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Assessment of Cactus Biosorption Potential of Cr (VI) ions Removal from Synthetic and Tannery wastewater

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ABSTRACT

Hexachromium Cr (VI) is environmentally mobile and causes ecotoxicological hazard. Chrome utilizing industries are a major source of Cr (VI) pollution. Adsorption using activated carbon prepared from biomaterials is a new technology for the treatment of heavy metals rich industrial effluents. Opuntia Ficus Indicus (OFI) activated with H₃PO₄ (45%) was evaluated for Cr (VI) removal capability from synthetic and tannery wastewater. The study employed batch experiment and residual Cr (VI) concentrations were analyzed using UV-Vis spectrophotometer. FTIR spectroscopy suggested contributions of hydroxyls and carboxyls in Cr (VI) adsorption. Maximum Cr (VI) removal efficiency of 99.5% was achieved by OFI. The % removal of Cr (VI) onto OFI increased with increase of the amount of sorbent, contact time, agitating speed, while observed increased at lower values of initial concentration of Cr (VI) and PH. Optimized values of sorbent dose, adsorbate concentration, pH, contact time and stirring speed were 0.125g, 6mg/L, 2, 60minuets and 150rpm at a temperature of 25°C, respectively. Langmuir isotherm with higher R² was best fitted to the experimental values with monolayer adsorption capacity of 4.587mg/g. RL values were in range of 0<RL<1, confirmed the favorability of adsorption process. About 88.7% Cr (VI) removal was detected when applied to the real wastewater. The reduction in percentage of removal might be due the matrix effect of the competing ions. The study revealed; activated OFI carbon is potent biosorbent of plant origin that holds distinct position for complete removal of Cr (VI) from aqueous solution.

Keywords: Hexachromium, Biosorption, Sorbent, OFI and Langmuir-Isotherm Model.

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1. INTRODUCTION

Chromium (Cr) is toxic metals and causes severe environmental and public health problems when it gets into natural water from a variety of industrial wastes [1]. Cr is considered as one of the 20 most noxious heavy metals [2]. It occurs in different valence states, but Cr (III) and Cr (VI) are the most common forms of chromium in the environment. In comparison to Cr (III), the chromate anions of Cr (VI) are highly soluble and 1000-fold times more toxic due to its carcinogenic and mutagenic properties to microorganism, plants, animals and humans [3,4]. Hence, concerns regarding the presence of chromium in the environment focus on the potential adverse public health and environmental effects of Cr (VI) [4].

Chromium, predominantly; gains access to water sources through discharges of industrial wastewater than the natural path [5]. Tanneries ranked the highest chromium pollutants of all other industries and generate effluents of about 75,000 m³/ day [6]. In India and Egypt, alone an amount of 2000-3000 and 2000–5000tons of elemental chromium annually escaped into the environment from tanneries and various industries respectively [7, 1]. Chromium concentrations from these sources range between 2000 and 5000mg/L in the aqueous effluent, while the limit to discharge into surface water is 2mg/l [6, 7]. More, specifically; Cr (VI) concentration in industrial wastewater ranges from 0.5 to 270 mg/l which is much higher when compared to tolerance limit of its discharge into inland water surface, 0.1and in potable water and bathing 0.05mg/l [8]. In Ethiopia, about 200-300 tons of chromium is released into the environment annually [6]. Indeed, more than 80% of industries in the city of Addis Ababa and its vicinity discharge their effluent into the environment without treatment [9].

Considering these facts, suitable removal of Cr (VI) metal from industrial wastewater is critical [4]. The most common conventional methods of Cr (VI) ions removal from aqueous system are neither effective nor economical, above all; most of them cause secondary pollution to the environment [4, 10]. Adsorption using activated carbon, on the other hand; is an effective and frequently used method for the treatment of wastewater rich in metals [1,10,11]. Nevertheless, commercial activated carbon is cost prohibitive [12]. Hence, exploring effective low-cost heavy metal removal methods is necessitated. Accordingly, in recent years removal of heavy metals by biosorption has been an emerging field of research and about 70 natural biosorbents have been tested [13]. Plant leaves characterized to have phosphate, hydroxyl, carboxylic and carbonyl groups are investigated show improved heavy metal biosorption [5, 10, 14]. Utilization of raw plant materials is limited, owing to leaching of their organic components like, cellulose lignin into the solution for which chemical modification is required to improve the physical, chemical and biosorption capacity [11]. Thoroughly; surveyed literatures indicate that the low cost and edible cactus leave of *O.Ficus-Indicus*/OFI characterized to contain above presented significant multifunctional groups; besides, OFI as biosorbent exhibits efficient primary coagulant [15-17].

Therefore, these unique characteristics potential of leaves/pads of OFI could make it an ideal candidate for investigating its enhanced adsorbent capacity in removal of chromium. In this context, the present study aimed to assess the biosorption potential of OFI carbon activated with H₃PO₄ for Cr (VI) from synthetic and tannery wastewater. The study also further attempted to describe the influences of optimized values of key parameters in the adsorption process and identify best fitted adsorption isotherm model.

2. METHODS AND MATERIALS

2.1. Materials and Reagents

All batch experiments were carried out by analytical reagent grades of checked shelf life: $K_2Cr_2O_7$, H_2SO_4 , NaOH, $KMnO_4$, NH_4OH and 1,5-diphenylcarbazide etc. As a precautionary exercise, standard procedures were followed (APHA 1998) and double distilled water/ DDW was used in all of the working solutions and respective washing by DDW was made after all glassware were soaked in HNO_3 (2%). Experimental blanks were also run in parallel for testing each study parameters and test experiments were performed in replicates from which average results were reported.

2.2. Biosorbent Collection and Preparation

Fresh *O. Ficus-indica* /OFI were collected from the banks of Bishoftu Lake; Bishoftu town, eastern Oromia Region. As first subsequent steps of adsorbent preparation, each pads/ leaves of OFI were washed, cut into strips of 1 cm width, chopped following spines removal and then dried in sun for two weeks and at $105^\circ C$ in electric oven for 24 hours. The dried OFI was impregnated with H_3PO_4 (45%) in W/V ratio of 2:1 and left soaked overnight then after was heated for 60 minutes at $450^\circ C$ in electrical furnace. The carbonized product was grinded and sieved with mesh size $<0.425mm$ and carbon powder was dried at $110^\circ C$ for 24 hours, after the removal of the activator, H_3PO_4 . Finally, the activated OFI powder was kept in tightly closed plastic bottles and was labeled to be ready for the preceding use of FTIR analysis and adsorption experimentation.

2.3 Characterization of Activated *O. Ficus Indicus* Carbon

2.3.1. Moisture Content

The moisture content of activated biosorbent was determined from the loss in mass of wet sample after drying in an oven at $110^\circ C$ for 60 minutes. One gram of A-OFI powder was taken in a previously weighed crucible then was placed in an electric hot air oven at about $110^\circ C$. Finally, the crucible was taken out after one hour, cooled in desiccator and weighed again. The moisture content in the sample was calculated using the following equation (ASTM D 2974-87).

$$\text{Moisture Content} = \frac{(W1 + W2) - W3 * 100}{W2}$$

Where, $W1$ = weight of crucible, $W2$ = weight of activated carbon and $W3$ = weight of residue after drying at $110^\circ C$.

2.3.2. Bulk Density

Determination of bulk density was carried out in which, dried activated OFI powder was filled in 50ml measuring cylinder and the amount taken by the cylinder was measured for calculating the bulk density. Bulk density = M/V , where; M = Amount (gram) of activated OFI placed in the cylinder; V = volume of the cylinder taken up by the activated *O. Ficus Indicus* powder.

2.3.3. FTIR (Fourier Transform Infrared Spectrometry)

FTIR analysis of OFI was carried out before and after adsorption processes; so as to identify surface functional groups and those involved for enhanced Cr(VI) metal biosorption efficiency.

2.4. Preparation of Stock Solution

Stock solution of Cr (VI) metal (1000mg/L) was prepared by dissolving 2.83g analytical reagent grade potassium dichromate ($K_2Cr_2O_7$) in 1000ml distilled water (APHA, 1998).

2.5. Batch Experiment Studies

Batch adsorption experiment was carried out in which different volume from stock solution were diluted to obtain required experimental solution of 50 ml of known Cr (VI) concentrations (2, 4, 6, 8, 10mg/L). The pH of each adsorbate solution added in the 100 mL conical flask was calibrated by buffer solution (pH =7 and 9) and adjusted to the desired values in the range (2-7) by adding 0.1M H_2SO_4 and NaOH solution and measured by a micro-processor pH meter model 210. After which, each measured amount of adsorbents (0.075, 0.125, 0.15, 0.2, 0.225g) was added into adsorbate solution and fixed in multi-functional orbital shaker of model PSU-20i for mixing the solution properly for predefined periods of time (30, 60, 90, 120, 150min) at fixed temperature (25°C) by setting the instrument at desired shaking speeds (50rpm, 100rpm, 150rpm, 200rpm). Accordingly, samples of the mixtures were filtered using Whatmann No. 41 filter paper into 100 ml volumetric flask. Finally; filtrate of the sample were analyzed calorimetrically in acidic media using 1,5 diphenyl carbazide solution to identify the residual Cr (VI) concentration in 1cm cuvette at wave length of 540 nm using Evolution 300 UV-Vis spectrophotometer (APHA, 1998).

2.6. Data Analysis

2.6.1. Analysis of Adsorption Data

The percent sorption of Cr (VI) and the amount of Cr (VI) ion adsorbed by O. Ficus-Indica carbon (q) were calculated by the following equations:

$$R = \frac{C_o - C_e}{C_o} * 100 \quad q_e = \frac{V * (C_o - C_e)}{M}$$

R=% removal efficiency, C_o and C_e =Initial and Final Cr (VI) concentration (mg/L) respectively, q_e =Adsorption capacity (mg/g), V=Volume of the solution (L), m = mass of the adsorbent (g).

2.6.2. Analysis of Adsorption Isotherm Data

Langmuir and Freundlich equations below described in linear form were used for analyzing isotherm data. Linear regression coefficient (R^2) and isotherm constants values were determined from the models and applicability of the isotherm models was judged from experimental data.

$\frac{C_e}{q_e} = \frac{1}{q_{max}} * b + \frac{C_e}{q_{max}}$ Langmuir; the constants b and q_{max} were calculated from the slope and intercept of the graph.

$RL = \frac{1}{1 + b * C_o}$ RL value is other essential characteristics of Langmuir Isotherm model: used to predict the affinity between the sorbate and sorbent as; unfavorable ($RL > 1$), linear ($RL = 1$), favorable ($0 < RL < 1$) or irreversible ($RL = 0$) adsorption.

$\log q_e = \log K_f + \frac{1}{n} \log C_e$ Franklin, where K_f and n are calculated from the slope and intercept of the linear plots of the graph.

2.6. Application to Tannery Wastewater

Sample of 100ml collected from Batu leather tannery industry's chrome liquor, Addis Ababa, was further checked for biosorption adoptability of the technique. The adsorbent removal efficiency of Cr (VI) metal was applied under previously optimized key parameters values; obtained from adsorption of synthetic Cr (VI) aqueous solution. Sample digestion and oxidation procedures were then employed for which analytical reagent grades; nitric- acid, methyl-orange indicator solution, ammonium hydroxide, sulfuric acid, potassium permanganate solution and sodium azid solution were used. Finally; 1 ml of sample was taken from reaction solution and diluted to 10ml by redistilled water, adsorbents were then separated from the solution by using filter paper (Whatmann No. 40). Accordingly, extraction of the total chromium concentration as residual Cr (VI) ion concentration in the solution was then analyzed by atomic-absorption spectrophotometer (AAS).

3. RESULT AND DISCUSSION

3.1. Characterization of Adsorbent

The high surface area, micro porous character and chemical surface nature of activated carbons, make them to have improved potential in removal of heavy metals [10]. The Proximate analysis of activated OFI-carbon powder of diameter of < 0.425mm was performed to understand the physicochemical characteristics, as provided by table-1below.

Table 1: Proximate analysis of activated OFI carbon powder

S.No	Physical characteristics	Unit	Value
1	Moisture content	%	1.685
2	Bulk density	g/ml	0.676

The higher (99.5%) uptake of Cr (VI) ion by *O. Ficus-Indicus* treated with H_3PO_4 (45%) could be attributed by its proximate characteristic values. Adsorption study result carried out with H_3PO_4 (40%) treated activated rice husk having moisture content (13.82%) and bulk density (0.68g/ml) is reported for maximum Cr (VI) removal (94 %) [18]. Though, both activated rice husk and OFI adsorbents have similarities with respect to the bulk density and activating agent, the low moisture content of activated OFI carbon contrasted with that of rice husk might have contributed to the better adsorption removal of Cr (VI) metallic ion. This can be explained, as higher moisture content increases, the internal pores spaces are filled with some water and interferes in pore structure development as a result prevents the diffusion of Cr (VI) ion on to the adsorbent site [19]. The lower the bulk density value indicates that the highly branched and porous structure with more void space. The American water work association has set a lower limit at 0.25g/ml for practical use of activated adsorbent. Therefore, the bulk density obtained from activated OFI carbon powder under study satisfies the condition.

3.2. Fourier Transform Infrared Spectrophotometer (FTIR) Test

IR technique is an essential tool to identify surface functional groups, particularly; those involved for enhanced Cr (VI) metal adsorption onto OFI carbon [11]. Samples of activated OFI carbon powder prior to and after the adsorption process were measured on spectrum 65 FT-IR (PerkinElmer) range 4000-400 cm^{-1} using KBr pellets. Accordingly, the FT-IR tests of both respective samples displayed; fig-1, demonstrated several absorption peaks. Accordingly, spectroscopic characteristics of the spectra of H_3PO_4 treated OFI carbon revealed, broad band at 3421 and 3419 cm^{-1} of H-bound hydroxyl (carbohydrate) before and after adsorption respectively.

Dropping in wave number in Cr (VI) laden OFI after sorption process ($3,419\text{cm}^{-1}$) in comparison to before adsorption ($3,421\text{cm}^{-1}$) signify, the role of H-bonded hydroxyl stretching of hydroxylates in Cr (VI) ion uptake. Consequently; hydrogen bonded OH stretching in finger print region of O.Ficus Indicus before adsorption (3421 cm^{-1}) likely supports the electrostatic bindings of negatively charged chromate ions. In that, a notable hydroxyl band shifting to a low wave number ($3,419\text{cm}^{-1}$) confirms its possible involvement in adsorption processes. Changes in the intensity and wave number; 2918 to 2924cm^{-1} and 1613 to 1620 cm^{-1} in OFI carbon spectra indicated that free C-H stretching and carboxyl C-O stretching vibrations probably get interacted with Cr (VI)ion. Besides, the vibrational shift of the functional group like, C-O bending vibrations of polysaccharides of $1,119\text{ cm}^{-1}$ to higher modes of $1,269\text{ cm}^{-1}$ bending frequencies indicates their contribution in Cr (VI) binding onto OFI. The findings are well supported with literatures reports and O.Ficus Indicus is confirmed to contain complex materials with multifunctional surface groups at varied absorption wave numbers [15, 17].

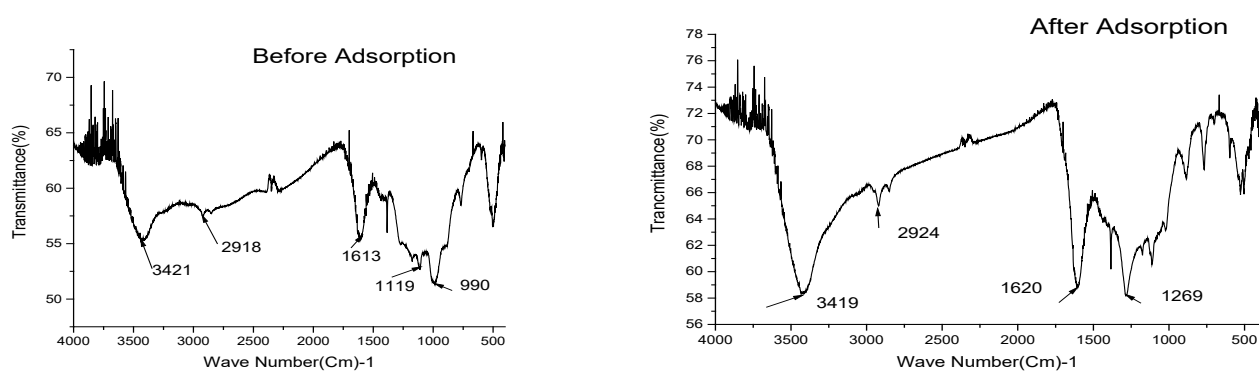


Figure 1: FTIR Spectrum of OFI using KBr Disc prior to and after adsorption process.

3.3 The Effect of Biosorbent Dose

The percentage adsorption of Cr (VI) ions increased from 89.63 to 99.5% with increased in OFI concentration and equilibrium was reached optimum dose at 0.125g (99.07%) under constant study parameters, fig 2. The increase in Cr (VI) removal with increase adsorbent amount is due to the increase in surface area and adsorption sites available for adsorption, thus makes easier penetration of Cr (VI) to the adsorption sites. This is in line with the literatures [8, 14]. However, the amount of metal uptake per unit gram decreases rapidly from 3.59 to 1.327 mg/g, as the mass of adsorbent dose added increases from 0.075 to 0.25g. Basically; the drop in adsorption capacity is due to the sites remaining are unsaturated during the adsorption process. The respective optimum values of Cr (VI) adsorption capacity of O.Ficus Indicus is found to be 3.378 mg/g occurred at adsorbent dose of 0.125g. The present study agrees with different literature reports [5]. It thus, the result revealed that adsorption percentage removal and adsorption capacity of Cr (VI) ion on O.Ficus Indicus is highly a function of the amount adsorbent used.

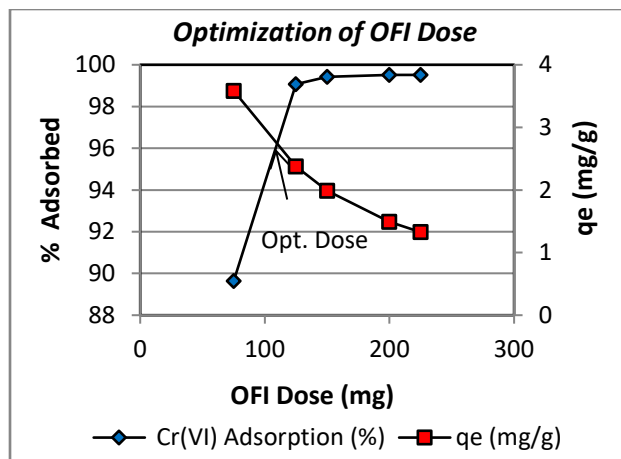


Figure 2: Illustrated the effect of adsorbent dose Vs removal % and capacity under initial Cr (VI) concentration; 6mg/l, pH; 2, contact time; 60min and shaking speed; 200rpm at temperature; 25°C.

3.4 The Effect of Initial Cr (VI) Concentration

The adsorption experiment study conducted reveals that with increases of Cr (VI) concentration from 2 to 10mg/L decreases the percentage removal from 98.6% to 94.02%. The maximum optimum Cr (VI) ion percentage removal of 98.6% was observed at lower initial concentration, 2mg/L. The decrease in percentage removal with increase of initial concentration can be due to the availability of limited number of unoccupied active sites on OFI surface per Cr (VI) ion at higher concentrations, which would have become saturated. The increase in adsorption capacity from 0.789 to 3.76 mg/g with increase in Cr (VI) concentration may be a higher initial concentration enhances the number of collisions between Cr (VI) ions and adsorbent resulting an increase adsorption rate and utilization of concentration [20,21].

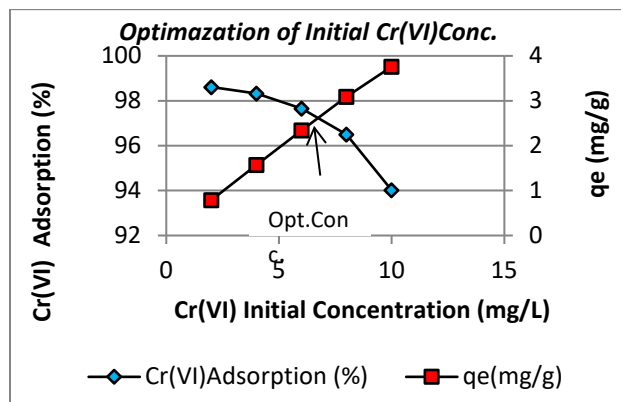
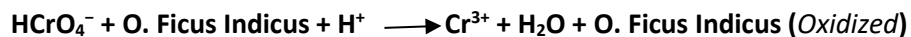


Figure 3: The effect of initial Cr (VI) ion concentration; studied under adsorbent dose; 0.125g, pH; 2, Contact time; 60minutes, and stirring speed; 200rpm at a temperature; 25°C.

3.5. The Effect of pH

The pH of a system is key parameter that controls the adsorption of Cr (VI) [12]. Sorption experiment was carried out to optimize the pH for maximum removal efficiency of Cr (VI) from 2 -7; such that it was not influenced by the metal precipitation. The experimental result revealed that the adsorption percentage removal increased as the pH was decreased and attended 99.24% at lower pH values from 2 to 3, hence optimum pH for maximum removal of Cr (VI) occurs at pH 2. When the pH increases above 3 the percentage removal observed to follow slight declining trend till the pH value reaches 6. This result resembles most with adsorption of Cr (VI) on activated carbon materials [22].

The favorable effect at low pH values is due to the fact that the surface of the adsorbent is highly protonated, thereby making the negatively charged surface of OFI to be saturated with positive charges enhancing the diffusion of Cr (VI) oxyanions and their subsequent adsorption by the electrostatic force of attraction [12]. Furthermore, the oxidative treatment of OFI carbon with H₃PO₄, introduces more oxygenated acidic surface at a lower pH value [10]. Accordingly, marked presence of various oxygenated acidic surface functional groups on OFI like, hydrogen bound hydroxyl groups increase the availability of active binding sites at low pH conditions, and hence increase the adsorption of oxyanions Cr (VI) ions. It is also postulated that at lower pH values (<3) Cr (VI) metal ion can be reduced to Cr (III) in the presence of activated carbon [20]. Consequently, Cr (VI) sorption and reduction to Cr (III) occur in that Cr (VI) starts to act as an oxidant and results in proportional released of the non-toxic Cr (III) from OFI surface by reaction mechanism described below.



Similar bioreduction process was observed in study report [14]. Reduction of Cr (VI) into Cr (III) is also clear from the aqueous chemistry of Cr (VI) at low pH value [22].



Here, anionic HCrO₄⁻ is dominantly sorbed as Cr (VI) metal ion on to OFI than the other its species. This can be well explained, HCrO₄⁻ is dominating Cr (VI) species at concentration of below 1g/L under acidic pH solution [12]. Furthermore; at pH of 2-3, HCrO₄⁻, is dominate and preferentially adsorbed over the other species of Cr(VI)ion on OFI due to its smaller ionic size and low adsorption energy, whereas; as the pH increases, this shifts to Cr₂O₇²⁻ and CrO₄²⁻ [22]. Thus, the dominate adsorption mechanism are anionic sorption and sorption coupled with reduction. The reduced adsorption efficiency at higher pH can be attributed due to increased negative charge density on surface OFI creating repulsive electrostatic with anionic Cr (VI) this is in conformity with many literature reports [5].

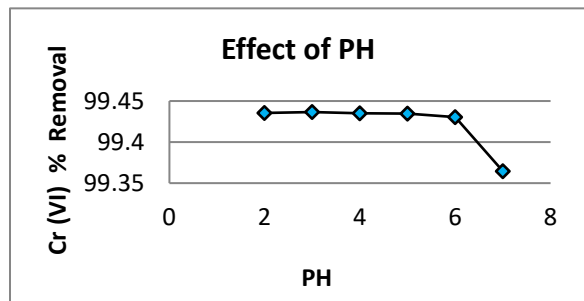


Figure 4: The effect of pH; under initial of Cr (VI) ion concentration; 6mg/L, adsorbent dose; 0.125g, contact time; 60minutes, stirring speed; 200rpm and temperature; 25°C.

3.6. The Effect of Stirring Time and Speed

The figure 5, shows increasing of percentage removal of Cr (VI) from 95.5 to 99.3%, while increasing the contact time from 30 to 150 minutes respectively. This agrees with various studies [5, 19]. Furthermore, a sharp increase of Cr (VI) adsorption efficiency was observed from 30 to 60 minutes, and thereafter begins to decline slowly till was reached the equilibrium time. Thus, the maximum percentage of adsorption was observed to be 99.3%. Whereas the optimal maximum was 98.3%, attended at 60 minutes of contact time and further increase in the contact time has a negligible effect on the removal of Cr (VI). Similar result observations have been reported in different literature studies [14, 19].

The effect of stirring speed was studied varying from 50-200 rpm, keeping the other previously optimized parameters constant. The removal efficiency of Cr (VI) found to increase from 95.6 to 99.4% along with increasing of the speed values in the range between 50-200rpm. The result also indicates that a shaking rate in the range 100-200 rpm is sufficient to assure that all the surface binding sites are made readily available for Cr (VI) uptake. Hence, a maximum of 99.36 % removal was reached at 200 rpm. Besides; it was shown that, further increase from the optimum removal of 99.35%, observed at 150rpm, has no significant effect on the adsorption of Cr (VI). This is in agreement with literature study reports [19].

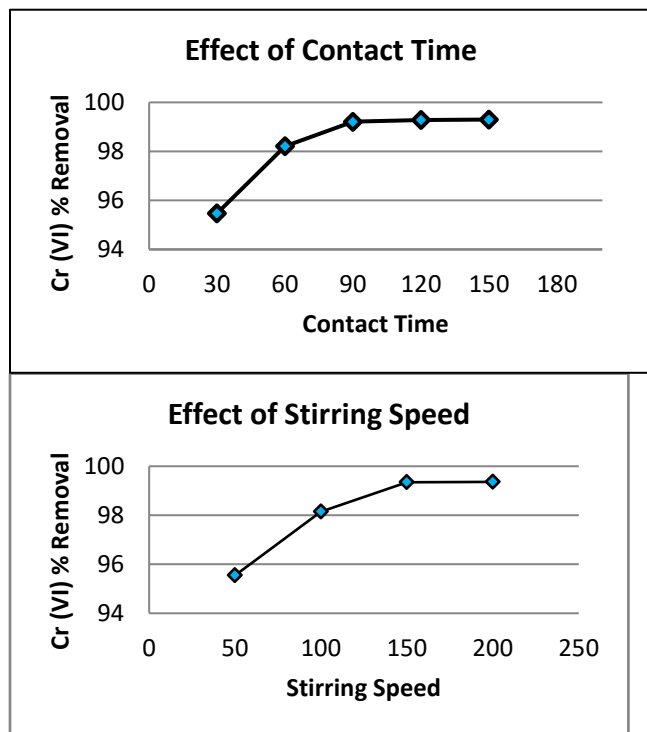


Figure 5: The effect of contact time; studied under adsorbent dose; 0.125g, initial Cr (VI) concentration; 6mg/L, pH;3, shaking speed; 200 rpm and temperature; 25°C.

Figure 6:The effect of Stirring speed studied under adsorbent dose; 0.125g, pH; 3, Initial Cr (VI)concentration;6mg/L, contact time; 60minutes and temperature; 25°C.

3.7. The Effect of Temperature

O. Ficus Indicus has showed a maximum percentage removed of about 99.5% of Cr (VI) ion from the solution at 25°C that further increase in excess of this temperature value could have little or negligible effect on additional removal of Cr (VI) ion. The result is consistency with the different research literatures

[10, 23]. It can be more explained; such that rising above the critical optimum value in monolayer dominated sorption process has no effect on adsorption system. This well supported with study reports [24].

3.8. Adsorption Isotherm Study

3.8.1. Langmuir Isotherm

Langmuir Isotherm basis on uptake of metal ions occurs on homogenous sites and forms monolayer adsorption and the adsorption of metal ion in one site is not affected by adjacent sites that all sites are energetically equivalent [4]. The Langmuir constants q_{max} and b which are measure of monolayer sorption capacity and adsorption energy, obtained from intercept and slop of the linear plot of C_e/q_e versus C_e to be 4.587 mg/g and 7.5 L/mg respectively. Higher maximum adsorption capacity (q_{max}), obtained by activated OFI when is compared with Pine leaves 0.198 mg/g and Sawdust activated carbon, 3.46mg/g [20, 21]. And the other: Cow Hooves, Chryseomonas Luteola, Modified Saw Dust and Waste Tea saw respectively, have 3.57,3,1.7and1.55mg/g of q_{max} values [5]. The higher regression correlation coefficient: $r^2=0.999$ is obtained indicating good agreement between the experimental data and isotherm parameters that confirms monolayer adsorption of Cr (VI) onto homogenous surface of OFI sorbent. The present result is in conformity with literature study on adsorption of Cr (VI) by Fe-modified activated carbon studied at 20°C [20]. The RL value of Langmuir isotherm lies in the ranges between 0.0131 and 0.0624. Hence, Langmuir isotherm model follows the condition $0 < RL < 1$ and implies the favorability of Cr (VI) removal in adsorption process by activated OFI carbon in that O. Ficus Indicus is a suitable adsorbent for removal of Cr (VI) metal.

3.8.2. Freundlich Isotherm

Describes the adsorbent heterogeneous surface is composed of different classes of sites with different energy [24]. Freundlich constants, K_f (L/mg) and $1/n$ are obtained by plotting the graph between $\log q_e$ versus $\log C_e$. The respective values of K_f and n are 5.57 and 1.980. Higher K_f values when comparing with potato peelings, 0.2985 and Bengal gram husk, 2.815mg/g, activated sugar beet bagasse, 1.108 mg/g [21]. Value of $1/n$ ranges between 0 and 1, for which the value of n lies between 1 and 10 that indicates the beneficial adsorption, suggesting relatively strong adsorption of Cr (VI) ions onto the surface of OFI carbon [5, 21]. Adsorption Isotherms with $n > 1$ is reflection of high affinity between adsorbent and adsorbate which is an indicative of chemisorptions [1]. The regression correlation coefficient ($r^2=0.956$) obtained from Freundlich isotherm model is lower than that of Langmuir isotherm model that Langmuir isotherm gives a better fit. This is in consistence with most of related studies reported that Langmuir model was suitable for describing the adsorption isotherm of Cr (VI) on adsorbents [1, 21].

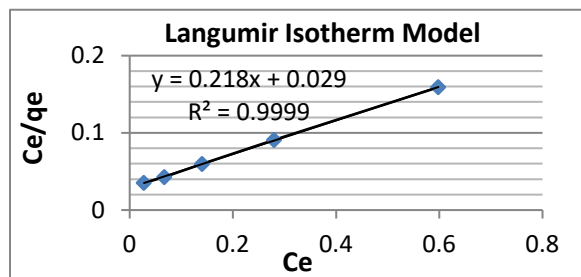


Figure 7: Langmuir Isotherm plot for the adsorption of Cr (VI) ion under optimum biosorbent dose; 0.125g, pH; 2, contact time; 60minutes, Stirring speed; 200rpm at 25°C.

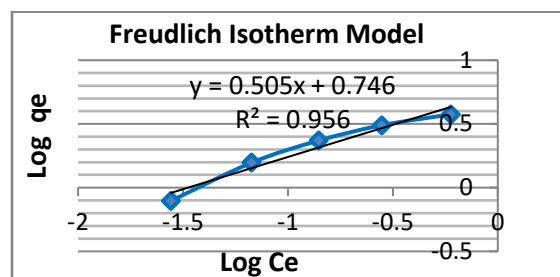


Figure 8: Freundlich Isotherm plot for the adsorption of Cr (VI) ion under optimum biosorbent dose; 0.125g, pH; 2, contact time; 60minutes; Stirring speed; 200rpm and at 25°C.

Table 2: Parameter and Correlation Coefficient of Adsorption Isotherm.

Adsorption Isotherms	Isotherms Parameters		R ²
Langmuir	q _{max} (mg/g)	4.587	0.999
	b(L/mg)	7.5	
	RL	0.062-0.013	
Freundlich	K _f	5.57	0.956
	1/n	0.505	
	n	1.98	

3.9. Application to Tannery Wastewater

The adsorbent was applied to real tannery wastewater and the removal efficiency was found to be 88.7%. The reduction in removal efficiency when applied to real tannery wastewater could be due to the presence of interfering ions such as chlorides and sulfites which might hinder the diffusion of Cr (VI) by competing with Cr (VI) for adsorption on to activated O. Ficus Indicus.

4. CONCLUSION

The present work shows that OFI activated with H₃PO₄ is sufficient to remove Cr (VI) from both synthetic and tannery wastewater. Higher removal efficiency of Cr (VI) was observed at lower adsorbate concentration and pH values and an increasing percentage adsorption was obtained with the rising of the adsorbent dose, contact time and Stirring speed values at a temperature of 25°C. About 99.5 % of maximum adsorption of Cr (VI) ions removal performance by OFI was accomplished within optimum 60 minutes, at initial Cr (VI) ion concentration of 2mg/l, 125mg of sorbent dose, pH of 2 and shaking speed of 150 rpm at room temperature. FTIR spectroscopy suggested the possible involvement of hydroxyls and carboxyls in Cr (VI) adsorption. The experimental equilibrium data better fitted Langmuir isotherm with regression correlation coefficient (R²=0.999) with monolayer adsorption capacity of 4.587mg/g. Besides; adsorption percentage removal of Cr (VI) onto O.Ficus Indicus found out to be 88.7% while, applied to real tannery waste water. The higher Cr (VI) % removal and adsorption capacity onto O. Ficus Indicus signifies the efficient removal performance of the adsorbent.

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6. REFERENCES

- [1]. S.Khedr, M.Shouman, N.Fathy, and A.Attia, Effect of Physical and Chemical Activation on the Removal of Hexavalent Chromium Ions Using Palm Tree Branches, Hindawi Publishing Corporation: ISRN Environmental Chemistry, 2014; Article ID 705069,10 pages, <http://dx.doi.org/10.1155/2014/705069>.
- [2]. R.J.Thilakar, J.Rathi, J. and, P.M.Pillai, Phytoaccumulation of Chromium and Copper by Pistia stratiotes L. and Salvinia natans (L.) All, J. Nat. Prod. Plant Resour., 2012; 2(6):725-730.
- [3]. B.D.Pandey,B. Dhal, H.Thatoi, and N.Das, Reduction of hexavalent chromium by Bacillus sp. isolated from chromite mine soils and characterization of reduced product, Journal of Chemical Technology & Biotechnology, 2010; doi: 10.1002/jctb.2451.

- [4]. M.A. Mohamed, S.A.Wanees, A.M.M. Ahmed, and M.S. Adam, Adsorption Studies on the Removal of Hexavalent Chromium-Contaminated Wastewater using Activated Carbon and Bentonite, *Journal of Chemistry*, 2012; Vol. 02, Issue 03, pp. 95-105.
- [5]. I.Osasona, A.O. Adebayo, and O.O.Ajayi, *Journal of Scientific Research & Reports*, 2013; 2(1): 288-303, Article no. JSRR. 2013.019.
- [6]. T.G.Amabye, Plant, Soil and Water Pollution Due to Tannery Effluent a Case Study From Sheb Tannery, P.L.C, Wukro Tigray, Ethiopia, *Science Journal of Analytical Chemistry*, 2015;3(5):47-51,doi: 10.11648/j.sjac.20150305.11.
- [7]. A.A. Belay, Impacts of Chromium from Tannery Effluent and Evaluation of Alternative Treatment Options, *Journal of Environmental Protection*, 2010; 1, 53-58, doi: 10.4236/jep.2010.11007.
- [8]. S.M. Desai, N.C.L.N Charyulu, and S.V. Suggala, Statistical Optimization of Adsorption Variables for Biosorption of Chromium (VI) Using Crude Tamarind Pod Shell and Activated carbon, *IJRET: International Journal of Research in Engineering and Technology*, 2014; Vol.03, Issue: 07/ Jul-2014.
- [9]. D.Woldemichael, F.Zewge, and S.Leta, Potential of Water Hyacinth (*Eichhornia Crassipes* (Mart.) Solms) for the Removal of Chromium from Tannery Effluent in Constructed Pond System, *SINET: Ethiop. J. Sci.*, 2011; 34(1): 49–62.
- [10]. M.Rahimizadeh, and A.Liaghat, Biosorbents for Adsorption of Heavy Metal, Paper Presented at International Conference of Environmental Science Engineering and Technology, 5-6 May 2015,Teheran University,Iran.
- [11].S.Mandina, F.Chigondo, M.Shumba, B. Chomunorwa N., E.Seбата, Removal of chromium(VI) from aqueous solution using chemically modified orange(*citrus cinensis*) peel, *Journal of Applied Chemistry*, 2013; Vol. 6, PP 66-75.
- [12]. K. Mulani, S. Daniels, K.Rajdeo, S.Tambe, and N. Chavan, Adsorption of Chromium(VI) from Aqueous Solutions by Coffee Polyphenol-Formaldehyde/Acetaldehyde Resins, Hindawi Publishing Corporation; *Journal of Polymers*, 2013; Article ID 798368, 11 pages, <http://dx.doi.org/10.1155/2013/798368>.
- [13]. T.P. Dhungana and P.N. Yadav, Determination of Chromium in Tannery Effluent and Study of Adsorption of Cr (VI) on Sawdust and Charcoal from Sugarcane Bagasses, *J. Nepal Chem. Soc.*, 2008/2009; Vol. 23.
- [14]. M. Kumar and, CB. Majumder, Biological Removal of Chromium(VI) from synthetic waste water using “Acid Treated Banana Peel”, *Research Journal of Pharmaceutical: Biological and Chemical Sciences*, 2014; RJPBCS 5(3), ISSN: 0975-8585.
- [15]. T. Nharingo and, M.Moy, Application of *Opuntia Ficus-indica* in Bioremediation of Waste Water, A critical review, *Journal of Environmental Management*, 2015; <http://dx.doi.org/10.1016/j.jenvman.2015.10.005>.
- [16]. A. buttice, J. stroot, D.lim, P.Stroot and, N.alcantar, Removal of Sediment and Bacteria from Water Using Green Chemistry, *Environ. Sci. Technol.* 2010, 44, 3514–3519.
- [17]. D. I.Fox, " Cactus Mucilage-Assisted Heavy Metal Separation: Design and Implementation", ph.D, Graduate Theses and Dissertations, 2011; University of South Florida, <http://scholarcommons.usf.edu/etd/3107>.
- [18]. Singh, S.R. and, Singh, A.P., Treatment of Water Containing Chromium (VI) Using Rice Husk Carbon As a New low Cost Adsorbent, *Int. J. Environ. Res.*, 2012; 6(4):917-924, Autumn 2012, ISSN: 1735-6865.
- [19]. B.V. Devi, A.A.Jahagirdar, M.N.Z.Ahmed, Adsorption of Chromium on Activated Carbon Prepared from Coconut Shell, *International Journal of Engineering Research and Applications*, 2012; (IJERA) ISSN: 2248-9622, Vol. 2, Pp.364-370.

- [20]. W.Liu, J.Zhang, C.Zhang, and, Y.Wang,Y.Li., Adsorptive removal of Cr (VI) by Fe-modified activated carbon prepared from *Trapa Natans* husk, *Chemical Engineering Journal*, 2010; 162(2010)677–684, doi:10.1016/j.cej.2010.06.020.
- [21]. F.Mutongo, O.Kuipa and, P.K.Kuipa, Removal of Cr(VI) from Aqueous Solutions Using Powder of Potato Peelings as a Low Cost Sorbent. Hindawi Publishing Corporation: *Bioinorganic Chemistry and Applications*, 2014; Article ID 973153, 7pages, <http://dx.doi.org/10.1155/2014/973153>.
- [22]. O.O.Kehinde,T.A.Oluwatoyin,and,O.O.Ader nke,Comparative analysis of the efficiencies of two low cost adsorbents in the removal of Cr (VI) and Ni(II) from aqueous solution, *African Journal of Environmental Science and Technology*,2009; Vol.3, Pp. 360-369.
- [23]. M.S.Sulaiman, Factors Affecting Biosorption of Cu (ii) Ions from Industrial Waste Water, *Applied Research*, 2015; Journal ISSN: 2423-4796, Vol.1, Issue, 5, pp.311-315.
- [24]. T.Dula,K.Siraj and, S.A.Kitte, Adsorption of Hexavalent Chromium from Aqueous Solution Using Chemically Activated Carbon Prepared from Locally Available Waste of Bamboo (*Oxytenanthera abyssinica*),Hindawi Publishing Corporation: ISRN Environmental Chemistry,2014; Article ID 438245, 9 pages, <http://dx.doi.org/10.1155/2014/438245>.