free Cr (VI) ions in the effluent is determined spectrophotometrically by developing a purple-violet color with 1, 5-diphenylcarboxide in acidic solution as a complexing agent. The absorbance of the purple-violet coloured solution is read at 540 nm after 20 min.

RESULTS AND DISCUSSION

Eucalyptus leaves ash: In order to increase the removal of chromium content from the aqueous solution, the eucalyptus leafs were burned in high temperature and ashes were added with various increasing percentage such as 4, 6, 8 and 10% by its dry weight. Also the contact time of aqueous solution and eucalyptus ash has been varied such as 1, 2 and 3 h in the view of obtaining the effect of contact time on the chromium removal.

Figure 5-8 are shows the results made out from the tests conducted on the aqueous solution with the various pH level and various increments in the dosage level such as 4, 6, 8 and 10% of eucalyptus ash and from the results it's been observed that the removal quantity of chromium from the aqueous solution has been constantly decreased up to 0.021% from the lower value of 4% to higher value of 10% in an hour of contact time. Also the same trend has been noted in the other contact periods of two hours and three hours. Here the value of chromium removal was gradually decreased with the increase in the contact time except in the presence of 6% additive.

Cow dung Ash: In the view of obtaining the effect of cow dung over the removal of chromium, the cow dung which is collected has been dried and burned with high temperature resulting as an ash has been added to the aqueous solution made with various pH levels. And the cow dung ash has been mixed with different proportions such as 4, 6, 8 and 10% by its dry weight to find out the optimum level of additive. In order to find out the effect of contact period over the effectiveness of chromium removal, the solution added with cow dung ash was kept in different time limits of 1, 2 and 3 h.

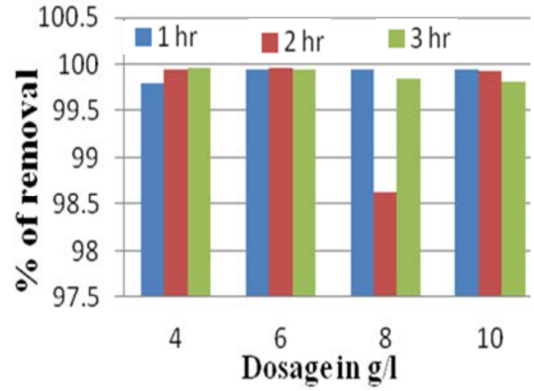

Fig. 5: Removal of chromium percentage with varying dosage of eucalyptus with pH of 6

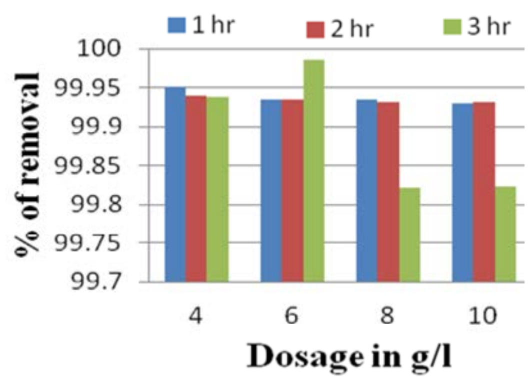

Fig. 6: Removal of chromium percentage with varying dosage of eucalyptus with pH of 7

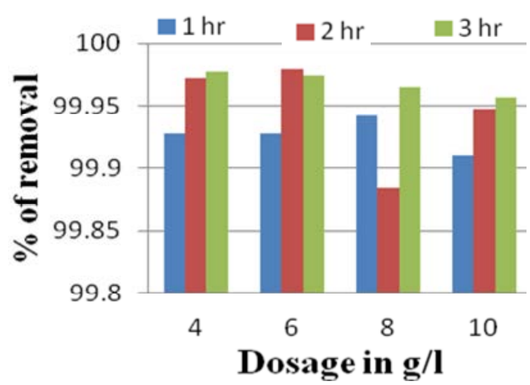

Fig. 7: Removal of chromium percentage with varying dosage of eucalyptus with pH of 8

Figure 9-12 are shows the results made out from the tests conducted on the aqueous solution with the various pH levels and with various increments in the dosage level

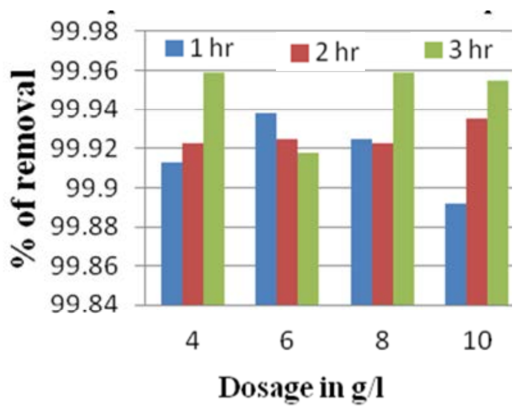

Fig. 8: Removal of chromium percentage with varying dosage of eucalyptus with pH of 9.2

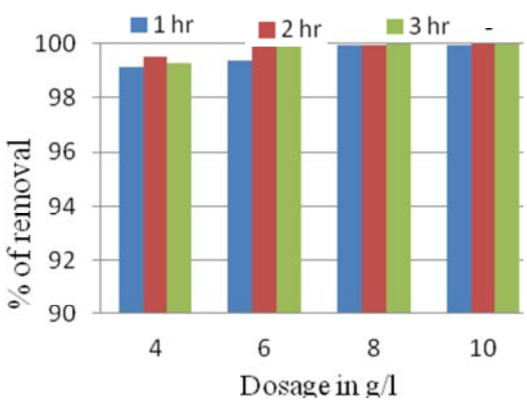

Fig. 9: Removal of chromium percentage with varying dosage of cow dung with pH of 6

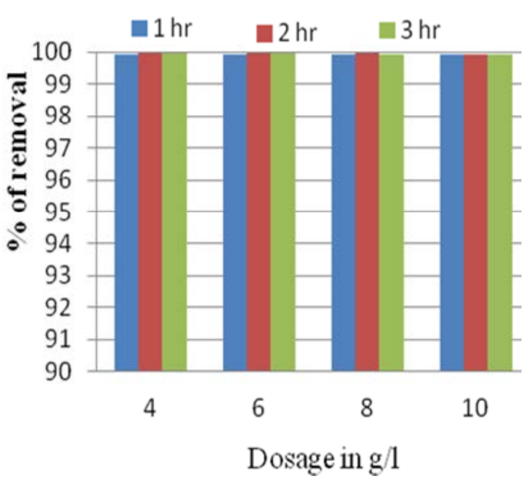

Fig. 10: Removal of chromium percentage with varying dosage of cow dung with pH of 7

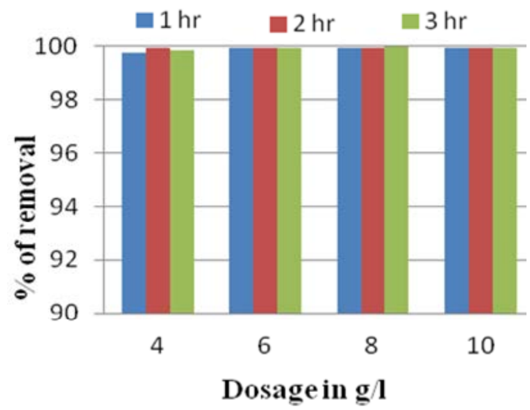

Fig. 11: Removal of chromium percentage with varying dosage of cow dung with pH of 8

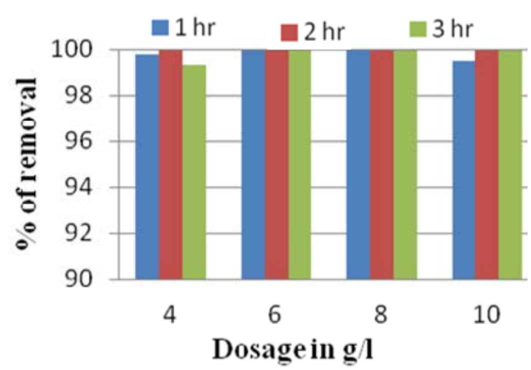

Fig. 12: Removal of chromium percentage with varying dosage of cow dung with pH of 9.2

such as 4, 6, 8 and 10% of cow dung ash. From the figures it has been observed that the chromium contaminant has effectively removed from the aqueous solution by adding the cow dung as a stabilizer than the eucalyptus leaf ash. In precise the chromium content removal percentage has been increased from 99.142-99.942% for the dosage level of 4-10%. And this 0.806% of increase in the removal percentage was found in the 1 h of contact period. In other hand, the increment in the contact time also made an effective role in contaminant removal. It has been more with 3 hours of contact time when compared with an hour of contact. Among all the level of dosages, 6% of dosage shows higher value of increase with respect to the contact time (0.595%).

From the careful study on the results and the interpretations the following conclusions have made. From Fig. 12-15, it can be concluded that for a constant level of pH Cow dung ashes effectively removed the chromium than the eucalyptus ash. And increment in the dosage level of eucalyptus.

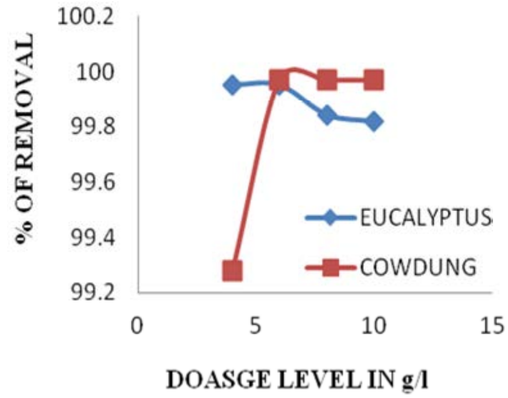

Fig. 13: Comparison between eucalyptus and cow dung with pH of 6

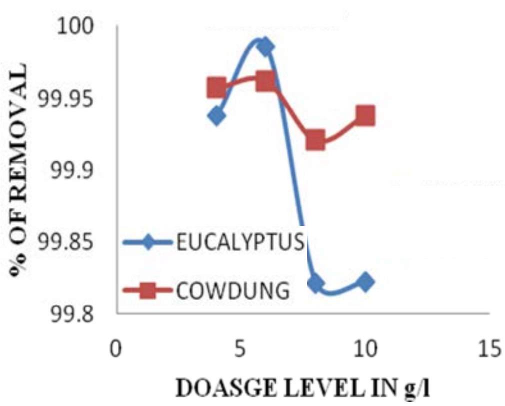

Fig. 14: Comparison between eucalyptus and cow dung with pH of 7

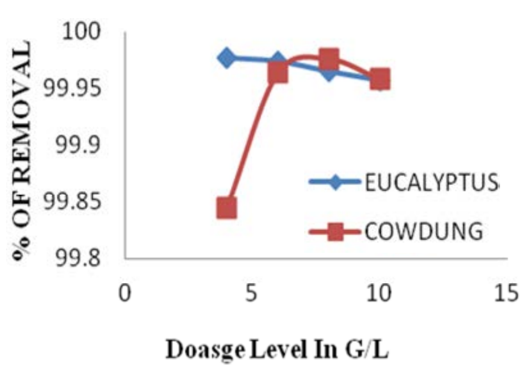

Fig. 15: Comparison between eucalyptus and cow dung with pH of 8

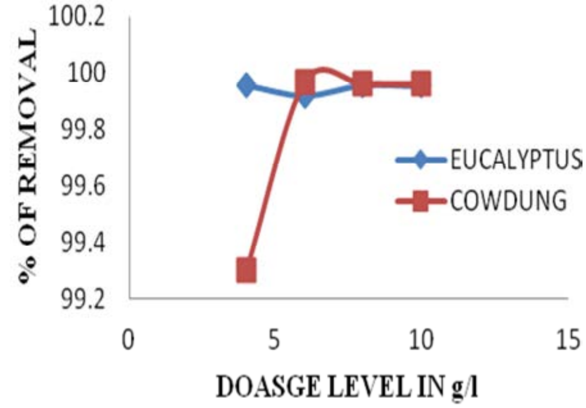

Fig. 16: Comparison between eucalyptus and cow dung with pH of 9.2

doesn't show the increase in the removal percentage meanwhile cow dung ash shown the increment in the removal percentage with the increase in the dosage level for some extent.

CONCLUSION

Finally, it can be concluded that Cow dung ash will be an effective adsorbent with proportion of 6 grams per litre at any level of pH.

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