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Removal of Chromium(VI) from Waste Water using Diospyros Lotus Seed Powder as a Biosorbent

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ABSTRACT

In the present study, biosorbent was prepared from the low-cost agricultural wastes which belongs to the Ebenaceae family of Date plum persimmon (Diospyros Lotus)

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seed powder was used for the removal of Cr(VI) from waste water. The adsorption of Cr(VI) was investigated from aqueous solutions of the Diospyros Lotus seed powder as a biosorbent. Aqueous solution of potassium dichromate ($K_2Cr_2O_7$) was used as a source of Cr(VI) ions. These experiments were conducted in a batch system and the effect of various parameters like temperature, pH, contact time, adsorbent dosage and concentration was investigated of Cr(VI). The prepared biosorbent was characterized by FT-IR, SEM, BET surface area and pore size analyzer. From the present study it could be concluded that the biomass of Diospyros Lotus seed powder is most efficient and can be used as potential biosorbent for the removal of Cr(VI) ions in aqueous solution and other waste water system.

Keywords: Diospyros Lotus, Biosorbent, Waste water, Cr(VI)

Introduction

A large amount of pollutants, whether coming out from inorganic or organic sources damage our environment to a huge extent. As heavy metal ions are considered environmental threat even in minor quantity. The elimination of this ion from solution is investigated as one of the sever issue in waste water treatment (Ahmad et al., 2017; Choudhury et al., 2022; Pakade, Tavengwa, & Madikizela, 2019; Vilela, Dalalibera, Duminelli, Becegato, & Paulino, 2019; Wang). The water quality is extremely affected by discharge of undesirable pollutants into the water bodies by chemical industries , mining areas such as, textiles, plastics, tanneries, pigments and battery manufacturing, electronic equipment, electroplating , dyes and catalysis (Gong et al., 2018; Zhao et al., 2019). The effect improved toxic waste of water rivers day by day (Vilela et al., 2019). The absorption series of Cr(VI) and over-all chromium in sewer water/industrial effluents of the abovementioned productions are regularly 3500–4500 mgL^{-1} and 3000–4000 mgL^{-1}, individually. Conferring to the Ecological Fortification Agency (EPA) of the Unified Statuses of America (USA) the acceptance boundary of Cr(VI) for issue into interior superficial aquatic is 0.1 mg L^{-1} and the suggested boundary for intake water is only 0.05 mg L^{-1} 3–5 A amount of methods such The chief idea of believed in a waste treatment Cr (VI) ability Heavy metals are

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Copper (Cu) Mercury (Hg) (Muhammad, Muhammad, Hoji, Yang, & Yigaimu, 2020) .Nickel (Ni) Cadmium (Cd) (Yin et al., 2017). Zinc (Zn), Lead (Pb) (Baile, Vidal, Aguirre, & Canals, 2018). and Chromium (Sunnapu et al., 2017). The release of heavy metals ions into drain water through industrial activities has developed a great problem for aquatic and humans live (Parlayici & Pehlivan, 2019). The most hazardous one is (Cr) is an element with the most harmful effects on humans, plants as well other animals (Vilela et al., 2019). Chromium exists in various oxidation states. The two most stable oxidation states are Cr(III) and Cr(VI). Cr(VI) is comparatively most poisonous than Cr(III) due to its teratogenicity and oncogenic behavior on the human beings and other animals. Over-exposure to Cr(VI) is causes irritation to the eyes, edema, irritation to the skin, , nervous damage, kidney failure (Kundu, Park, Ray, Oh, & Jun, 2019; Shorie, Kaur, Chadha, Singh, & Sabherwal, 2019). Numerous techniques such as electro dialysis ,membrane process , ultrafiltration, ion exchange , and reverse osmosis are possible to eliminate dangerous metals from the west water medium (Mekonnen, Yitbarek, & Soreta, 2015; Pshinko, Puzyrnaya, Yatsyk, Kosorukov, & Goncharuk, 2014) oxidation and reduction (Bayuo, Pelig-Ba, & Abukari, 2019). Removal of (Cr) has also been investigated using precipitation as well as adsorption (Tiadi, Mohanty, Mohanty, & H. Panda, 2017). These techniques are inexpensive when Cr(VI) exists in the wastewater at a low absorption. Adsorption, a quantity transmission method in wide-ranging (Dubey, Gusain, & Sharma, 2016). The adsorption method stops the most ideal method because of its inefficiency, low-priced technique (Altun & Pehlivan, 2012; Kaya, Pehlivan, Schmidt, & Bahadir, 2014). However, these must have some limits as well as high operational cost, great elimination productivity (Srivastava, Weng, Singh, & Sharma, 2011). In the type of low-cost adsorbents, both are bio-adsorbents and natural adsorbents are used (Tamjidi, Esmaeili, & Moghadas, 2019). Numerous agricultural constituents have been used for the adsorption of heavy metals containing as plants seeds (Edokpayi, Odiyo, Msagati, & Popoola, 2015). Biosorbents prepared after agricultural waste take organic insoluble compounds and poly functional groups such as $-COO^-$, ^-OH, PO_4^{2-}

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and $-NH_2$, these ions relate with Cr(VI) ions over the electrostatic force of attraction.

The main sources of bio-sorbents study will provide complete information almost the use of low-cost adsorbent as well as easily available, result oriented, reproducible adsorbents for the removal of heavy metal ions (Foroutan, Oujifard, Papari, & Esmaeili, 2019). adsorption of heavy metals from wastewaters due to its highly toxic the research and application of several adsorbent materials for the renewal of toxic hexavalent chromium (Cr(VI)) from eco-friendly examples have established huge consideration from researchers (Benhelal et al., 2019; Miretzky & Cirelli, 2010; Mortazavian, An, Chun, & Moon, 2018; Pradhan, Sukla, Sawyer, & Rahman, 2017; Zhou et al., 2018).

In the present work we used Diospyros lotus (Toor Amlook) seed powder as bio sorbent. To the best of our knowledge this bio sorbent has not been used for the removal of Cr(IV) metal ion from waste water.

2. Experimental

2.1 Reagents

All of the chemicals used in the current work were of high proportion concentration and remained used as conventional short of additional distillation. Sulphuric acid (H_2SO_4), Potassium dichromate ($K_2Cr_2O_7$), 1,5diphenylcarbazide ($C_{13}H_{14}N_4O$), hydrochloric acid (HCl), sodium hydroxide (NaOH),and acetone (C_2H_6O).

2.2 Preparation of the Biosorbents

The diospyrous lotus powder used in the present study. The composed biosorbent were crushed and sieved (170 mesh, size 0.297nm). The separated constituent part of all of the biosorbent were wash away numerous periods with rap water to eliminate dust particles shadowed by wash with deionized water independently. Then they were dried at 383 K in an oven over nightly and used when we well prepare different stocks solution stocks solution of Cr(IV) $K_2Cr_2O_7$ for this purposed in 1.415g $K_2Cr_2O_7$ dissolve in 500mg of distal water the test solution of various solution we prepare from stock solution by dilution .

2.3 Characterization

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Scanning electron microscopy (SEM) was cast-off to examine the external geomorphology of the adsorbents. Fourier-transform infrared spectroscopy (FT-IR) was accomplished for authorization of the superficial functional sets which were in charge for the approval of Cr metal ions from aqueous solutions. External examines of all of the examples be situated prearranged by means of Chrome NOVA 1200e. Earlier external area purpose individually sample was vented at 423K for 60 min in a nitrogen troposphere.

2.4 Batch Biosorption Experiments

A standard solution result (1000 mg L^{-1}) of chromium was organized by dissolving 1.415 g of $K_2Cr_2O_7$ in distilled water. Examination solutions of numerous absorptions were organized from the stock solution by dilution. In a characteristic biosorption experimentation, 40 mg L^{-1} and 30 mg L^{-1} test solution was taken in a tapering flask and 0.4 g of biosorbent was added to it. The pH of these solutions was used to using 0.1 M HCl and 0.1 M NaOH. Then bunch biosorption researches were achieved at 303K with a shaky speed of 130 rpm for 360 min. Later divisions, the interruptions were filtered followed by analysis with a UV-Visible spectrophometer. For analysis, the Cr(VI) was changed to a dyed compound by the adding of 1,5-diphenyl carbazide in an acidic solution medium. The transmission density and absorptions of the resultant mixtures (filtrates of the test solutions) were strong-minded at a wavelength of 540 nm. The amounts of Cr(VI) adsorbed in in each sample (mg g^{-1}) were considered using eqn (1) and (2). A characteristic batch biosorption trial is obtainable in Arrangement equation

$$R\% = \left(\frac{C_i - C_e}{C_i} \right) \text{x } 100 \qquad (1)$$

$$Q_{ad} = \left(\frac{C_i - C_e}{W} \right) \text{x } V \qquad (2)$$

Where C_i (mg/L), C_e (mg/L), V(mL) and W(g) are the initial Cr(VI) concentration, equilibrium Cr(VI) concentration, volume (mL) of Cr(VI) solutions taken in conical

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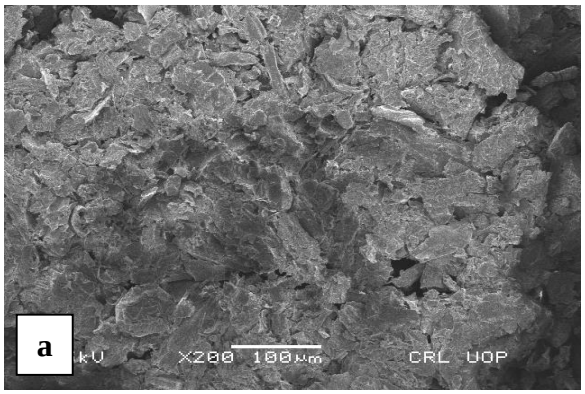
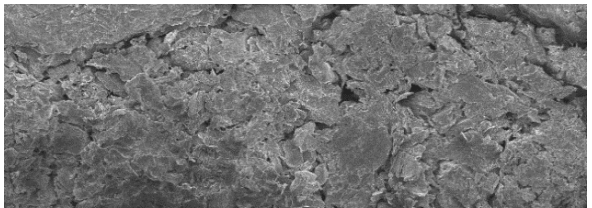
flask and dry weight of the biosorbents respectively.

3. Results and Discussion

3.1 Characterizations

SEM simplified the shortest reflection of the microstructure of the adsorbents' surfaces. The SEM procedure was hand-me-down to confirm the superficial word structure of the studied biosorbents already and after adsorption (Fig.1). The microstructure of the unused diospyros lotus seed powder biosorbent presented an irregular morphology of the surface particles (Fig. 1a). This proposes the existence of a substantial superficial part for the adsorption of Cr(VI) ions. From the micrograph of the used diospyros lotus' seeds powder a minor standardization in the external was experiential, representing the growth of chromium ions confidential its obtainable openings (Fig. 1b). Additionally, the particles could not resist the acidic medium (pH = 4) and dissolved to some amount. Furthermore, whereas the SEM image of the same external occupied afterward adsorption presented a plane external of the biosorbent constituent part interested in the minute opening of the external atoms. From now, since the SEM investigation it was established that biosorbent sides have no substantial microstructures and consequently adsorb a low amount of nitrogen which chiefs to a low BET surface area. As the SEM images examined biosorbents with great atom size besides the BET external extents were meaningfully lesser associated to the shallow areas of initiated carbon, it was long-established that the results of the SEM and superficial extent analyzer were slightly comparable.





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b

Figure 1. a) SEM images of unused diospyrous lotus seeds biosorbents b) SEM images of used diospyrous lotus powder biosorbents.

FT-IR remained approved obtainable to recognize the external efficient groups in charge used for the Cr(VI) adsorption. Fig. 2 show the FT-IR spectra of the unused diospyros lotus seeds powder biosorbent. The peaks at around 3400 cm^{1-} can be given to –OH stretch vibrations indicative of the occurrence of carbolic acid and alcohols, which checks the existence of cellulose .The peaks at around 2900 cm^{1-} looked due to C–H stretch vibrations, which show the existence of methyl and methylene groups. General, the FTIR ranges of the unused diospyros lout's seeds powder biosorbents show a number of points which to be their multipart nature The conceivable presence of –OH, COO–, CO– and –C–C– theatres a vital role in the biosorption of Cr(VI) from aqueous solutions on the surfaces of as-prepared biosorbents. Furthermore, the whole spectra of the used biosorbents did not show a clear change in functional groups, but a percentage of the full biosorbents' spectra (around 600–800 cm^{1-}) indicated

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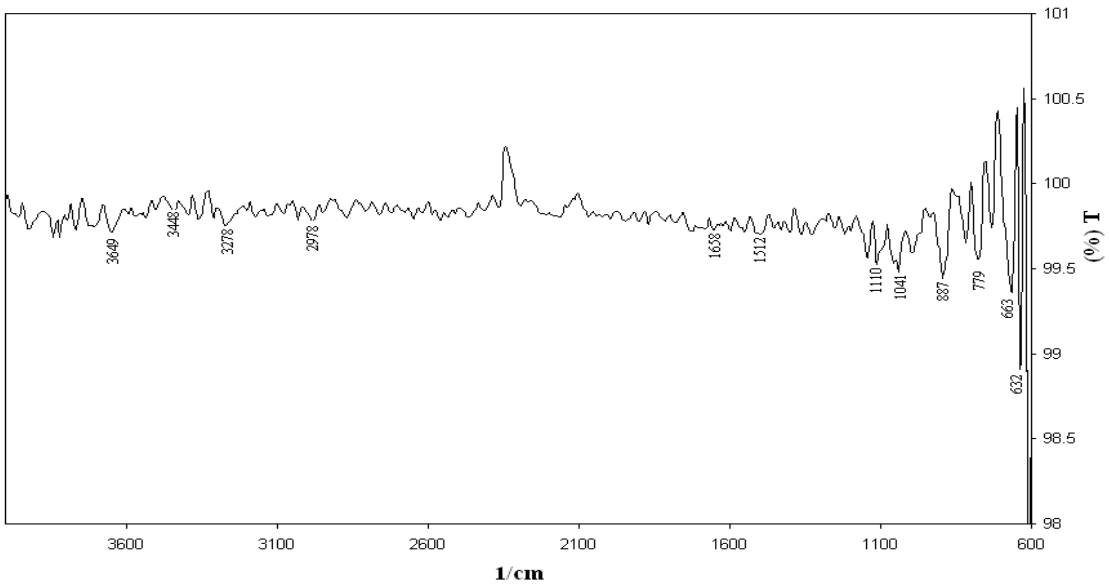

Figure 2: FT-IR spectra of the unused diospyros lotus seeds powder biosorbent

Cr–O bonds, which shows that individuals functional groups are castoff up for the detention of chromium ions from aqueous solutions. The BET surface area and pore size were resolute from a nitrogen adsorption warm obverse at 77 K using a surface area and pore size analyzer (NOVA 1200e). Already the surface area capacities, respectively model was vented at 423 K for 60 min in a nitrogen atmosphere. The surface areas of the, se diospyros lotus seeds powder biosorbent were 1.78. The diospyros lotus seeds powder had a large surface area compared to the other biosorbent this indicated that the diospyros lotus seeds powder produced better results than the other biosorbents due to its larger maximum surface area. Similarly, the pore volumes of the diospyros lotus seeds powder biosorbents were 0.003 cm^3g^{1-},

3.2. Effect of Initial pH of the Solution

To examine the effect of early pH, bunch adsorption revisions be located accomplished at a pH range as of 2–7 by means of 40.00± 2.00 mgL^{1-} as the early concentration of Cr(VI). The approval of Cr(VI) reduced with the rise in the result pH (Fig. 3). Determined adsorption was experimental at pH 2.0. At small pH the external develops

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more positive and the interaction amongst the positive surface and the dichromate anions becomes stronger, later the sorption capacity increases. At high pH the dichromate species CrO_4^{2-} and $Cr_2O_7^{2-}$ reside in the active sites of the adsorbents and delay the inward types of the identical nature, which leads to a reduction in Cr(VI) adsorption. Table 1 summarizes the effect of pH on the adsorption of Cr(VI) in aqueous media.

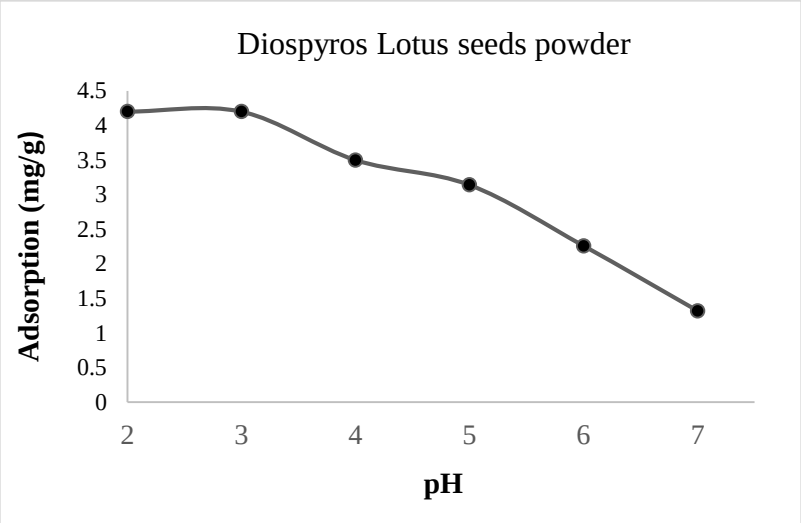

Figure 3. Effect of pH on the adsorption of Cr(VI) for use biosorbents

Table 1 Tabulated data of the effect of pH on the removal efficiency of the biosorbents for Cr(VI) removal

S. No	pH value	diospyros lotus seeds (mg/g)
1	2.00	4.20
2	3.00	4.20
3	4.00	3.50
4	5.00	3.14
5	6.00	2.26
6	7.00	1.32

Temperature = 28±1 °C, shaking- speed = 130 rpm, concentration = 40.00± 2.00 mg/L. adsorbent dosage = 0.4 g Reaction Conditions: contact time = 24 hours,

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3.3. Effect of Contact Time

Exchange time is single of the features which affects the sorption singularity. Consequently, the contact time for the biosorption of Cr(VI) was wide-ranging since 10 to 360 min while keeping the other parameters constant, i.e., 0.4 g of biosorbent at pH=2 using 40 mL of 40 mgL^{1-} Cr(VI) resolution at 303K. A distinct batch biosorption research was directed to clarify the symmetry while essential for the superficial load of the used adsorbents with hexavalent chromium. Figure 4 shows the time essential to attain equilibrium for the approval of Cr(VI) the present biosorbent. The equilibrium time of the adsorbent was 360 min. At the begning of the experimentations, maximum Cr(VI) removal was attained for the adsorbent due to the large surface area with untenanted functional groups (–OH, COO –NH_2, –C–C– and CO) which are accountable for the detention of Cr(VI) from artificial solutions. Nevertheless, as the period was long, the surfaces of the diospyros lout's seeds powder is biosorbent were working by the adsorbable (chromium) and equilibrium was conventional at 360 min (Figure 4). Next the symmetry was conventional, the exteriors converted saturated, and consequently, the amount of adsorption was measured by the rate at which the Cr(VI) removed from the external places to the internal seats of the adsorbents. It was initiate that the diospyros lotus' seeds powder adsorbent had a greater maximum adsorption capacity than the other adsorbents.

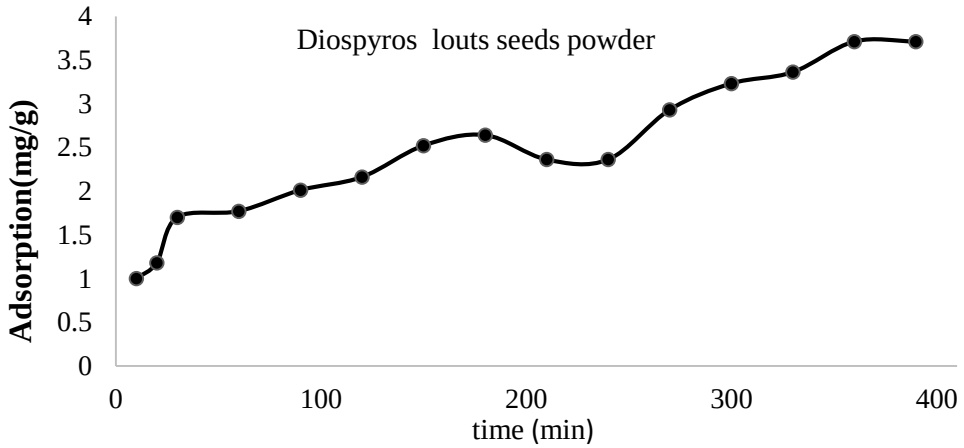

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Figure 4. Effect of contact time on the adsorption of Cr (VI) on diospyros lotus seeds powder as biosorbent

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Table 2. Contact time Effect of the removal of Cr (VI) biosorbents.

S. No	Time (min)	diospyros lotus seeds powder (mg/g)
1	10	1.00
2	20	1.18
3	30	1.70
4	60	1.77
5	90	2.01
6	120	2.16
7	150	2.52
8	180	2.64
9	210	2.36
10	240	2.36
11	270	2.93
12	300	3.23
13	330	3.63
14	360	3.71

Reaction Conditions: temperature = 28±1, concentration = 40.00± 2.00 mg/L, adsorbent dosage = 0.4 g, pH = 4, shaking speed = 130 rpm.

3.4 Effect of Adsorbent Dose

Dose studies were approved out on the arranged adsorbents keeping all of the other parameters constant. The adsorbent amount was wide-ranging from 0.2 to 1.0 g for 40 mL (40 mgL^{1-}) of Cr(VI) solution. Figure 5 characterizes the adsorption efficiency of the biosorbent. It was experimental that the elimination efficiency of the adsorbents usually decreased with an increase in the adsorbent quantity. This happened because

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the adsorbent measurements of the obtainable adsorbent were non fully used at a developed adsorbent dosage in contrast to a lower adsorbent dosage. Consequently, its strength be conceivable that the adsorption bulk reductions as the adsorbent dosage increases. In such environments, it is productive to study varying the method limitations such as temperature or pH

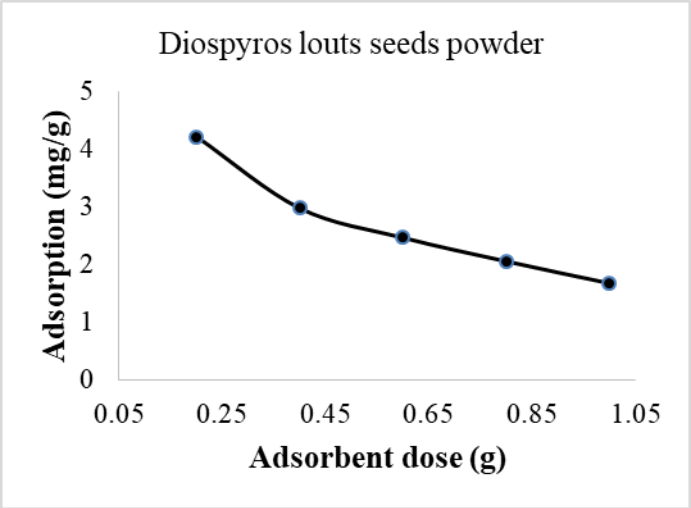

Figure 5. Effect of biosorbent dosage on the biosorption of Cr(VI).

Table 3. Relative Conclusion Removal of Biosorbents Quantity used for Cr(VI).

S. No	Adsorbent dosage (g)	Diospyros lotus' seeds powder (mg/g)
1	0.20	4.22
2	0.40	2.98
3	0.60	2.47
4	0.80	2.06
5	1.00	1.68

Reaction Conditions: temperature = 28±1 °C, connection period = 24 hours, absorption = 40.00± 2.00 mg/L, pH = 4, shaking speed = 130 rpm.

3.5 Adsorption Isotherms

Table representing quantity adsorbed against compression for concentration on instance of adsorption since solution, temperature is constant is known as an isotherm of adsorption. The experimental results have been studied using a wide variety of

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adsorption isotherms. The Freundlich and Langmuir adsorption isotherms are the two that apply the most. The Freundlich adsorption isotherm model predicts that adsorption will occur in a monolayer with a varied distribution of functional groups and contact amongst the molecules that are being adsorbed. The Freundlich model's basic equation is

$$\theta = K_f C^{1/n} \qquad (3)$$

Anywhere the Xa is quantity on the adsorbed of the absorbable symmetry Xm, (mg/g) is the quantity of absorbable obligatory monolayer meant for the attention next to adsorptive outward and adsorption strength is n, superficial attention is the once is which equivalent to = Xa/Xm. Kf is a Freundlich constant. Equation 3 becomes after applying the value.

$$\frac{X_a}{X_m} = K_f C^{1/n} \qquad (4)$$

$$X_a = X_m K_f C^{1/n} \qquad (5)$$

As $K_f X_m = K'_f$

$$X_a = K'_f C^{1/n} \qquad (6)$$

$$\log X_a = \log K'_f + \frac{1}{n} \log C_e \qquad (7)$$

The Langmuir model proposed monolayer adsorption on the standardized surface of the adsorbent. Langmuir adsorption isotherm can be characterized basically in the procedure of comparison 8 as given below:

$$X_e = \frac{q_m K_l C_e}{1 + K_l C_e} \qquad (8)$$

Where (mg/g) and qm be located over-all quantity on adsorbable necessary used for full attention of monolayer and Xe (mg/g) is the amount of adsorbate adsorbed at equilibrium, Ce (mg/L) is the equilibrium concentration, Kl (L/mg) is the Langmuir equilibrium constant, and Ce (mg/L) is the equilibrium concentration. 8 equation is

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linearized in the direction of give the resulting formula.

$$\frac{C_e}{X_e} = \frac{1}{K_l q_m} + \frac{1}{q_m} C_e \qquad (9)$$

Equations 7 and 9 were used to apply the Langmuir and Freundlich isotherms, as shown in Figures 14 and 15 It is strong that the amount of Cr(VI) maintained in solution is exactly proportional to the quantity of Cr(VI) adsorbed per element mass of the adsorbent. The values for the Langmuir and Freundlich models' qm, Kl, K/f, and n. The Langmuir isotherm model was clearly additional relevant than the Freundlich isotherm model, as shown by the correlation coefficient (R2) values. Equation 10 connected to equation the Langmuir constant (kl) on the way high temperature of adsorption as

$$K_l = K_o \exp\left(\frac{Q_{ad}}{RT}\right) \qquad (10)$$

Somewhere Q_{ad} high temperature of the adsorption, is the T of total disease and common gas continuous. R is the value of $(8.314\ J\ mol^{-1}\ k^{-1})$.

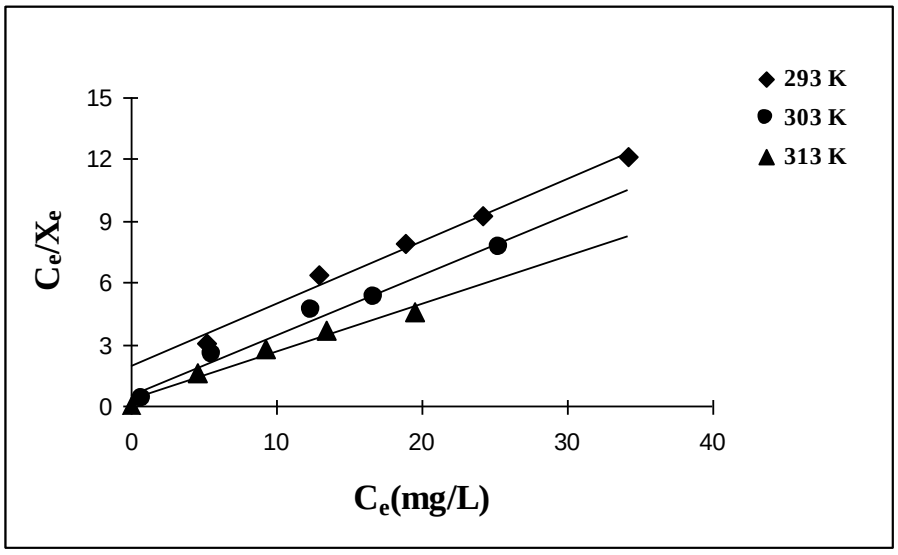

Figure 1. Adsorption Langmuir isotherms used for the elimination of Chromium (VI) on diospyros lotus seeds powder biosorbent

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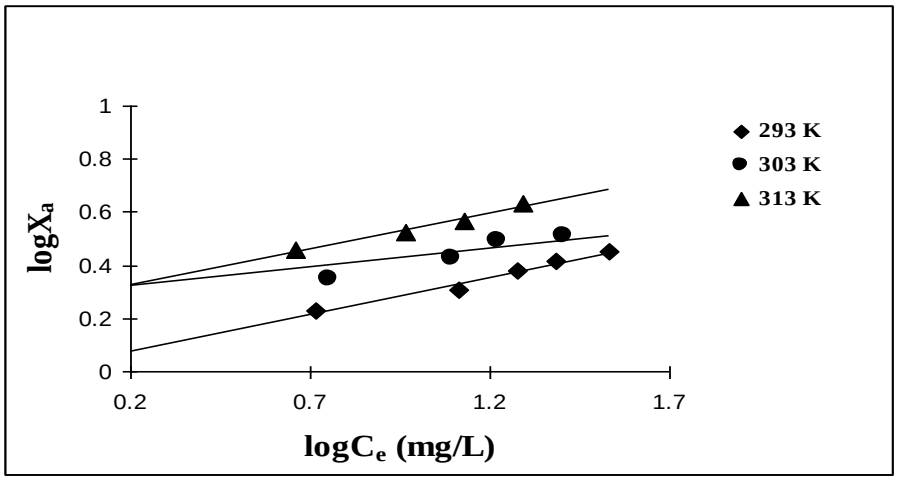

Figure 2. Adsorption Freundlich isotherms used for the elimination of Chromium(VI) on diospyros lotus seeds powders biosorbent

4. Conclusions

The adsorption productivity remained improved through the increase in temperature from 293 to 303 K (endothermic in nature). Adsorption measurements were enlarged by the rise of adsorbents amount unpaid to the occurrence of great quantity of vigorous positions. The equipoise while for the biosorbent was 360 minutes. Freundlich and Langmuir adsorption isotherms remained functional to the investigational information. The results exposed healthier suitable to the Langmuir adsorption isotherm by decent relationship constants (R^2) as compared to the Freundlich adsorption isotherm. Resolute uptake of Cr(VI) was realized at 1 g/40 mL of biosorbent. Determined adsorption capacity of diospyros lotus seed powder biosorbents was gritty in the method of monolayer treatment (q_{max}) that is 4.32 mg/g .Freundlich and Langmuir adsorption isotherms remained practical to the investigational information. The outcomes presented improved appropriate on the way to the Langmuir adsorption isotherm by means of respectable association coefficients (R^2) as related to the Freundlich adsorption isotherm. Maximum adsorption volume of diospyros lotus seed powder biosorbents was single-minded monolayer attention (q_{max}) is that 4.32 mg/g .The thermodynamically strictures like

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ΔS, ΔH and ΔG remained resolute. Since constructive ideals of ΔG, ΔH the problem remained examined. Adsorption procedure endothermal. But, organization special treatment extemporaneity at high temperatures. Adsorption power of the adsorbent remained derivative from q_{max} values. Adsorbent set from diospyros lotus' seeds powder displayed improved outcomes associated to the other adsorbents organized owing to big external area of diospyros lotus' seeds powder. Pseudo-first order and pseudo-second order equations be located practical on the method to the investigational information. Diospyros lotus seeds powder is biosorbent was found to be effective and better than numerous biosorbents stated in the works for chromium removal from aqueous solution.

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