NIPES Journal of Science and Technology Research 3(1) 2021 pp.52 - 57 pISSN-2682-5821, eISSN-2682-5821

NIPES

Journal of Science and Technology Research

Journal homepage: www.nipesjournals.org.ng

Effects of Some Experimental Variables on the Adsorption of Hexavalent Chromium from Aqueous Solution Using Red Mangrove (*Rhizophora mangle*)

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Article Info

Keywords:
hexavalent chromium, mangrove biomass, particle size, pH, initial concentration, aqueous solution

Received 23 January 2021
Revised 08 February 2021
Accepted 16 February 2021
Available online 01 March 2021

https://doi.org/10.37933/nipes/3.1.2021.6

https://nipesjournals.org.ng

Abstract

The effects of particle size, pH and initial concentration of adsorbate on the adsorption of hexavalent chromium from aqueous solution using red mangrove biomass (leaves, bark and root) as adsorbents were investigated by batch adsorption method. The main objective was to analyze and report the efficiency of red mangrove leaves, bark and root in removing hexavalent chromium ion from aqueous solution in terms of particle size of adsorbent, initial concentration of hexavalent chromium and pH of solution. The adsorption was found to be dependent on all the variables. The percentage hexavalent chromium adsorbed decreased as particle size of red mangrove biomass powder, initial concentration of hexavalent chromium and pH of solution increased. Maximum adsorptions were observed at particle size of 150μm, initial concentration of 20ppm and pH of 2. Minimum adsorptions were obtained at particle size of 2000μm, initial concentration of 100ppm and pH of 9. However, results show greater adsorption by red mangrove root and leaves than the bark, suggesting that red mangrove biomass especially the root and leaves can be used as low-cost adsorbent for the removal of hexavalent chromium ion from aqueous solution. Protonation/deprotonation and surface association have been mentioned as possible reaction pathways in the pH and in the non-pH-controlled adsorptions.

1. Introduction

Adsorption, the attraction of a substance (adsorbate) on the surface of a solid or liquid (adsorbent), is a powerful technique for treating domestic and industrial effluents [1]. Adsorption process can be influenced by manipulation of any or some of its several operating conditions including nature and physical condition of the adsorbent material, initial concentration of adsorbate, temperature, pH of the medium, contact time and distribution coefficient [2 - 8].

Hexavalent chromium, a highly soluble chromate anion, is of great concern to man due to its high level of toxicity, non-biodegradability and thus significant danger to human health [9, 10]. Therefore, it is necessary to device ways of reducing the concentration of hexavalent chromium in our environment to acceptable levels. Technologies often used by researchers for the removal of hexavalent chromium ion from waste water such as ion-exchange, electrolytic method and reverse osmosis are exorbitant. Moreover, adsorbents used in the past were synthetic and non-biodegradable, not readily available and pose some health challenges. For these reasons, researchers are continually looking for cheaper technologies including readily available, environmentally friendly, effective and low-cost agricultural materials as adsorbent for the removal of hexavalent chromium ion from aqueous solution. In a recent article [11] on the evaluation of the effects of some parts of red mangrove on the adsorption of Cr (vi) ion in aqueous medium, it was reported that the leaves and roots of the plant could act as adsorbents for the removal of Cr (vi) ion in aqueous solution.

Red Mangrove *(Rhizophora mangle*) is a dominant mangrove specie that grows abundantly in the coastal areas of southern Nigeria. The present study aims at evaluating the effects of the size of adsorbents, initial concentration of hexavalent chromium ion and pH of solution on the removal of hexavalent chromium ion by red mangrove biomass in aqueous solution. In continuation, the adsorption process was carried out by batch method.

2. Methodology

The collection and processing of fresh red mangrove leaves, bark and root samples as well as the instrumentation employed in this work are similar to that by Iboroma *et al.* [11] but with slight modification of experimental procedures to describe the effects of particle size, initial concentration of hexavalent chromium ion and pH of medium. Dried mangrove samples were ground to powder with mechanical grinder and sieved into five different sizes using test sieves of different mesh sizes (1.5×10^2, 5.0×10^2, 10×10^2, 12×10^2 and 20×10^2 μm) and stored fresh in tightly covered plastic container without modification. Stock solution (1000ppm) of hexavalent chromium ion ($Cr_2O_7^{2-}$) was prepared by dissolving 2.828g of potassium dichromate ($K_2Cr_2O_7$) in 1 liter of deionized water. Working solutions (10ppm, 20ppm, 40ppm, 60ppm and 100ppm) were prepared using appropriate dilutions of the stock solution. All pH measurements were made using pocket-sized pH Meter (HANNA instrument: H196107 pH). Atomic absorption spectrophotometer, AAS (Agilent MP-AES 42100) was used to measure the concentration of hexavalent chromium ion in test solution after each adsorption process. For particle size variation, exactly 0.5g of the adsorbent materials of size 1.5×10^2µm was weighed into a beaker containing 20ml of 100ppm hexavalent chromium solution and the mixture equilibrated on an orbital shaker (Stuart orbital shaker) at 150rpm for 90 minutes. The procedure was repeated for other particle sizes (5.0×10^2, 10×10^2, 12×10^2 and 20×10^2µm). For concentration of hexavalent chromium, 20ml of 10ppm of the hexavalent chromium ion solution was added to 0.2g of the mangrove sample of particle size 500µm. The sample bottle was covered and mixture equilibrated for 90 minutes. The procedure was repeated using 20, 40, 60 and 100ppm of the hexavalent chromium ion solutions. The effect pH was analyzed by adding 0.5g of 500μm mangrove powder to a beaker containing 20ml of 40ppm hexavalent chromium ion solution. The pH of the mixture was adjusted to 2 by adding few drops of either 0.1M HCl or 0.1M NaOH solution and the resulting mixture equilibrated at the speed of 150rpm for 90 minutes. The mixture was filtered and the residual concentration of hexavalent chromium ion in solution after adsorption determined using AAS. The procedure was repeated at other pH values (4.0, 5.0, 8.0 and 9.0). Experimental procedures for particle size and hexavalent chromium ion concentration were carried out at ambient solution pH and temperature. The percentage (%) of hexavalent chromium ion adsorbed on various parts of red mangrove was calculated from the difference between the initial (C_o) and final (C_f) hexavalent chromium concentrations using equation 1.

$$\%\, Hexavalent\ Chromium\ Adsorbed = \left(\frac{C_0 - C_f}{C_o}\right) \times 100 \qquad (1)$$

3. Results and Discussion

3.1 Effects of experimental variables on the adsorption of hexavalent chromium ion

a. Particle Size:

The amount of materials adsorbed by a given mass of adsorbent in an adsorption process depends largely on the nature and porosity of the adsorbent [12, 13]. Influence of particle size accounts for surface area as well as porosity. Thus, % hexavalent of chromium ions adsorbed are plotted against particle size of red mangrove leaves, bark and root powder adsorbents (Figure 1).

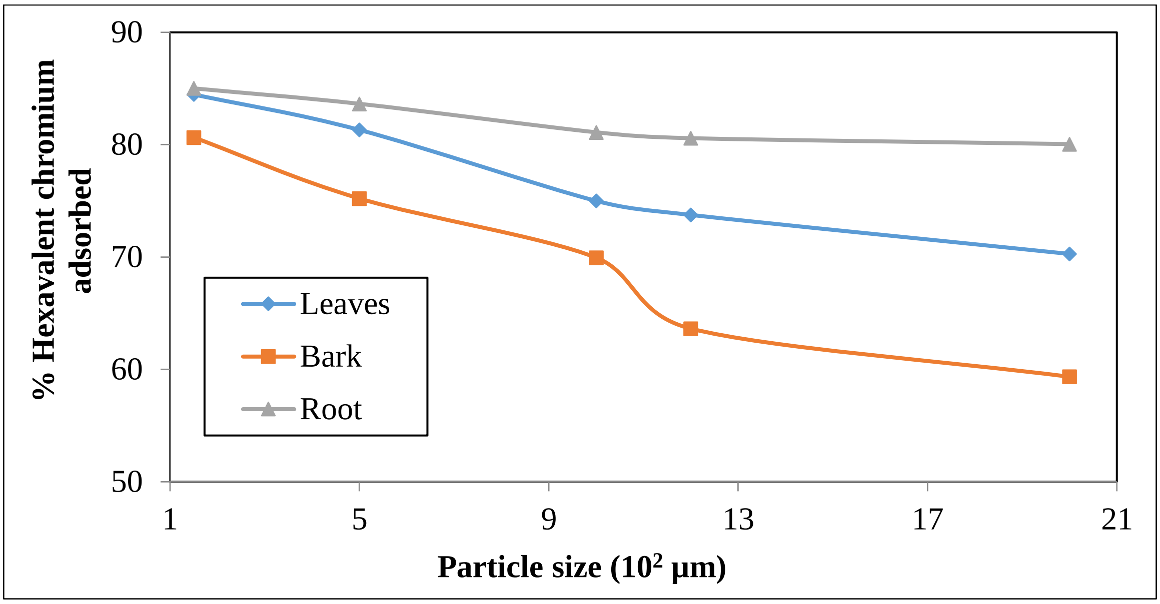

Figure 1: Graph of % Hexavalent Chromium Ion Adsorbed against Particle Size, for the Adsorption of 100ppm Hexavalent Chromium Ion using 0.5g Red Mangrove Biomass Sorbents

As can be seen, the adsorption of hexavalent chromium ion is inversely proportional to the particle size of red mangrove powder. Maximum adsorptions obtained were 85.01% for root, 84.47% for leaves and 80.65% for bark at particle size of 150µm. In all biomaterials studied, the least adsorption was observed for the largest particle size of 2000µm which were 80.05, 70.28 and 59.35% for roots, leaves and bark respectively. The decrease in adsorption with increase in particle size may be attributed to the fact that smaller particles have wider surface area than larger ones such that the adsorbate molecules have greater contact with adsorbent surface. According to Heys, [3] surface phenomenon accounts for the effect of particle size on adsorption. Thus, greater hexavalent chromium (adsorbate) adsorption occurred when red mangrove biomass was more porous and finely divided.

b. Initial Concentration of Hexavalent Chromium ion:

The effect of initial concentration on adsorption of hexavalent chromium ion is displayed in Figure 2.

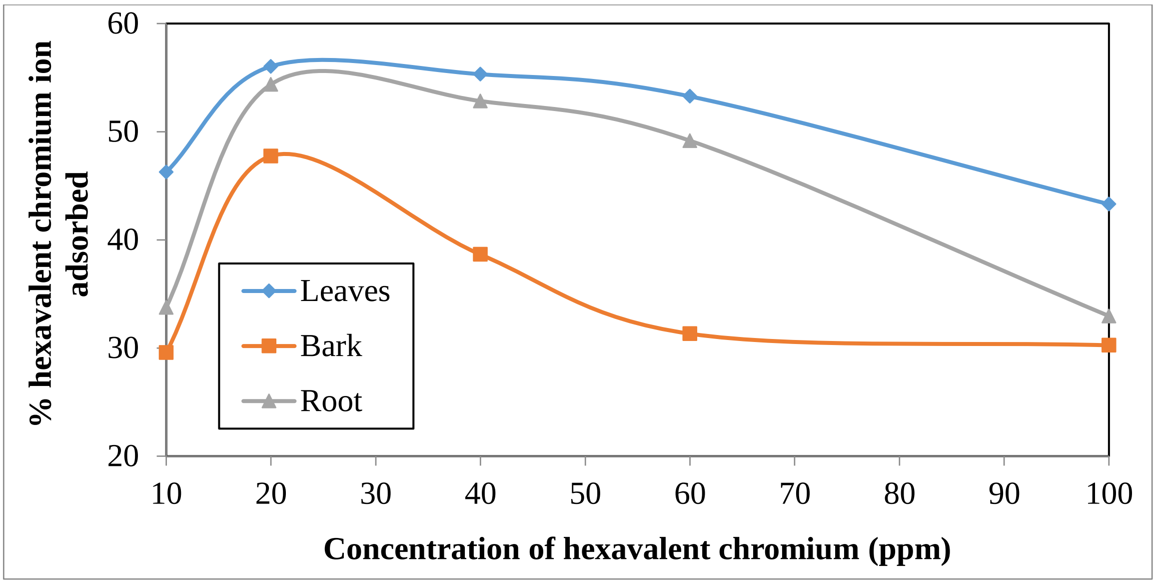

Figure 2: Graph of % Hexavalent Chromium Ion Adsorbed against Initial Concentration of Hexavalent Chromium in Solution using 0.2g Red Mangrove Biomass Sorbents

The plots indicate that % hexavalent chromium ion adsorbed by the various biomass materials increased from 46.25 to 56.04, for leaves; 29.58 to 47.75, for bark and 33.75 to 54.36, for root as concentration of hexavalent chromium ion was increased from 10ppm to 20ppm. Presence of unsatisfied active sites on the adsorbents ready to adsorb more hexavalent chromium ion may be responsible for the initial increase in adsorption and thus, 20ppm was the optimal concentration required to saturate or fill up active sites on 0.2g of the red mangrove biomass studied. Above 20ppm, the concentration adsorbed gradually decreased in each case. Furthermore, the chromate anions need to migrate to the biomass surface through intra-particle diffusion. Therefore, observed decrease in % adsorption above the optimal concentration may be due to saturation or shortage of active sites on the adsorbents or slower intra-particle diffusion rate as the concentration of hexavalent chromium ions greatly increased.

c. pH: It has been reported [14] that the pH of test solutions influences the adsorption of a material on the surface of another. Thus, % hexavalent chromium adsorbed on red mangrove leaves, bark and root powders were plotted against pH (Figure 3).

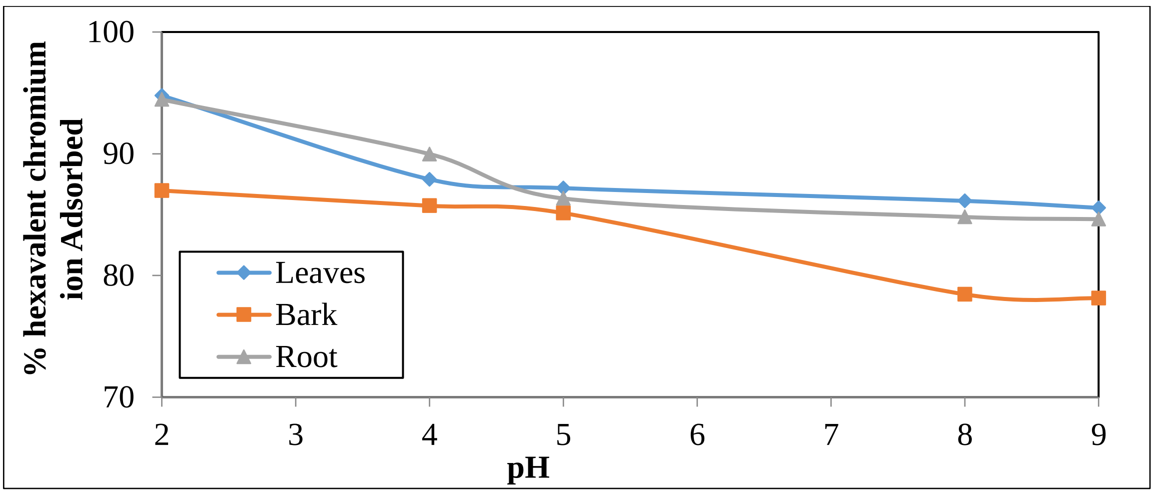

Figure 3: Graph of % Hexavalent Chromium Ion Adsorbed against pH, for Adsorption of (40ppm) Hexavalent Chromium using 0.5g Red Mangrove Biomass Sorbents

As may be observed, adsorption of hexavalent chromium ion on red mangrove biomass is pH dependent, increasing with decrease in pH. Maximum adsorptions of 94.78% for leaves, 94.45%, for root and 86.99% for bark were observed at pH of 2. At pH of 9, minimum adsorptions of 85.55%, 84.63% and 78.13% were respectively obtained for leaves, root and bark biomass. The results suggest that low pH favours the adsorption of hexavalent chromium ion on these biological materials. Protonation/deprotonation of functional groups on binding sites accounts for the role of pH in adsorption processes [14]. Low pH of solution implies high acidity and hence high concentration of hydrogen ions. This in-turn enhances adsorption by protonation of any negatively charged functional groups on an adsorbate. Subsequently, electrostatic attraction between anionic hexavalent chromium ion and positively charged biomass is suspected. At high solution pH, deprotonation of functional groups occur which makes adsorbent surface become negatively charged, thus repulsive interactions dominate. However, in non pH-controlled adsorptions such as the case of particle size and initial concentration of hexavalent chromium ion at ambient solution pH, described earlier in this work, surface associations between the numerous acidic phenolic hydroxyl ions and other functional groups in mangrove [1, 15] plus the anionic hexavalent chromium are possible interaction pathways.

In addition to the observed effects that small adsorbent particle size, low solution pH and low concentration of hexavalent chromium ion favour adsorption of hexavalent chromium ion on red mangrove, this study also shows that generally greater hexavalent chromium ion adsorption occurred on the root and leaves than bark. This observation clearly confirms an earlier report by Iboroma *et al.* [11] that red mangrove biomass especially the root and leaves could be used as natural adsorbents for the removal of hexavalent chromium ion from aqueous solution.

4. Conclusion

The effects of some experimental variables- particle size, initial concentration of hexavalent chromium ion and pH- on the adsorption of hexavalent chromium ion from aqueous solution using red mangrove biomass (leaves, bark and root) powder have been evaluated by batch adsorption method. It was found that small adsorbent particle size, low solution pH and low concentration of hexavalent chromium ion favoured adsorption of hexavalent chromium ion from aqueous solution. The results also showed greater hexavalent chromium adsorption on red mangrove root and leaves than mangrove bark. Therefore, it can be suggested that red mangrove biomass especially the root and leaves are good adsorbents for removing hexavalent chromium ion from aqueous solution.

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