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Comparative Study of Removal of Chromium -IV Ion from Aqueous Solution Using Eucalyptus, Neem and Mango Leaves

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Abstract:- The present work was focused on investigation of effect of solution concentration, contact time and pH variation on ability of the eucalyptus, neem and mango leaves in removing chromium ions form aqueous solution. The dried leaves were washed with deionised water, air-dried and ground using ball mill then sieved. The leaf powder was added to 1M stock metal ion solution made from potassium dichromate. The concentrations, contact time and pH of each stock solution were varied. These mixtures were shaken at a constant rate of 250 rpm, filtered and analyzed by Avanta Atomic Absorption Spectrophotometer. All the experiments were carried out in duplicated and the average value were used for further calculation. For Cr-VI, the maximum adsorption was obtained at pH 2 and 7, agitation rate of 150 rpm, particle size of 75 μm, initial concentration of Cr ions of 5 mg/l and contact time 20 min.

I. INTRODUCTION

One of the heavy metals is chromium (Cr-VI) is present in waste water from several industries such as metal cleaning and plating baths, refineries, paper and pulp, tanning, dyes and pigments, wood preserving, glass, ceramic paints, catalysis chemical manufacturing etc. which is present from 5 to 220 mg/dm^3 which leave into environment [1-3]. The effluent from industries containing Cr-VI is considered by the International Agency for Research on Cancer (IARC) (1982) as powerful carcinogenic agent that modifies the DNA transcription process causing important chromosomic aberration [4, 5].

Various technologies are employed for removing toxic ions from water, which include chemical precipitation, reverse osmosis, ion-flotation, evaporation, ion-exchange and adsorption [6, 7]. Most of these methods suffer from drawbacks such as incomplete metal removal, high capital and operational costs, requirements of expensive equipment and monitoring system, high reagent and energy requirements, generation of toxic sludge, other waste products that require disposal, membrane scaling, fouling and blocking [8, 9]. Adsorption by activated carbon is one of the effective techniques for chromium removal from waste water because of high surface area, highly porous character and relatively low-cost. The use of activated carbon for removing chromium from waste water has been received a great attention from decades [10, 11]. Thus this study is aimed at utilizing waste eucalyptus, neem and mango leaves as adsorbents in the removal of Cr-VI in aqueous solution by varying the experimental conditions such as contact time, metal ion concentration, pH which could be applied in reduction of heavy metal pollution in the environment.

II. EXPERIMENTAL STUDIES

2.1 Preparation of bio-absorbent

Standard stock solution of 1 mg/mL of chromium (VI) was prepared from potassium dichromate [12]. Sample of eucalyptus, neem and mango leaves was collected from respective trees. The leaves were separated from their branches washed thoroughly with deionised water and dried in air-drier. After through drying, the leaves ground using ball mill and sieved to produce 500 μ to 1 mm size of powder. The ground leaves powder were soaked in H_2SO_4 in the ratio of 1: 2 (H_2SO_4: leaves powder) for 24 hours. Then leaves powder were washed with deionized water and was kept in muffle furnace at 120 °C for 1 hour for removal of water.

2.2 Batch sorption experiment

Batch experiments were carried out at room temperature using a conical flask by shaking a mixture of 0.1 g of prepared leaves powder and 20 mL of Cr solution in a centrifuge tube, at agitation rate of 150 rpm for allowing sufficient time for adsorption equilibrium. All samples were carried out in duplicate under the same conditions and the average results were taken. After agitation, the powder was removed by filtration using filter paper. The concentration of Cr in the filtrates as well as in the control samples were determined by using GBC Avanta Flame atomic Absorption Spectroscopy (AAS) spectrometer. Percentage removal of metal ions can also be computed using the following equation:

$$\%R = \frac{C_0 - C_e}{C_0} X\ 100$$

Where Co =Initial concentration of Cu (mg/L), Ce = Concentration of Cu at equilibrium state (mg/L)

2.3 Determination of the effect of pH

A 20.0 ml of the standard Cr solution was poured into each of six conical flasks and the pH condition varied from 2 to 10 as 2, 4, 6, 8 and 10, respectively by the addition of either dilute HC1 or NaOH using a pH meter at constant particles average size 75 μm, initial metal concentration 5mg/l, contact time 20 min, agitation rate 150 rpm for 20 ml solution. Then 0.1 g of the pretreated biomass (leaf powder) was added to the standard metal ion solutions of Cu and the flasks tightly covered with cellophane and shaken vigorously for 2 h to reach equilibrium and agitation speed was maintained at 150 rpm. The suspensions were filtered and analyzed by using pH Meter.

2.4 Determination of the effect of Cu concentration

Study on effect of initial metal concentration 5 mg/l, 10 mg/l and 15 ml/g on % of removal of Cr-VI ions for eucalyptus, neem and mango leaves at constant contact time of 20 min, agitation rate of 150 rpm , pH value of 7, average particle size of 75 μm for 20 ml solution

2.5 Determination of the effect of contact time

A 20 ml solution of the standard Cr solution was poured into each eight conical flasks and the contact time varied from 5, 10, 15, 30, 60, 120, 180 and 360 min at constant particles average size 75 μm, initial metal concentration 5mg/l, pH value of 7, agitation rate 150 rpm for 20 ml solution

2.6 Determination of the effect of agitation rate

Study the effect of agitation rate (50 rpm, 150 rpm and 250 rpm) on % of removal of Cr-VI ions for eucalyptus, neem and mango leaves at constant contact time of 20 min, initial metal concentration 5mg/l, pH value of 7, average particle size of 75 μm for 20 ml solution.

2.7 Determination of the effect of particle size

The effect of particle size was studied by using four different sizes of leaves powder, which are 50-100 μm, 100-250 μm, 250-500 μm, 500-1000 μm of leaves powder which were sieved into desired size was agitated at constant contact time of 20 min, initial metal concentration 5mg/l, pH value of 7, agitation rate 150 rpm for 20 ml solution

III. RESULTS AND DISCUSSION

3.1 Effect of pH

Fig. 1 shows the effects of pH on the adsorption of Cr-VI by eucalyptus, neem and mango leaves. The pH of the aqueous solution is an important operational parameter governing the adsorption process of metal ions in solution. This is because it affects the solubility of the metal ions concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of adsorbate during reaction. The pH was varied from 2 to 11, while the other operational parameters such asadsorbent dosage, agitation time, initial ion concentration and particle size were kept at the optimum. The % removal decreased initially between 2 to 4 then increases 4 to 11. At neutral solution the removal rate very nominal just below 20%. Maximum adsorption of Cr-VI was observed at the both acidic and basic solution. This is because at lower pH there is increase in H+ ions on the carbon surface, similarly OH^{-1} ions increases in basic solution on the carbon surface resulting in significant strong electrostatic attraction.

3.2 Determination of the effect of contact time

The Fig. 2 shows the effect of contact time on sorption of Cr-VI ions by eucalyptus, neem and mago leaves and also tabulated in Table 2 and other parameters were kept constant. For these cases, pH of 11 was used for Cr-VI solution solution and Cr concentration in water was 5 mg/L. For Cr removal rate reaches up to 98.32 by neem leaves, when contact time was 20 min and then little change of sorption rate was observed. This result revealed that adsorption of Cr was fast and the equilibrium was achieved after 20 min of contact time. Taking into account these results, a contact time of 20 min was chosen throughout experiments.

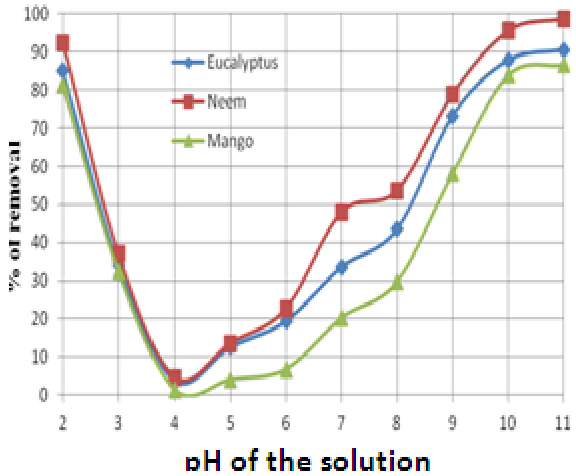

Fig.1 Effect of pH on % removal of Cr ions by eucalyptus, neem and mango leaves at particle size of 75 µm, initial metal concentration of 5mg/l, contact time of 20 min, agitation rate of 150 rpm for 20 ml solution

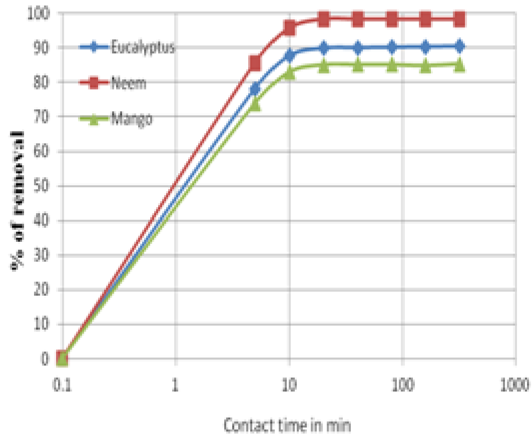

Fig. 2 Effect of contact time on % removal of Cr-VI ions by eucalyptus, neem and mango leaves at particle size of 75 µm, initial metal concentration of 5mg/l, pH values of 11, agitation rate of 150 rpm for 20 ml solution.

The fast initial % removal occurred in the early stage of adsorption was due to the fact that most of the binding sites on leaves were free which allowed quick binding of Cr-VI ions on the biomass.. As the binding sites became exhausted, the uptake rate slowed down due to competition for decreasing availability of actives sites by metal ions. According to the test results, agitation time was fixed at 20 minutes for the rest of the batch experiment to ensure equilibrium was achieved. The plots of metal removal as a function of time are single, smooth, and continuous, suggesting the possibility of the formation of monolayer coverage of Cr ions at the outer surface of adsorbent.

3.3 Determination of the effect of particle size

The particle size of adsorbents is one of important factors affecting the adsorption capacity as it influences the surface area of adsorbent. The lower the particle size higher the surface area hence it absorbs more metal ions. The present study the average particle size was used in the range of 75µm to 750 µm. Fig. 3 shows the variation of Cr-VI removal rate with different particle size and other parameters kept constant.

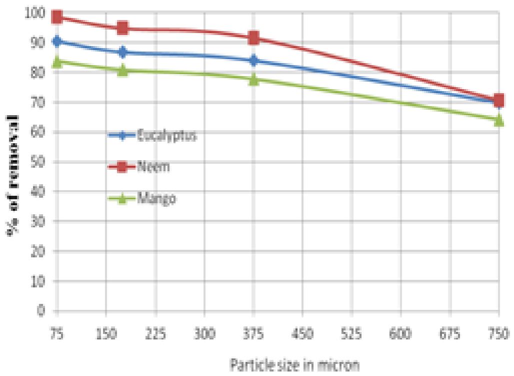

Fig. 3 Effect of particle size on % removal of Cr ions by eucalyptus, neem and mango leaves at pH values of 11, initial metal concentration of 5mg/l, contact time of 20 min, agitation rate of 150 rpm for 20 ml solution.

The results indicated that the metal ions uptake increased with decreasing particle size. When the particle size decreased from 750 µm to 75 µm the % removal of Cr-VI ions increased 85% to 98 % for neem leaves. The higher uptake with decreasing particle size was attributed to the fact that smaller particles had larger external surface area compared to larger particles, hence more binding sites were exposed on the surface and thus, leading to higher adsorption capacity since adsorption is a surface process. Apart from that, particles with smaller size also moved faster in the solution compared to larger particles, consequently, the adsorption rate was faster.

3.4 Determination of the effect of agitation rate

Agitation is also one of the important parameters in adsorption phenomena as it influences the distribution of the solute in the bulk solution and the formation of the external boundary film. The effect of agitation rate on sorption was investigated by conducting experiments at agitation rate of 50 rpm to 200 rpm at constant parameters. Fig. 4 shows the variation of Cr-VI ions uptake with agitation rate for different leaves. It was observed that the percentage uptake increased when the agitation rate was increased while after 150 rpm it decreased hence 150 rpm is taken as optimum value for complete experiments. For 150 rpm the % removal was 90.59%, 98.60% and 86.54% for the eucalyptus, neem and magno leaves respectively. This was because increasing the agitation rate reduced the boundary layer resistance to mass transfer surrounding the sorbent particles, resulting in higher sorption rate. In addition to that, higher agitation rate also spread the Cr-VI ions in the solution, providing better access to the active sites on adsorbent surface.

They investigated the uptake of metal ions by varying the agitation rate at 50 rpm and 150 rpm reported an increase in the percentage removal with increasing agitation rate due to reduction in film boundary layer of sorbent particles, which increased the external mass transfer coefficient.

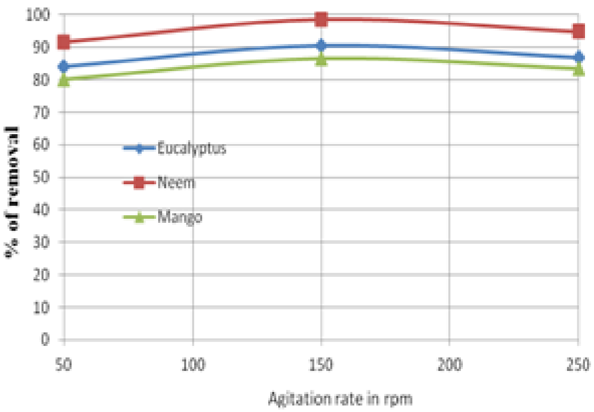

Fig. 4 Effect of agitation rate on % removal of Cr-VI ions by eucalyptus, neem and mango leaves at particle size of 75 µm, initial metal concentration of 5mg/l, contact time of 20 min, pH values of 11 for 20 ml solution**.**

3.5 Determination of the effect of Cr-VI concentration

The impact of adsorbent dose on the adsorption of Cr-VI in shown is Fig. 5. From Fig. 5, it can be observed that there is a general increase in the adsorption of Cr-VI as the adsorbent dose increased. The other parameters like in previous investigations were kept constant during the contact process. But the results showed that the % of removal Cr-VI ions decreased from 98.36% to 75.02 % with the increment of initial Cr-VI ions concentration from 5 mg/L to 10 mg/L for neem leaves.

According to Gupta *et al*.[11], at lower metal ions concentration, the percentage removal was higher due to larger surface area of adsorbent being available for adsorption. When the concentration of Cr-VI ions became higher, the percentage removal decreased since the available sites for adsorption became less due to saturation of adsorption sites. At a higher concentration of Cr-VI ions, the ratio of initial number of moles of Cr-VI ions to the adsorption sites available was higher, resulting in lower adsorption percentage.

IV. CONCLUSION

- The removal of Cr-VI from aqueous solutions strongly depended on pH of the solution, agitation rate, initial Cu concentration, contact time and particle size.
- For Cr-VI, the maximum adsorption was obtained at pH 2 and 11, agitation rate of 150 rpm, particle size of 75 μm, initial concentration of Cu ions of 5 mg/l and contact time 20 min.
- Maximum removal of Cr-VI from aqueous solutions can be obtained if all of the five process parameters are optimized.
- From this study, it was observed that neem leaves can be used as an alternative low cost adsorbent for Cu remediation for polluted water and wastewater.

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