



Adsorption of Chromium (VI) from aqueous solution by using *Eleusine coracana* (Ragi) seed powder

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ABSTRACT: Chromium is a dietary requirement for many organisms. It applies only for a trivalent chromium but not hexavalent chromium. Hexavalent chromium is very toxic to flora and fauna. Discharging the untreated chromium waste water in rivers causes environmental disasters. Taking that factor into consideration, the present study investigates the possibility of controlling Cr (VI) by using *Eleusine coracana* (Ragi) seed powder by using adsorption process. The experimental study carried out with respect to effect of contact time, concentration, adsorbent dosage, pH of the solution and temperature of the medium. The studies were proved that the adsorption efficiency is increase with increase in contact time, initial chromium concentration and adsorbent dosage. The maximum adsorption of chromium is observed at pH 7. The adsorption efficiency decreased with increase in temperature. The experimental data were tested with adsorption kinetic and adsorption isotherm models and from that it is concluded that adsorption of chromium by *Eleusine coracana* powder as an adsorbent can be described by pseudo first order kinetic model and isotherm studies reveals that adsorption of chromium is perfectly fitted with Temkin and Freundlich adsorption isotherm models.

KEY WORDS: Chromium, trivalent chromium Cr (III), hexavalent chromium Cr(VI), Adsorption, *Eleusine coracana*,

1. INTRODUCTION:

Chromium is a dietary requirement for many organisms. It applies only for a trivalent chromium but not hexavalent chromium. Hexavalent chromium is very toxic to flora and fauna. Discharging the untreated chromium waste water in rivers causes environmental disasters [1]. In the present study it was found that one of the paint manufacturing industry in Hyderabad have chromium content of 20 mg. taking that factor into consideration, the present study investigates the possibility of controlling Cr (VI) by using *Eleusine coracana* (Ragi) seed powder by using adsorption process. The study reveals the percentage removal of Chromium [Cr (VI)] increases with increase in contact time, concentration and adsorbent dosage.

2. METHODS & MATERIALS:

2.1. Selection of Adsorbent

Eleusine coracana commonly known as finger millet, or *Eleusine coracana* belongs to the family Gramineae, The grains of *Eleusine* are unusual in that the outer layer (pericarp) is not fused and can be easily removed from the seed coat (testa) below (Van Wyk & Gericke 2000) [2]. Per 100 g, the straw is reported to contain (ZMB): 3.7 g protein, 0.9 g fat, 87.3 g total carbohydrate, 35.9 g fiber, 8.1 g ash, 1110 mg Ca, 160 mg P, 260 mg Na, and 1500 mg K (C.S.I.R., 1948-1976) [3]. Potassium level in *Eleusine coracana* seeds are high this may bind with Chromium present in aqueous solution. Taking all these factors into consideration *Eleusine coracana* seed powder is selected as an adsorbent.

2.2. Selection of optimum Contact time

The contact time strongly influences the adsorption process, for this study an 1000 ml of different concentrations of chromium solutions were taken separately and they were mixed with optimum adsorbent dosage and stirred for different period of contact time i.e. for 1hr and time interval varies as 3,5,10,15.....60 min. After completion of 60 mints contact time the samples were filtered through watt man NO.1 filter paper and analyzed for chromium concentration using spectrophotometer method [4].



2.3. Determination of Optimum Dosage of Adsorbent

The effect of adsorbent dose on the removal of chromium, is studied in neutral condition (pH 7), at ambient temperature ($25 \pm 2^\circ\text{C}$) and contact time of 60 minutes for initial chromium concentration of 4 mg/L. The added amount of adsorbent was varied from 0.2 g – 1.2 g. After completion of optimum contact time period the solutions were filtered and analyzed for residual and removal of chromium concentrations respectively. The dosage which gives minimum residual concentration is chosen as optimum dosage [5].

2.4. Effect of Initial Concentration of ion

The adsorption of chromium onto various selected adsorbents was studied by varying initial chromium concentration using optimum adsorbent dosage, at ambient temperature ($25 \pm 2^\circ\text{C}$) and contact time of 60 minutes. The filtered solutions were analyzed for residual and removal of chromium concentrations respectively [6].

2.5. Determination of Optimum pH

A series of conical flasks were taken with 1000 ml of 4 mg/L of chromium solution to determine the optimum pH by adding optimum adsorbent dosage at different pH. The pH of the flasks was adjusted ranging from 3.0 to 10.0. The flasks were kept at room temperature for optimum contact time. After stirring the samples are filtered and analyzed for the chromium and chromium concentration. The flask which gives minimum and less concentrations (Cr) is selected as the optimum pH [7].

2.6. Effect of Temperature

Temperature has an important effect on the process of adsorption. The percentage of chromium adsorption is studied as a function of temperature. The batch experiments were performed at temperatures of 0°C , 30°C , 40°C , 50°C , at different initial (1, 2, 3 and 4 mg/L) concentrations of chromium.

2.7. Adsorption Isotherm Models

The parameters obtained from the different models gives important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption isotherm models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid phase concentration were tested with the Langmuir, Freundlich and Temkin isotherm equations [8]. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

(A) Temkin Adsorption Isotherm Model

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface [9 - 11]. The assumptions made by Temkin are

- ✓ Heat of adsorption decreases with surface coverage due to the interactions between adsorbent and adsorbate [12].
- ✓ Bonding energies are uniformly distributed up to certain binding energies. Depending upon these two factors Temkin proposed an empirical equation which is represented as follows [13 – 14]

$$q_e = B_T \ln K_T C_e \dots\dots(i)$$

The linear form of temkin equation is as follows (Temkin and Pyzhav)

$$q_e = B_T \ln K_T + B_T \ln C_e \dots(ii)$$

Where T is absolute temperature (K), R is universal gas constant (8.314 J/mol.k), K_T is equilibrium binding constant (L/mg), b_T is Variation of adsorption energy (kJ/mol) B_T is Temkin constant (kJ/mol).The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates. If the adsorption process follows Temkin adsorption isotherm model the graph between C_e versus q_e has to show a linear relationship.

(B) Langmuir Adsorption Isotherm Model

Langmuir adsorption isotherm explains quantitatively the formation of monolayer adsorbate on outer surface of the adsorbent, and after that no further adsorption takes place. The theoretical Langmuir isotherm is valid for adsorption of solute from a liquid solution as monolayer adsorption on a surface containing a large number of identical sites. Langmuir isotherm model [15] explains uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. The Langmuir isotherm has an assumption that the adsorption occurs within adsorbent at specific homogeneous site. The linear form of Langmuir equation is as follows:



$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \dots\dots(iii)$$

Where q_e is adsorption capacity equilibrium, q_m is the maximum adsorption capacity, C_e is the solution concentration at equilibrium k_L is Langmuir constant

(C) Freundlich Adsorption Isotherm Model

The Freundlich equation is basically empirical but is often useful as a mean for data description. The equation generally agrees with the Langmuir equation and experimental data over moderate ranges of concentration [16]. This is commonly used to describe the adsorption characteristics for the heterogeneous surface [17]. The data often fit the empirical equation proposed by Freundlich.

$$q_e = k_f C_e^{1/n} \dots\dots(iv)$$

The linear form of Freundlich equation is as follows [18]

$$\log q_e = \log k_f + 1/n (\log C_e) \dots\dots(v)$$

Where k_f is the Freundlich adsorption capacity and n is the adsorption intensity. A plot of $\log q_e$ versus $\log C_e$ gives a linear line with slope of $1/n$ and intercept of $\log k_f$.

2.8. Adsorption Kinetic models

In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, several kinetic models are used to test experimental data. The mechanism of adsorption involves the chemical reaction of functional groups present on the surface of the adsorbent and adsorbate. In present study the experimental data were tested with pseudo first order, pseudo Second order, Elovich model and intra particle diffusion models [19].

(i). Pseudo first order equation:

Pseudo-first-order kinetic model, the Lagergren rate equation, has been the most widely used rate equation for assigning the adsorption of an adsorbate from a liquid phase since 1898 [20]. A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form [21 - 22].

$$dq_t/dt = k_1 (q_e - q_t) \dots\dots(vi)$$

Where k_1 is the rate constant of pseudo-first-order adsorption and q_e denotes the amount of adsorption at equilibrium. After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the linear equation is as follows

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} X t \dots\dots(vii)$$

The plot of $\log (q_e - q_t)$ versus t should give a straight line with slope of $-k/2.303$ and intercept $\log q_e$. Pseudo first-order kinetic equation differs from a true first-order equation in following ways

- ✓ The parameter, $k (q_e - q_t)$ does not represent the number of available sites,
- ✓ The parameter, $\log (q_e)$ is an adjustable parameter and often it is found that it is not equal to the intercept of the plot of $\log (q_e - q_t)$ versus t , whereas in a true first order model the value of $\log q_e$ should be equal to the intercept.

Hence, pseudo first order kinetic model is used for estimating k alone, which is considered as mass transfer coefficient in the design calculations [23].

(ii). Pseudo second-order kinetics

As pseudo first-order kinetic model gives only k and as q_e cannot be estimated using this model, applicability of the pseudo second-order kinetics has to be tested for the estimation of q_e with the rate equation given by Ho 1995, [24]. The pseudo second order kinetic order equation expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots\dots(viii)$$

Where k_2 is the rate constant of pseudo second order adsorption (g/mg/min) and q_e is the equilibrium adsorption capacity (mg/gm) [25]. The plot of t/q_t versus t should give a linear relationship which allows the computation of a second-order rate constant, k_2 and q_e . The pseudo-second order model is based on the assumption that the rate limiting step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbent and adsorbate [26].

(iii). Elovich Model

Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate-adsorbent [27 -28]. It has extensively been accepted that the chemisorption process can be described



by this semi-empirical equation [29]. The Elovich or Roginsky–Zeldovich equation is generally expressed as follows [30 -32, 11]

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \dots \dots (ix)$$

Where, α is the initial adsorption rate (mg/g/min), β is the desorption constant (g/mg). If the adsorption fits to the Elovich model, a plot of q_t versus $\ln(t)$ should give a linear relationship with a slope of $(1/\beta)$ and an intercept of $1/\beta \ln(\alpha\beta)$.

(iv). Intraparticle Diffusion Model

In adsorption studies it is mandatory to find out the rate limiting step. Therefore the results obtained from the batch adsorption experiments were used to study the rate limiting step. The rate limiting step might be film or intraparticle diffusion which was tested by plotting a graph between amount of ion adsorbed and square root of time [33].

$$q_t = K_{id} t^{1/2} + I \dots \dots (x)$$

Where q_t is the amount of chromium and chromium adsorbed (mg/g) at time t (min), and I is the intercept (mg/g). k_{id} and I values are obtained from the slopes and intercept of the linear plot. If the postulated mechanism is correct, then a linear plot passing through the origin is obtained. Additionally, the value of the rate constant for diffusion is obtained from the slope of the line. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. In general, a mass transfer process is diffusion controlled and its rate is dependent upon the rate at which components diffuse towards one another. The intra-particle diffusion model has been applied in three different forms:

- (i) The amount of adsorption at any time, q_t is plotted against $t^{1/2}$ to get a straight line passing through origin. This means that A is equal to zero which implies that the rate is not limited by mass transfer across the boundary layer. This occurs when a system is agitated and mixed to a sufficient extent (high turbulence);
- (ii) Multi-linearity in q_t versus $t^{1/2}$ plot is considered (that is, two or three steps are involved). In this form, the external surface adsorption or instantaneous adsorption occurs in the first step; the second step is the gradual adsorption step, where intra-particle diffusion is controlling; and the third step is the final equilibrium step, where the solute moves slowly from larger pores to micro pores causing a slow adsorption rate. The time required for the second step usually depends on the variations of the system parameters such as solute concentration, temperature, and adsorbent particle size;
- (iii) q_t is plotted against $t^{1/2}$ to obtain a straight line but does not necessarily pass through the origin; that is, there is an intercept [34]. This implies that the rate is limited by mass transfer across the boundary layer. This occurs in a slowly stirred batch adsorption process.

2.9. Thermodynamic parameters

Thermodynamic parameters were calculated from the variation of the equilibrium constant, K_c , at different temperature by using following equation.

$$K_c = \frac{q_e}{C_e} \dots \dots (xi)$$

K_c (L/g) values were obtained using the Khan and Sing method [35] by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero. The intercept of the straight line with the vertical axis gives the values of K_c . The Gibbs free energy change of the adsorption process is related to K_c as in equation given below [36].

$$\Delta G^\circ = -RT \ln K_c \dots \dots (xii)$$

The changes in enthalpy (ΔH°) and entropy (ΔS°) for chromium and chromium adsorption were calculated from the slope and intercept of the plot of $\ln K_c$ against $1/T$ according to the van't Hoff equation [37].

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \dots \dots (xiii)$$

Where ΔS° is change in entropy, ΔH° is change in enthalpy ΔG° is change in free energy. Plotting $\ln K_c$ versus $1/T$ shows straight lines. From their slope and intercept, ΔH° and ΔS° are determined. The negative values of ΔG° indicate a favourable and spontaneous process [30, 38].

2.10. Equilibrium parameter

In order to find out the efficiency of adsorption process, the dimensionless equilibrium parameter, R_L is calculated by using following equation [8, 39].

$$R_L = \frac{1}{1 + K_c C_e}$$



$$1 + bC_0 \dots(xiv)$$

Where C_0 = Initial concentration (mg/L), b is Langmuir isotherm constant. Values of the dimensionless equilibrium parameter explain the differences in the shapes of the isotherm. The R_L values lies between 0 and 1 indicate favourable adsorption. The R_L value above 1 indicates unfavourable.

Non-linear regression analysis

In this experimental study, a non-linear regression analysis was conducted to determine the isotherm and kinetic constants and statistical comparison values such as determination coefficient (R^2), standard error of the estimate (SEE) and Absolute sum of squares (ASS). The batch adsorption data was evaluated using Graphpad prism scientific software. As regression models were solved, they were automatically sorted according to the goodness-of-fit system into a graphical interface. To determine the statistical significance of the predicted results 95 % confidence was used in the non-linear regression analysis.

3. RESULTS & DISCUSSION:

3.1. Effect of Contact time between Chromium and *Eleusine coracana* Seed Powder

The experimental studies measuring the effect of contact time on the batch adsorption of Cr (VI) and at initial concentration of 85 mg/L, indicated that increase in contact time from 2 to 30 minute enhanced the percent removal of Cr (VI) significantly. The initial rapid adsorption gives away a very slow approach to equilibrium. The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium. For *Eleusine coracana* seed powder this time was 30 minute. Results are given in figure-1, in a graph mode by taking contact time on X- axis and % removal on Y-axis.

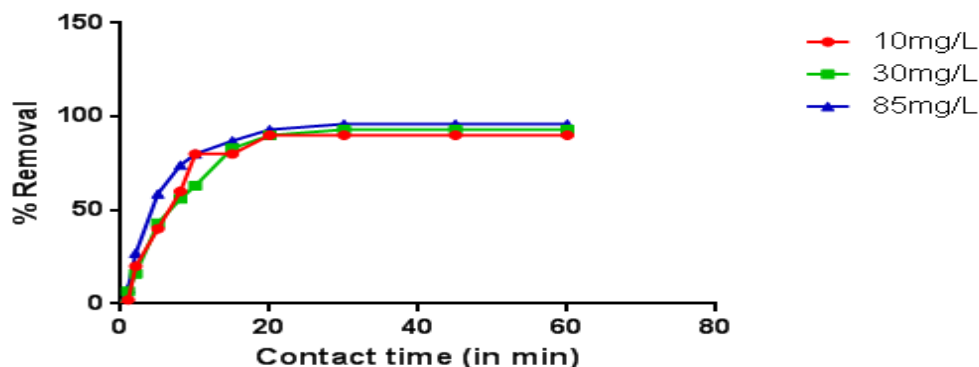


Figure – 1: Variation of contact time between Chromium and *Eleusine coracana* seed powder

3.2. Effect of Initial Chromium Concentration on *Eleusine coracana* Seed Powder

The adsorption data of Cr (VI) at different initial concentrations ranging from 50-200 mg. However, the experimental data were measured at 60 minutes to make sure that full equilibrium was attained. It is well known that by increasing the concentration of metal, the adsorbed amount increases. Results are given in figure-2.

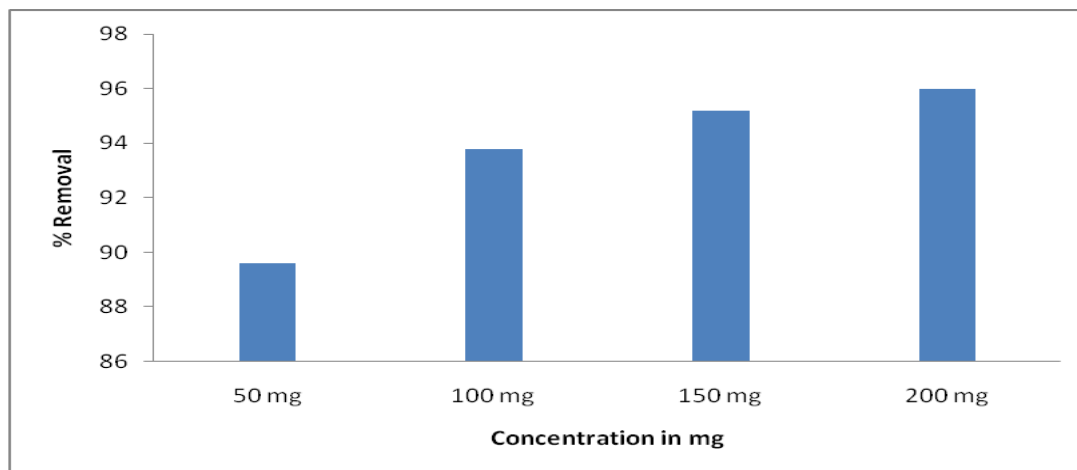


Figure – 2: Variation of initial concentration of Chromium on Adsorption



3.3. Effect of *Eleusine coracana* Seed Powder Dosages

To study the effect of adsorbent dose(g) on the uptake of Cr (VI), experiments were done with 100 ml of 85 mg solutions, while the amount of adsorbent added was varied from (0.2 – 1.2 g). Results in Figure-3 showed that the percentage removal of Cr (VI) from aqueous solution increased with the adsorbent dose and reached a optimum at 0.8 gm of sorbent. The increase in ion removal was due to the increase in the available sorption surface area [40-42].

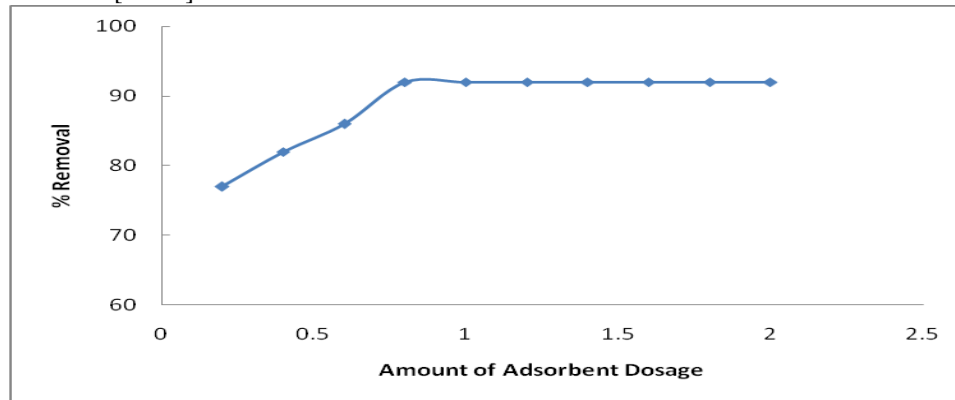


Figure –3: Variation of *Eleusine coracana* seed powder dosages on chromium adsorption

3.4. Effect of pH:

The pH of the solution is an important variable which controls the adsorption of the metal ions at the solid-water interface. Hence, the influence of pH on the adsorption of Cr+6 ions onto *Eleusine coracana* seed powder was examined in the pH range of 2-9. These results were represented in Figure 4, which showed that the adsorption capacities of Cr⁺⁶ ions onto *Eleusine coracana* seed powder increased significantly, with increasing pH value and the maximum removals of Cr⁺⁶ ions by *Eleusine coracana* seed powder for contact time (60 min) were carried out at room temperature. The improved removal of Cr (VI) at neutral pH (pH 7) is probably due to the acidic nature of *Eleusine coracana* seed powder [43-44].

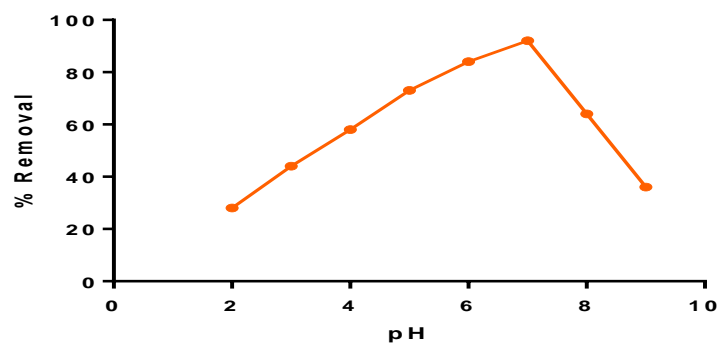


Figure-4: Effect of pH on adsorption of chromium

3.5. Effect of Temperature:

Figure 5 indicates the effect of temperature on the removal efficiency of Cr+6 ions from wastewater using *Eleusine coracana* seed powder. Six different temperatures were considered in this study (0, 30, 40, 50, 60 and 80°C). The figure showed that the removal efficiency increased by increasing the temperature, where the maximum adsorption (88% approx.) is achieved at 50°C. The adsorption process does not usually operate at high temperature (more than 50°C) and this may be due to the damage of active binding sites and because of high operational cost, so experiments were performed at the temperature range (35-50°C). Also, it is mentioned that, the metal cations become more faster with increasing temperature. While, in the adsorption of Cr (IV) onto *Eleusine coracana* seed powder at 50°C, probably the available binding sites have been saturated and the adsorbent no longer can bind further ions as the number of sites available on the adsorbent is constant. The augmentation of the removal efficiency by stepping up the temperature are due to: Firstly, the higher temperatures activate the metal ions for enhancing adsorption at the coordinating sites of the adsorbent, and the metal cations became more faster (45-46). Secondly, acceleration of some originally slow step(s) and creation of some new activation sites on the adsorbent surface (47). Herein, the phenomenon can be observed in effect of temperature on removal of chromium by *Eleusine coracana* seed powder.

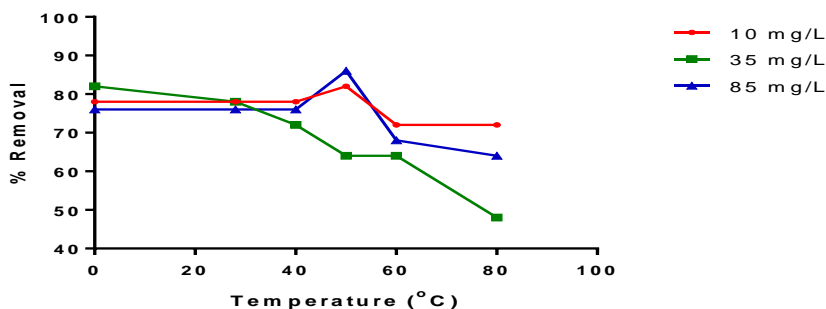


Figure-5: Effect of temperature on adsorption of chromium

3.6. Adsorption Isotherm Studies: Langmuir Adsorption Isotherm

The plot of C_e/q_e versus C_e gives a linear relationship if adsorption follows Langmuir isotherm model. The experimental data which were tested with Langmuir plot shown in figure-6. The parameter b and q_m were calculated from the intercept and slope of the plot respectively and their values at various temperatures are listed in Table-4.7.1. As shown in table-1, R^2 values at different temperatures were determined in the range of 0.708 to 0.915, more over the q_m calculated from the Langmuir isotherm was for higher than the experimental values. Therefore the Langmuir model does not describe the adsorption of Chromium onto *Eleusine coracana* seeds powder.

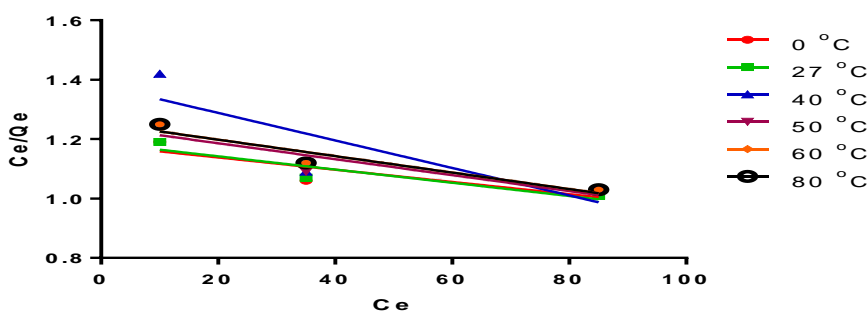


Figure-6: Langmuir Adsorption isotherm plot of adsorption of chromium by *Eleusine coracana* Seed Powder

Freundlich Isotherm Model:

The plot of $\log q_e$ against $\log C_e$ gives a straight relationship if adsorption of chromium follows Freundlich isotherm onto *Eleusine coracana* seed powder. The figure-7 shows a straight relationship indicating follows Freundlich isotherm model. The n_f and k_f values were calculated from the slope and intercept of the plot respectively. The results are presented in table-1. The correlation coefficients (R^2) are higher than those of Langmuir model (> 0.915), which confirms that experimental data can be well described by Freundlich model. The n_f values are above 1.2, which illustrates that chromium favourably adsorbed by *Eleusine coracana* seed powder.

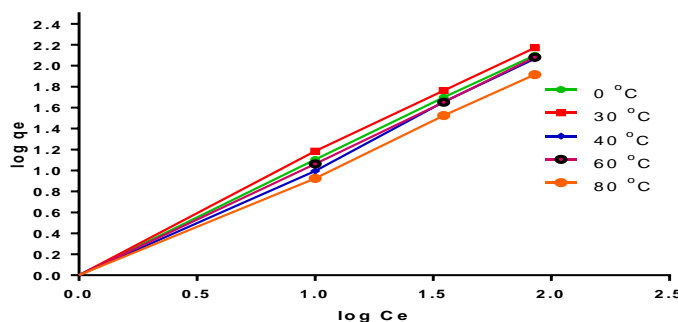


Figure-7: Freundlich adsorption isotherm plot of adsorption of chromium by *Eleusine coracana* Seed Powder



Temkin Adsorption Isotherm:

The values of A_T and B_T can be calculated from the intercept and the slope of the linear plots obtained by plotting q_e versus C_e in figure-8 (a) & (b), respectively and the results are listed in table-1. The linear regression correlation coefficients (R^2) are higher than those of the other isotherms that are the equilibrium data can be better interpreted by Temkin isotherm than the other isotherms, suggesting a uniform distribution of binding energy arising due to interaction of the chromium metal ions.

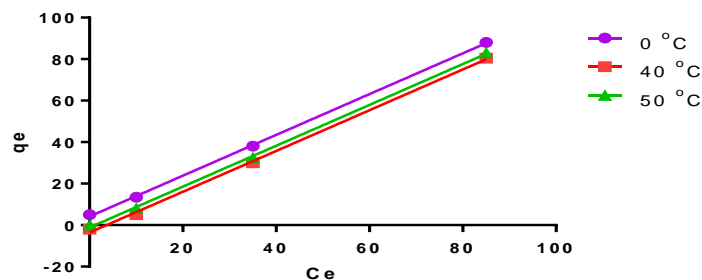


Figure-8 (a): Temkin adsorption isotherm for removal of chromium by *Eleusine coracana* seed powder at 0, 40 and 50°C

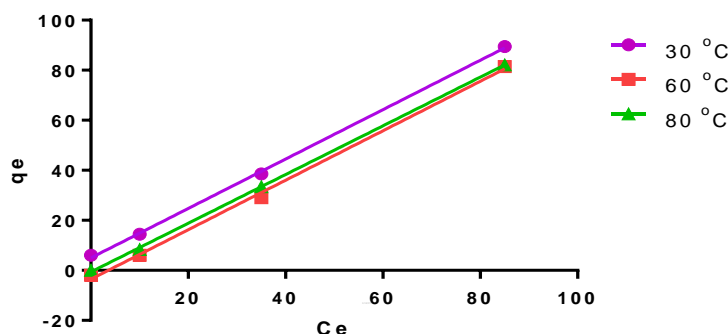


Figure-8 (b): Temkin adsorption isotherm for removal of chromium by *Eleusine coracana* seed powder at 30, 60 and 80°C

3.7. Adsorption Kinetics Models:

Pseudo first order, pseudo second order, Elovich model and Intraparticle diffusion kinetic models were selected to fit the experimental kinetic data. The linear plots and constants of all kinetic models are shown in figures -9 to figure-12 and the calculated constant values of tested kinetic models were listed in table-2.

The linear plots of $\log (q_e - q_t)$ versus t and t/q_t versus t are shown in figure-9 and figure -10, respectively. The values of q_e , k_1 and k_2 can be determined from the slope and intercept of the plots. Although the correlation coefficient (R^2) at different concentrations (10, 35, and 85 mg/L) were listed in table-2. The R^2 values of pseudo first order kinetic models were higher than that of R^2 values of pseudo second order kinetic model. However the graphical values of pseudo first order kinetic model were perfectly agrees with experimental values. The result indicating the experimental kinetic data is better describes by pseudo first order kinetic model than the pseudo second order kinetic model. The results show that the rate limiting step may be the adsorption mechanism.

Adsorption data can also be analyzed using the Elovich equation. If the adsorption of aqueous Chromium solution by *Eleusine coracana* seed powder fits to the Elovich model, a plot of q_t versus $\ln(t)$ should give a linear relationship with a slope of $(1/\beta)$ and an intercept of $1/\beta \ln(\alpha\beta)$. The results for Elovich model represented in figure-11. It was evident from the figure; the adsorption process does not fit for Elovich model. The R^2 and ASS (Absolute Sum of Squares) values are given in table-2.

The intraparticle diffusion model (31) proposed by Weber for removal chromium by *Eleusine coracana* seed powder shown in Figure-12 represents the plots of q_t versus $t^{1/2}$ for adsorption of Chromium solution by *Eleusine coracana* seed powder at various initial Chromium concentrations. It is essential for the plots to pass through origin if intraparticle diffusion is rate limiting step. The values of q_t increases quickly in the beginning and then increases slowly, indicating that the adsorption of chromium on *Eleusine coracana* seed powder is a multi step process, which adsorption on external surface, diffusion into the interior and the final equilibrium stage included [48-50].

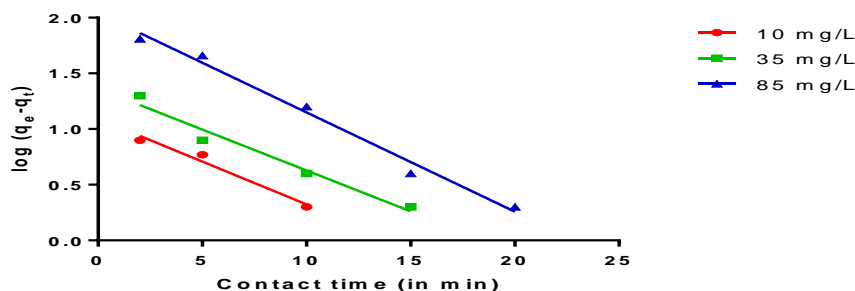


Figure-9: Pseudo first order kinetic model plot of adsorption of chromium by *Eleusine coracana* Seed Powder

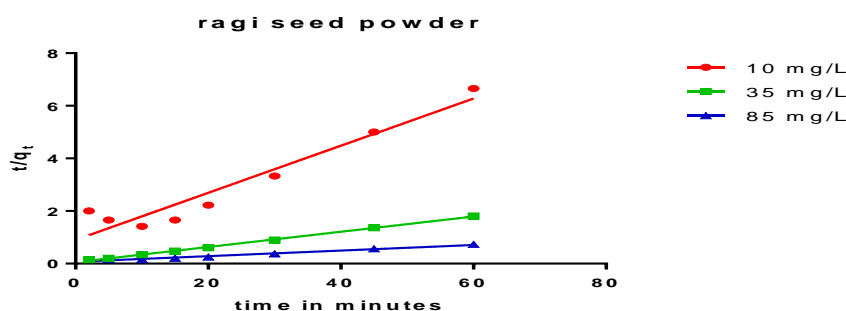


Figure-10: Pseudo Second order kinetic model plot of adsorption of chromium by *Eleusine coracana* Seed Powder

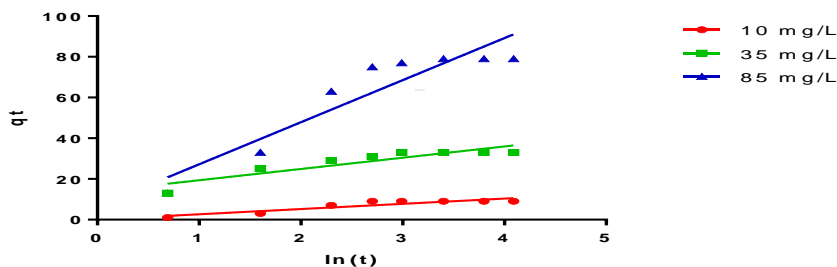


Figure-11: Elovich model plot of adsorption of chromium by *Eleusine coracana* Seed Powder

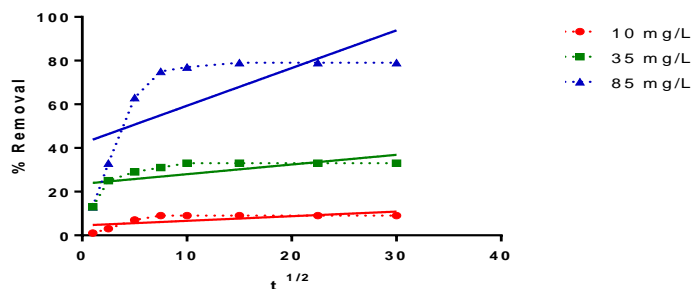


Figure-12: Intraparticle Diffusion plot of adsorption of chromium by *Eleusine coracana* Seed Powder

3.8. Thermodynamic parameters:

Thermodynamic studies of the adsorption of chromium onto *Eleusine coracana* seed powder were performed at temperatures of 273, 303, 313, 323, 333 and 353 K. Plotting $\ln K_c$ versus $1/T$ for *Eleusine coracana* seed powder shows straight lines (Figure-14). From their slope and intercept, ΔH° and ΔS° are determined. The negative values of ΔG° indicate a favorite and spontaneous process.

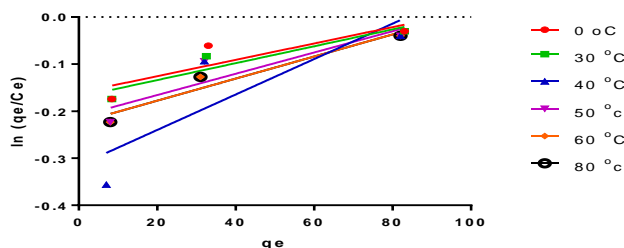


Figure-13. Relationship between $\ln(qe/Ce)$ and qe for the removal of chromium by *Eleusine coracana* seed powder

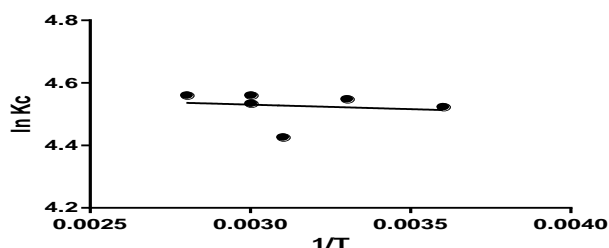


Figure-14. Relationship between $\ln(Kc)$ and $1/T$ for the removal of chromium by *Eleusine coracana* seed powder

3.9. Equilibrium parameters

Values of Dimensionless equilibrium parameter R_L at different temperatures and concentration are shown in table-4.

3.10. Fourier Transform Infrared Spectroscopy:

The FTIR spectra of chalk powder before adsorption and after adsorption were shown in figure-15. From the spectrum it is observed that the peaks at 3408 cm^{-1} is due to -OH stretching of polymeric compounds, the peak at 2927.94 cm^{-1} is due to asymmetric and symmetric vibration of methylene group (CH_2). The peaks between the regions of $1400 - 1700\text{ cm}^{-1}$, represent the functional groups of lignin, cellulose and proteins and the peaks at $1250 - 1080\text{ cm}^{-1}$ is due to stretching of C-O of carboxylic acids. The electro negative functional groups such as hydroxyl (OH) amine (NH) are capable to binding with chromium molecules, which were confirmed by shift in the peaks mainly in the region of $1800\text{-}2000\text{ cm}^{-1}$ and $1400\text{-}1600\text{ cm}^{-1}$.

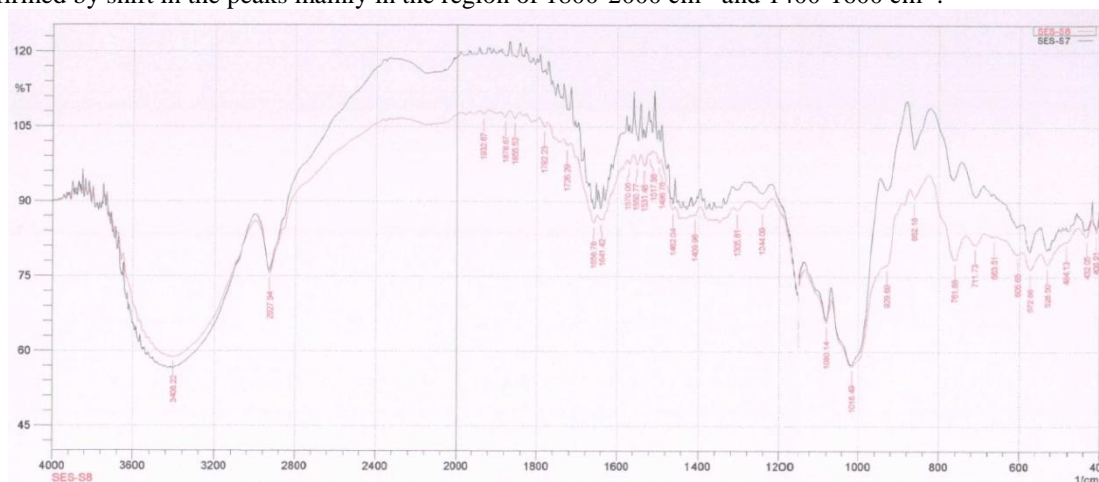


Figure-15: FTIR spectrum of *Eleusine coracana* seed powder before and after adsorption of chromium

Table-1: Isotherm kinetics for adsorption of Chromium (VI) by *Eleusine coracana* seed powder

| S.No | Parameters | Temperature °C | | | | | |
|-----------------------------------|------------|----------------|-------|-------|-------|-------|-------|
| | | 0 | 30 | 40 | 50 | 60 | 80 |
| Temkin Adsorption Isotherm | | | | | | | |
| 01 | R^2 | 0.999 | 0.999 | 0.998 | 0.999 | 0.998 | 0.999 |



| | | | | | | | |
|---------------------------------------|--------------------|---------|---------|---------|---------|---------|--------|
| | ASS | 1.454 | 2.567 | 4.197 | 7.565 | 2.848 | 0.902 |
| | a _T | -0.843 | -1.017 | -1.575 | -1.150 | -1.532 | -0.635 |
| | b _T | 0.982 | 0.987 | 0.982 | 0.984 | 0.988 | 0.973 |
| Langmuir Adsorption Isotherm | | | | | | | |
| 02 | R ² | 0.781 | 0.862 | 0.708 | 0.813 | 0.915 | 0.915 |
| | ASS | 0.003 | 0.002 | 0.025 | 0.004 | 0.002 | 0.002 |
| | Q ₀ | 1.179 | 1.187 | 1.381 | 1.240 | 1.853 | 1.253 |
| | b _L | -0.0020 | -0.0022 | -0.0046 | -0.0026 | -0.0027 | -0.002 |
| Freundlich Adsorption Isotherm | | | | | | | |
| 03 | R ² | 0.999 | 0.999 | 0.998 | 0.999 | 0.999 | 0.999 |
| | ASS | 0.064 | 0.000 | 0.000 | 0.025 | 0.000 | 0.000 |
| | Log k _f | -0.144 | -0.127 | -0.302 | -0.193 | -0.138 | -0.138 |
| | 1/n | 1.072 | 1.062 | 1.156 | 1.095 | 1.068 | 1.068 |

Table-2: Kinetic parameters for adsorption of Chromium by *Eleusine coracana* seed powder

| S.No | Parameters | Chromium concentration (10 mg/L) | Chromium concentration (35 mg/L) | Chromium concentration (85 mg/L) |
|--|-----------------|----------------------------------|----------------------------------|----------------------------------|
| Pseudo first order kinetic model | | | | |
| 01 | R ² | 0.970 | 0.966 | 0.987 |
| | ASS | 0.005 | 0.018 | 0.022 |
| | K ₁ | 0.076 | 0.073 | 0.089 |
| Pseudo Second order kinetic model | | | | |
| 02 | R ² | 0.925 | 0.998 | 0.976 |
| | ASS | 1.869 | 0.003 | 0.007 |
| | K ₂ | 8.801 x 10 ⁻³ | 1.351 x 10 ⁻³ | 1.388 x 10 ⁻³ |
| Elovich model | | | | |
| 03 | R ² | 0.834 | 0.822 | 0.865 |
| | ASS | 11.90 | 6.36 | 606.9 |
| | α | 0.757 | 1.091 | 1.310 |
| | β | 0.389 | 0.180 | 0.048 |
| Intraparticle diffusion model | | | | |
| 04 | R ² | 0.239 | 0.445 | 0.409 |
| | ASS | 15.03 | 359 | 2177 |
| | k _{id} | 0.080 | 0.629 | 1.441 |
| | I | 8.157 | 21.29 | 45.89 |

Table-3: Thermodynamic parameters of Chromium adsorption by *Eleusine coracana* seed powder

| S. No | Temperature | ΔG° (KJ/ mol) | ΔS° (KJ/ mol) | ΔH° (KJ/ mol) |
|-------|-------------|---------------|----------------|---------------|
| 01 | 273 | -1268.3 | 4.616 | -28.31 |
| 02 | 303 | -1402.1 | | |
| 03 | 313 | -1448.4 | | |
| 04 | 323 | -1494.7 | | |
| 05 | 333 | -1540.9 | | |
| 06 | 353 | -1633.5 | | |

Table-4: Equilibrium parameter R_L values at different concentration and different temperatures

| S.No | Temperature (°C) | Concentration of Chromium (mg/L) and R _L values | | |
|------|------------------|--|---------|---------|
| | | 10 mg/L | 35 mg/L | 85 mg/L |
| 01 | 0 | 0.1002 | 0.286 | 0.117 |
| 02 | 30 | 0.1002 | 0.285 | 0.117 |
| 03 | 40 | 0.1004 | 0.287 | 0.118 |
| 04 | 50 | 0.1003 | 0.286 | 0.117 |
| 05 | 60 | 0.1003 | 0.286 | 0.117 |
| 06 | 80 | 0.1001 | 0.286 | 0.117 |



4. REFERENCE:

- [1]. N. Gandhi, D. Sirisha and K.B. Chandra Sekhar, Adsorption studies of Chromium by Using Low Cost Adsorbents.. *Our Nature*, 11(1), 2013, 11-16.
- [2]. B.E. Van Wyk and N. Gericke, People's Plants. A Guide to Useful Plants of Southern Africa. (Briza Publications, Pretoria 2000).
- [3]. C.S.I.R. The Wealth of India – An Encyclopedia of India's raw Materials Resources.1948-1976.
- [4]. V. Marry priyanka, D. Sirisha and N. Gandhi, Sulphur dioxide adsorption using *Macrtyloma uniflorum* Lam. Seed powder. *Proceedings of the International Academy of Ecology and Environmental Sciences*, 2(4), 2012, 251-254.
- [5]. D. Sirisha, K. Mukkanti and N. Gandhi, Adsorption Studies on Alum Sludge. *Advances in Applied Science Research*, 3(5), 2012, 3362-3366.
- [6]. V. Marry priyanka, D. Sirisha and N. Gandhi, Adsorption studies on *Mangifera indica* controlling of SO₂ pollution. *Journal of Chemical and Pharmaceutical Research*, 4(3), 2012, 1768-1771.
- [7]. N. Gandhi, D. Sirisha, Smita Asthana, and A. Manjusha, Adsorption studies of fluoride on multani matti and red soil. *Research Journal of Chemical Sciences*, 2(10), 2012,1-4.
- [8]. M.I. Temkin and V. Pyzhev, Kinetic of Ammonia Synthesis on Promoted Iron Catalyst, *Acta Phy. Chem*, URSS 12, 1940, 327 – 356.
- [9]. Y.S. Ho, J.F. Porter, and G. Mckay, Equilibrium Isotherm Studies for Sorption of Divalent Metal ions onto Peat, Copper, Nickel and Lead single Component Systems, *Water, Air, Soil, Pollu.* 141, 2002, 1 – 33.
- [10]. Z. Chen, W. Ma, and M. Han, Biosorption of Nickel and Copper onto Treated Alga (*Undriapinnarlifida*). Application of Isotherm and Kinetic Models, *J. Hazar. Mater.* 155, 2008, 327 – 333.
- [11]. P. Brow, I. Jetcoat, D. Parrisha, S. Gilla, and E. Grahams, Evaluation of the Adsorptive Capacity of Peanut hull Pellets for Heavy Metals in Solution, *Advanc. Envir. Res.* 4, 2008, 19 – 29.
- [12]. E.S. Cossich, C.R.G. Tavares and T.M.K. Ravagnani, Biosorption of Chromium (III) by *Sargassun* Sp. Biomass, *Elctro. J. Biotech.* 5, 2002, 133 – 140.
- [13]. I. Langmuir, The Adsorption of Gases on Plane Surfaces of Glass Mic and Platinum. *J. American Chem. Soci.* 40, 1918, 1361 – 1403.
- [14]. A.R. Tembhurkar, and D. Shipa, Studies on Fluoride Removal using Adsorption Process, *J. Envir. Sci. Eng.* 48, 2006, 151 – 156.
- [15]. M. Dakiky, M. Khamis, A. Manassra and M. Mereb, Selective Adsorption of Chromium (VI) in Industrial Wastewater using Low – Cost Abundantly Available Adsorbents, *Advanc. Envir. Res.* 6, 2002, 533 – 543.
- [16]. H.M.F. Freundlich, Over the Adsorption in Solution, *J. Phy. Chem.* 57, 1906, 385 – 470.
- [17]. E. Demirbas, M. Kobya, E. Sentark and T. Ozkan, Adsorption Kinetics for the Removal of Chromium (VI) from Aqueous Solution on the Activated Carbons Prepared from Agricultural Waste, *Water SA*, 30, 2004, 533 – 539.
- [18]. S. Lagergren, About the Theory of so Called Adsorption of Soluble Substances, *Kungliga Svenska Vetenskapsakademiens Handlingar*, 24, 1898, 1 – 39.
- [19]. L. Deng, Y. Su, H. Su, X. Wang and X. Zhu, Sorption and Desorption of Lead (II) from Wastewater by Green Algae (*Cladophora fascicularis*), *J. Hazar. Mater.* 143, 2007, 220 – 225.
- [20]. S. Doyurum and A. Celik, Pb (II) and Cd (II) Removal from Aqueous Solution by Olive Cakes, *J. Hazar. Mater. B.* 138, 2006, 22 – 28.
- [21]. G. Suresh and B.V. Babu, Removal of Toxic Metal Cr (VI) from Aqueous Solutions using Saw Dust as Adsorbent. Equilibrium, Kinetics and Regeneration Studies. *Chem. Eng. J.* 150, 2009, 352 – 365.
- [22]. Y.S. Ho, Adsorption of Heavy Metals from Waste Streams by Peat, Ph.D. Thesis, University of Birmingham, Birmingham UK, (1995).
- [23]. H. Elifantz and E. Telor, Heavy Metal Biosorption by Plant Biomass of the Macrophyte (*Ludwigia stolonifera*), *Water Air and Soil Pollution*, 141, 2002, 207 – 218.
- [24]. Y.S. Ho and G. Mcay, Study of the Sorption of Divalent Metal ions to Peat. *Adsorption Sci. Technol.* 18, 2008, 639 – 650.
- [25]. S.M. Yakout and E. Elsherif, Batch Kinetics, Isotherm and Thermodynamic Studies of Adsorption of Strontium from Aqueous Solutions onto Low –Cost rice Straw Based Carbons. *Carbon Sci. Technol-* 1, 2010, 144 – 153.
- [26]. D.L. Sparks, Kinetics of Soil Chemical Process, Academic Press, New York, (1989).
- [27]. J. Zhang and R. Stan forth, Slow Adsorption Reaction between Arsenic Species and Geothite. Diffusion or Heterogeneous Surface Reaction Control, *Langmuir* 21, 2005, 2895 – 2901.
- [28]. M.J.D. Low, Kinetics of Chemisorption of Gases on Solids, *Chem. Rev.* 60, 1960, 267 – 312.



- [29]. S.H. Chien and W.R. Clayton, Application of Elovich Equation to the Kinetics of Phosphate Release and Sorption on Soils, *Soil Sci. Soci. American J.* 44, 1980, 265 – 268.
- [30]. D.L. Sparks, Kinetics of Reaction in Pure and Mixed Systems in Soil Physical Chemistry, (CRC Press, Boca Raton, 1986).
- [31]. W.J. Weber, and J.C. Morris, Kinetics of Adsorption on Carbon from Solution, *J. Sanitary Eng. Div. American Soci. Chem. Eng.* 89, 1963, 31 – 39.
- [32]. F. Wu, R. Tseng, and R. Juang, Initial behaviour of Intraparticle Diffusion Model used in the Description of Adsorption Kinetics, *Chem. Eng. J.* 153, 2009, 1 – 8.
- [33]. A.A. Khan and R.P. Singh, Adsorption Thermodynamics of Carbofuran on Sn (IV) Arseno silicate in H⁺, Na⁺ and Ca⁺² forms, *Colloids. Surface.* 24, 1987, 33 – 42.
- [34]. H. Uslu and I. Inci, Adsorption Equilibria of L – (+) – Tartaric Acid onto Alumina. *J. Chem. Eng. Data*, 54, 2009, 1997 – 2001.
- [35]. P.N. Palanisamy and P. Sivakumar, Adsorption Studies of Basic red 29 by a Non _Conventional Activated Carbon Prepared from Euphorbia Antiguorum L. *Inter. J. Chemtech. Res.* 1, 2009, 502 – 506.
- [36]. M. Karthikeyan and K.P. Elongo, Removal of Fluoride from Aqueous Solution using Graphite. A Kinetic and thermodynamic Study, *Indian J. Chem. Technol.* 15, 2008, 525 – 532.
- [37]. N. Gandhi, D. Sirisha, M. Hasheena and Smita Asthana, Eco-friendly Method for Synthesis of Copper Nanoparticles and Application for removal of Aqueous Sulphur Dioxide (SO₂) and Nitrogen Dioxide (NO₂). *International Journal of Engineering Research and Technology.* 3(11), 2014, 1253-1262.
- [38]. N. Gandhi, D. Sirisha and K.B. Chandra Sekhar, Bioremediation of Wastewater by using *Strychnos Potatorum* Seeds (Clearing nuts) as Bio Adsorbent and Natural Coagulant for Removal of Fluoride and Chromium. *Journal of International Academic Research for Multidisciplinary*, 3(1), 2014, 253-272.
- [39]. N. Gandhi, D. Sirisha and Vikas Chandra Sharma, Microwave-Mediated Green Synthesis of Silver Nanoparticles Using *Ficus Elastica* Leaf Extract and Application in Air pollution Controlling Studies. *International Journal of Engineering Research and Applications.* 4(1), 2014, 01-12.
- [40]. N. Gandhi, D. Sirisha and K.B. Chandra Sekhar, Adsorption of Fluoride from aqueous solution by using chalk powder. *World Journal of Pharmacy and Pharmaceutical Sciences*, 2(5), 2013, 3897-3914.
- [41]. N. Gandhi, D. Sirisha and K.B. Chandra Sekhar, Adsorption of Chromium (VI) from aqueous solution by using brick powder. *Asian Academic Research Journal of Multidisciplinary*, 1(15), 2013, 112-137.
- [42]. N. Gandhi, D. Sirisha, Smita Asthana and A. Manjusha, Adsorption studies of fluoride on multani matti and red soil. *Research Journal of Chemical Sciences*, 2(10), 2012, 1-4.
- [43]. A. Manjusha, N. Gandhi and D. Sirisha, Removal of Chromium (VI) from paint manufacturing industry waste water by using papaya peel powder. *International Journal of Pharma world Research*, 3(2), 2012, 1-4.
- [44]. A. Manjusha, N. Gandhi and D. Sirisha, Adsorption of Chromium (VI) from aqueous solution by using *mangifera indica* bark dust. *Universal Journal of Environmental Research and Technology.* 2(1), 2012, 1-6.
- [45]. S. Babel and T. A. Kurniawan, “Low-cost adsorbents for heavy metal uptake from contaminated water: a review,” *J Hazard. Mater.*, 97(1-3), Feb. 2003, pp. 219-243,
- [46]. V.J. Inglezakis, K.J. Hadjiandreou, M.D. Loizidou, H.P. Grigoropoulou, Pretreatment of Natural Clinoptilolite in a Laboratory-scale ion-exchange Packed Bed. Department of Chemical Engineering, National Technical University of Athens, Zografou Campus, Athens, Greece, 2000.
- [47]. P.A. Domenico and F.W. Schwertz, Physical and Chemical Hydrology. (John Wiley and Sons, Inc., New York, NY, 1990).
- [48]. Gandhi, N., Sirisha, D., and Chandra Shekar, K.B., Adsorption of Fluoride from aqueous solution by using chalk powder. *World Journal of Pharmacy and Pharmaceutical Sciences*, 2(5), 2013, 3897-3914.
- [49]. N. Gandhi, D. Sirisha and K.B. Chandra Sekhar, Adsorption of Chromium (VI) from aqueous solution by using brick powder. *Asian Academic Research Journal of Multidisciplinary*, 1(15), 2013, 112-137.
- [50]. N. Gandhi, D. Sirisha and K.B. Chandra Sekhar, Adsorption of Chromium (VI) from aqueous solution by using Multani miti. *International Journal of Research in Pharmacy and Chemistry.* 4(1), 2014, 168-180.