



Chief Editor

Dr. A. Singaraj, M.A., M.Phil., Ph.D.

Editor

Mrs.M.Josephin Immaculate Ruba

Editorial Advisors

1. **Dr.Yi-Lin Yu**, Ph. D
Associate Professor,
Department of Advertising & Public Relations,
Fu Jen Catholic University,
Taipei, Taiwan.
2. **Dr.G. Badri Narayanan**, PhD,
Research Economist,
Center for Global Trade Analysis,
Purdue University,
West Lafayette,
Indiana, USA.
3. **Dr. Gajendra Naidu.J.**, M.Com, LL.M., M.B.A., PhD. MHRM
Professor & Head,
Faculty of Finance, Botho University,
Gaborone Campus, Botho Education Park,
Kgale, Gaborone, Botswana.
4. **Dr. Ahmed Sebihi**
Associate Professor
Islamic Culture and Social Sciences (ICSS),
Department of General Education (DGE),
Gulf Medical University (GMU), UAE.
5. **Dr. Pradeep Kumar Choudhury**,
Assistant Professor,
Institute for Studies in Industrial Development,
An ICSSR Research Institute,
New Delhi- 110070.India.
6. **Dr. Sumita Bharat Goyal**
Assistant Professor,
Department of Commerce,
Central University of Rajasthan,
Bandar Sindri, Dist-Ajmer,
Rajasthan, India
7. **Dr. C. Muniyandi**, M.Sc., M. Phil., Ph. D,
Assistant Professor,
Department of Econometrics,
School of Economics,
Madurai Kamaraj University,
Madurai-625021, Tamil Nadu, India.
8. **Dr. B. Ravi Kumar**,
Assistant Professor
Department of GBEH,
Sree Vidyanikethan Engineering College,
A.Rangampet, Tirupati,
Andhra Pradesh, India
9. **Dr. Gyanendra Awasthi**, M.Sc., Ph.D., NET
Associate Professor & HOD
Department of Biochemistry,
Dolphin (PG) Institute of Biomedical & Natural Sciences,
Dehradun, Uttarakhand, India.
10. **Dr. D.K. Awasthi**, M.SC., Ph.D.
Associate Professor
Department of Chemistry, Sri J.N.P.G. College,
Charbagh, Lucknow,
Uttar Pradesh. India

ISSN (Online) : 2455 - 3662
SJIF Impact Factor :4.924

EPRA International Journal of **Multidisciplinary Research**

Monthly Peer Reviewed & Indexed
International Online Journal

Volume: 4 Issue:6 June 2018



Published By :
EPRA Journals

CC License



**EPRA International Journal of
Multidisciplinary Research (IJMR)**

ADSORPTIVE REMOVAL OF CHROMIUM (VI) BY LOW –COST MATERIAL CONCRETE POWDER

N. Gandhi¹

¹Centre for environment and climate
change,
School of environmental sciences,
Jawaharlal Nehru institute of advanced
studies (JNIAS-JNTUA),
Hyderabad, Telangana & Jawaharlal
Nehru Technological University
Anantapur, Ananthapuram A.P, India

D. Sirisha²

Centre for environment and climate change,
School of environmental sciences,
Jawaharlal Nehru institute of advanced
studies,
Hyderabad, Telangana, India

ABSTRACT

Hexavalent chromium is a heavy metal found in low levels in drinking water in many places of India. Chromium is entering into sources of water from industrial plants and hazardous waste sites. It was found to cause cancer in laboratory mice and rates when they were exposed through drinking water. The present study investigates the possibility of controlling chromium (VI) by most cost effective process such as batch adsorption process by using concrete as an adsorbent. When concrete powder is used as adsorbent, it could successfully remove 72 % of Cr (VI) at the concentration of permissible limit and 82 % at the above permissible limit. The investigations were carried out with various parameters, such as effect of contact time, initial chromium concentration, concrete powder dosage, pH of the solution and temperature of the medium. The results reveals that percentage removal Cr (VI) by concrete is directly proportional to contact time, concentration of the solution and dosage of concrete powder. The efficiency of adsorption was found to decrease with temperature. The experimental data was also tested with different adsorption kinetic models and adsorption isotherm models. The adsorption of chromium by concrete powder followed pseudo first order kinetic model and Freundlich adsorption isotherm.

KEY WORDS: *Chromium, Adsorption, Concrete, Kinetic models, Isotherm models, FTIR, low-cost method.*

INTRODUCTION

Most of the divisions of our communities like industry, agriculture, mining, energy, transportation, construction and consumers producing waste and resulting in environmental pollution. These wastes contain pollutants which are discarded materials, process materials or chemicals. Pollution could be caused by these pollutants when they are released beyond the assimilation capacity of the environment [1]. Tannery and paint manufacturing effluents contains the highest pollutants among all industrial wastes. They are especially large contributors of chromium pollution. Urbanization, Civilization and industrialization has brought tremendous changes in the life style of many communities, which has lead to many environmental pollution [2].

Chromium can significantly affect the ecological environment when present in large amount [3]. Therefore chromium pollution has recently received much attention in industries such as the leather, paint and metal finishing industry. The heavy metal chromium is a carcinogenic, tasteless and odourless chemical that is associated with industrial waste from metal plating operations and other manufacturing concerns. In higher doses it may result in the manifestation of certain abnormalities. Chromium has been linked to concern and other serious health problems through inhalation, ingestion and contact. Chromium is found in many effluents and is found to be highly toxic to living organisms. It also causes chromosome abnormalities [4].

Various traditional precipitation and ion exchange processes have been developed for removal and recovery of heavy metal ions from the wastewater [5]. However, the precipitation process is costly and does not always provide a satisfactory removal rate to meet the pollution control limits for the treatment of wastewater. The synthetic ion exchange resins are often quit expensive also. Adsorption has become one of the most useful methods for wastewater treatment [6]. Moreover numerous investigations have proved the feasibility of using agricultural products, industrial waste biomass and natural substances to decontaminate wastewater that contain metal ion [7-10]. In addition these materials are readily available and inexpensive. Therefore adsorption with relevant adsorbents can be adopted to treat wastewater.

METHODS AND MATERIALS

Selection of Adsorbent:

The components of concrete powder are silica, stones and cement in the ratio 1:2:4 and consists 2.5% of MgO, 62% of CaO, 22% of SiO₂, 1% of K₂O, 7.2% of Al₂O₃, 2.5% of Fe₂O₃ and SO₃. Whenever modifications of buildings and structures are under taken solid waste such as dismantled concrete cement consists of calcium and cement is obtained. As this mixture consists of Al, Mg, Fe, Ca it is considered for the study of removal of chromium. Physical and mechanical properties of an adsorbent is depends on its porosity and porosity

structure. The porosity of concrete is high, considering this factor and concrete selected for adsorption studies to remove chromium from aqueous solution.

Selection of optimum contact time

To find out the effect of contact time on adsorption of chromium by concrete powder, batch adsorption experiments were conducted with 1000 ml of Cr (VI) solution of different concentrated solution of Cr (VI) and constant concrete powder dosage. The final residual concentration of chromium after adsorption at regular time intervals (2,5,...60 min) were determined by spectrophotometer.

Determination of Optimum Dosage of Adsorbent

The experiments were conducted at neutral pH, at constant dosage of concrete powder and room temperature for 60 minutes and concentration was maintained as 4 mg/L. The addition of concrete powder is varied between 0.2 gm – 1.2 gm. After 60 minutes contact time period the change in concentration and percentage removal were determined by spectrophotometer using diphenylcarbazide method. The dosage which gives minimum residual concentration is chosen as optimum dosage.

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.

Determination of Optimum pH

A series of conical flasks were taken 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 batch adsorption experiments were conducted at room temperature and optimum contact time. The better pH for removal of chromium by concrete powder was found from the results.

Effect of Temperature

The adsorption influenced by the temperature. In the present investigation the batch adsorption studies were conducted at constant chromium concentration, concrete dosage and neutral pH by varying temperature between 0 - 80°C.

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 Tempkin isotherm equations [11]. 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 [12 - 14]. The assumptions made by Temkin are

- ✓ Heat of adsorption decreases with surface coverage due to the interactions between adsorbent and adsorbate [15].
- ✓ 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 [16 – 17]

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

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 [18] 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 [19]. This is commonly used to describe the adsorption characteristics for the heterogeneous surface [20].

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 [21]

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

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 $\log k_f$.

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 [22].

(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 [23]. A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form [24 - 25].

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

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 [26].

(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, [27]. 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) [28]. 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 [29].

(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 [30 -31]. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation [32]. The Elovich or Roginsky-Zeldovich equation is generally expressed as follows [33 -35, 14]

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

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 [36].

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

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 [37]. This implies that the rate is limited by mass transfer across the boundary layer. This occurs in a slowly stirred batch adsorption process.

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 [38] 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 [39].

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

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 [39].

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

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 [33, 40].

Equilibrium parameter

In order to find out the efficiency of adsorption process, the dimensionless equilibrium parameter, R_L is calculated by using following equation [11, 41].

$$R_L = \frac{1}{1 + bC_0} \dots(xiv)$$

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.

RESULTS & DISCUSSION

Effect of Contact time between Chromium and Concrete Powder

The experimental runs 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 figure-1, shows the percentage removal increases with increase in contact time initially and slows down with time indicates attachment of equilibrium between adsorbent and adsorbate. The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium. For this concrete powder time was 30-40 minutes.

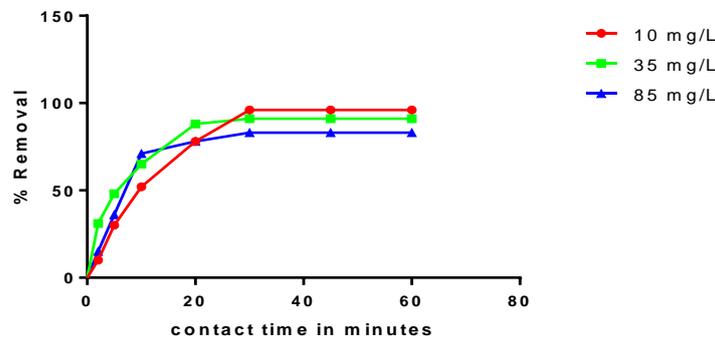


Figure - 1: Variation of contact time between Chromium and Concrete powder

Effect of Initial Chromium Concentration on Concrete 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.

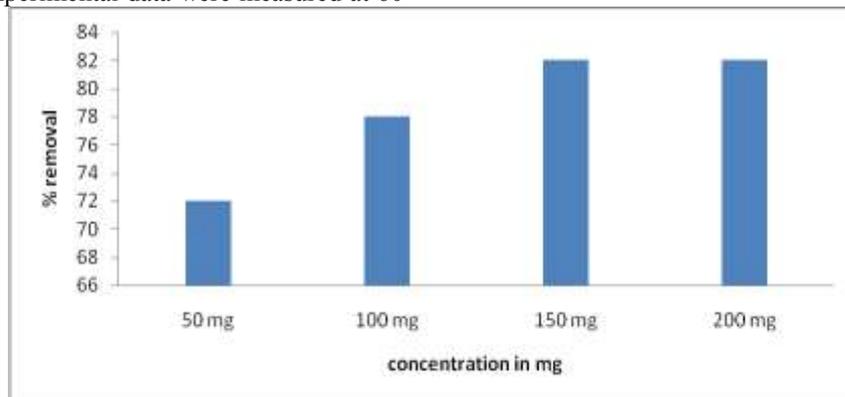


Figure -2: Variation of initial concentration of Chromium (VI) on adsorption

Effect of Concrete Powder Dosages

To study the effect of adsorbent dose on the uptake of Cr (VI), experiments were done with 1000 ml of 85 mg solutions, while the amount of adsorbent added was varied from (0.2 – 0.8 g). Results in figure-3, showed that the percentage

removal of Cr (VI) from aqueous solution increased with the adsorbent dose and reached an optimum at 0.8 gm of sorbent. The increase in ion removal was due to the increase in the available sorption surface area.

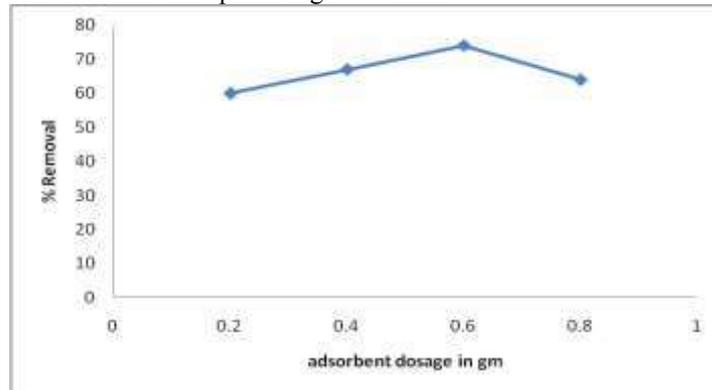


Figure – 3: Variation of Concrete powder dosages on adsorption of chromium

Effect of pH

The Fig.5.5.4 shows the adsorption efficiency of concrete powder at different pH. The adsorption experiments followed the expected trend of increasing metal retention with increasing medium pH. When the pH of the adsorbing medium is increased from 2 – 9, there was a corresponding increase in deprotonation of the concrete surface

leading to a decrease in H⁺ ion on the surface. This creates more negative charges on the surface, which favours adsorption of positively charge species as a result of less repulsion between the positively charge species and the positive sites on the surface [42-43]. At initial pH 2, adsorption of Cr (VI) was < 10 %, it increased to as high as 47 % adsorption at pH 6.

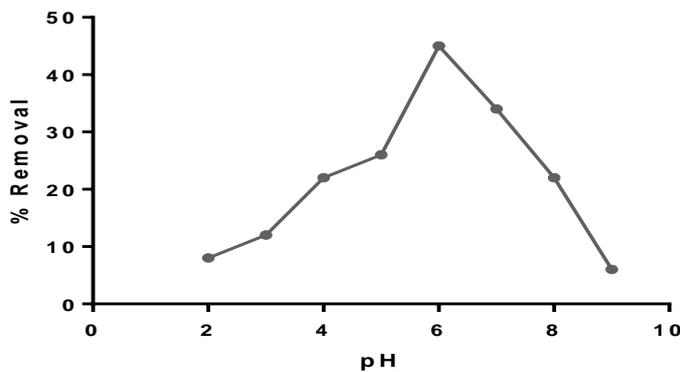


Figure- 4. Effect of pH on adsorption process

Effect of Temperature

The Fig.5.5.5 shows the adsorption efficiency of concrete powder at different temperatures. The adsorption experiments at different temperatures concluding that removal of chromium by concrete is a physical adsorption process. The more adsorption

efficiency observes at lower temperatures and the efficiency is keep decreased as increase in temperature. This observation stating that adsorption of chromium by concrete will shows high efficiency at lower temperatures only.

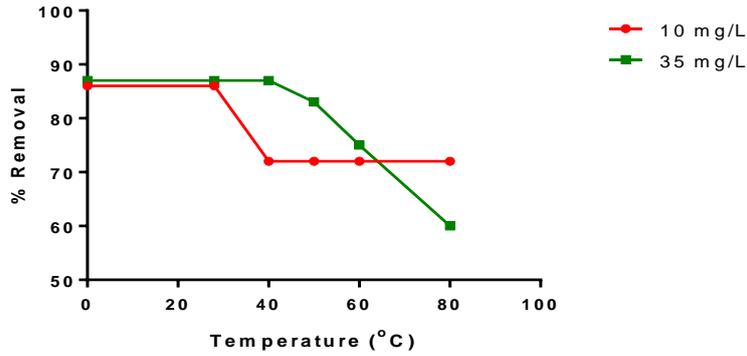


Figure-5: Effect of temperature on adsorption of chromium

Adsorption Isotherm Studies:

The experimental data tested with Langmuir, Freundlich and Temkin adsorption isotherm models. The results are shown in figure-6 to 8. The constant values obtained from the graphs were tabulated in table-5.5.1. The Correlation coefficient (R^2) values and calculated constant values were compared with obtained values from graph and concluded that adsorption of Cr (VI) by concrete can be perfectly described by Temkin and Freundlich adsorption isotherm models.

Langmuir Adsorption Isotherm Model

The plot of C_e/q_e versus C_e gives a linear relationship if adsorption follows Langmuir isotherm model. The experimental data 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-1. As shown in table-1, R^2 values at different temperatures were determined in the range of 0.708 to 0.927, 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 concrete seeds powder.

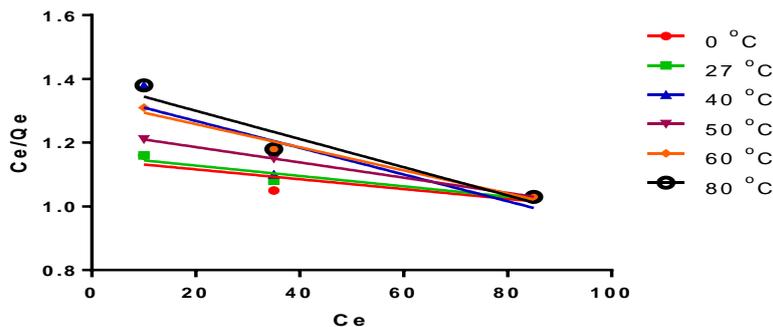


Figure-6: Langmuir Adsorption isotherm plot of adsorption of chromium by concrete powder

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 concrete. The figure-7 shows a straight relationship which 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 ($> \dots$), 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 concrete.

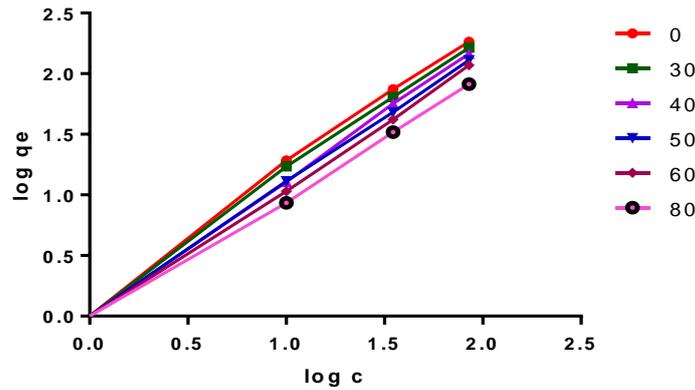


Figure-7: Freundlich adsorption isotherm plot of adsorption of chromium by concrete powder

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 is 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.

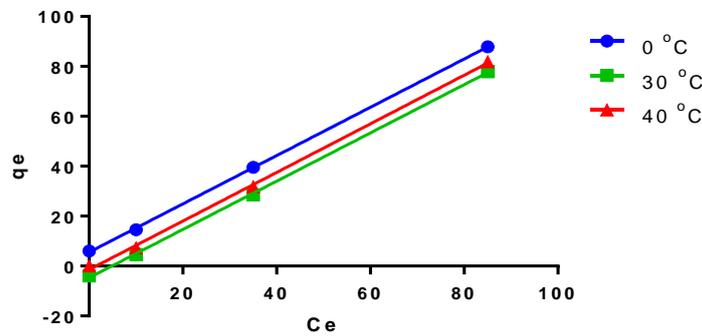


Figure-8 (a): Temkin adsorption isotherm for removal of chromium by concrete at 0, 30 and 40°C.

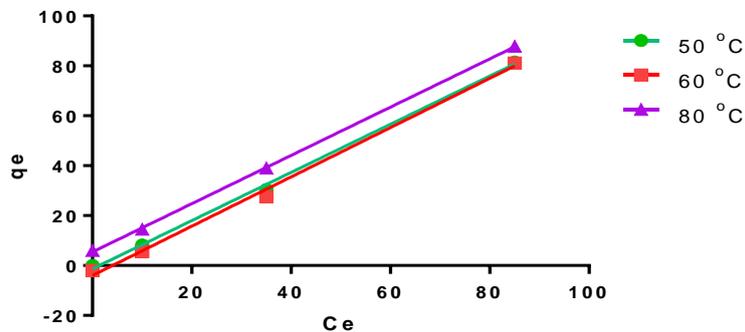


Figure-8 (b): Temkin adsorption isotherm for removal of chromium by concrete at 50, 60 and 80°C.

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 12 and calculated values of standards were tabulated in table-2 respectively.

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.

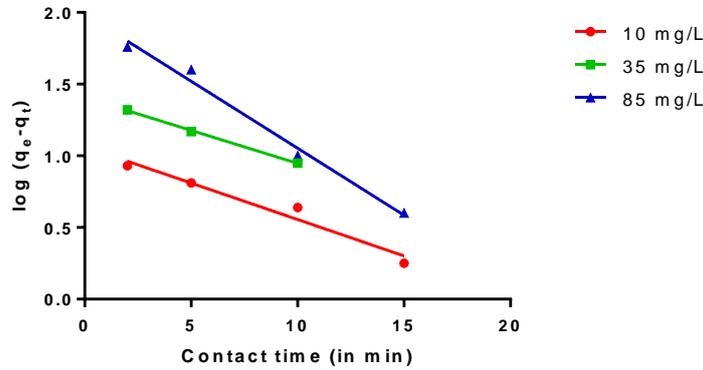


Figure-9: Pseudo first order kinetic model plot of adsorption of chromium by concrete

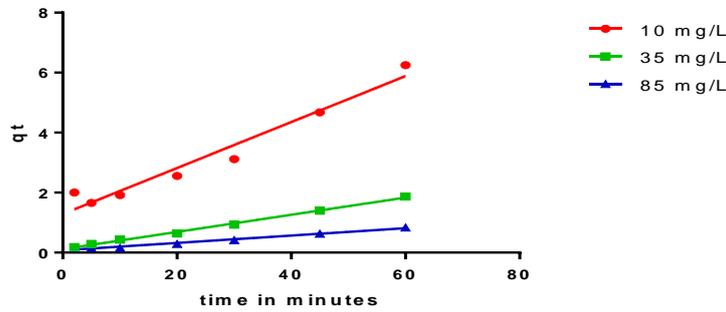


Figure-10: Pseudo Second order kinetic model plot of adsorption of chromium by concrete

Adsorption data can also be analyzed using the Elovich equation. If the adsorption of aqueous Chromium solution by concrete 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 (Weber and Morris 1963) proposed by Weder and Morris can

be linear plot. Figure-12 represents the plots of q_t versus $t^{1/2}$ for adsorption of Chromium solution by concrete 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 concrete powder is a multi step process, which adsorption on external surface, diffusion into the interior and the final equilibrium stage included.

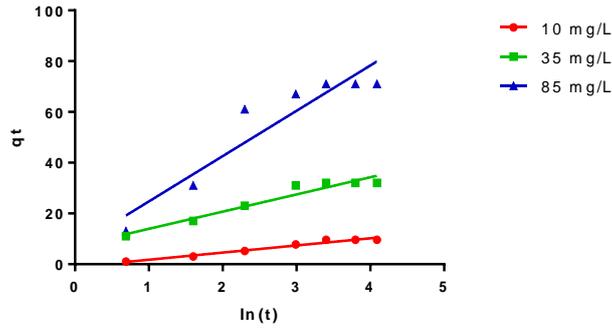


Figure-11: Elovich model plot of adsorption of chromium by concrete powder

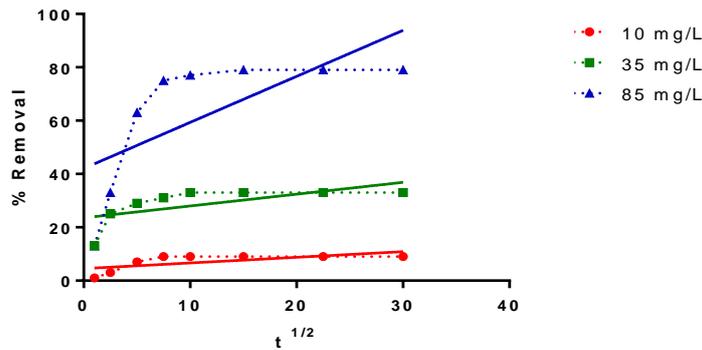


Figure-12: Intraparticle diffusion model plot for removal of Cr(VI) by concrete

Thermodynamic parameters:

Thermodynamic studies of the adsorption of chromium onto concrete powder, were performed at temperatures of 273, 303, 313, 323, 333 and 353 K.

the parameters, including ΔG° , ΔH° and ΔS° were calculated and tabulated (Figure-4.8.14). The negative values of ΔG° indicate a favourite and spontaneous process (21-22).

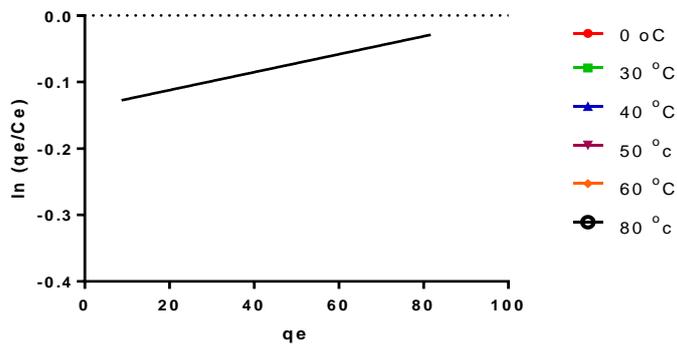


Figure-13. Relationship between $\ln(q_e/C_e)$ and q_e for the removal of chromium by concrete

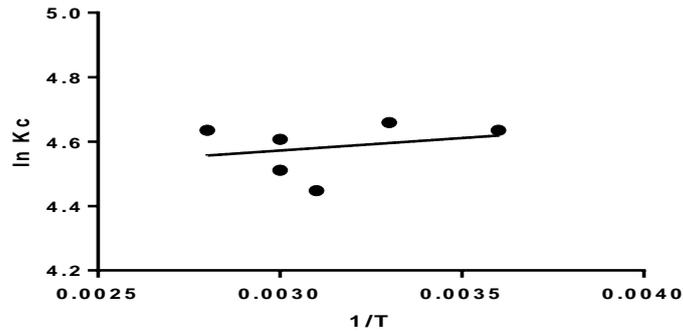


Figure-14. Relationship between $\ln(Kc)$ and $1/T$ for the removal of chromium by concrete Equilibrium parameter:

Values of the dimensionless equilibrium parameter, R_L , of different temperatures are calculated for the initial concentrations of Chromium (VI) and are given in table-4.8.4. The parameters explain the differences in the shapes of the isotherm. The observed R_L values for Chromium (VI) are between 0 to 1 and it indicative of the favourable adsorption.

Mechanism of adsorption of Chromium (VI) by concrete powder:

Different mechanisms for adsorption were proposed depending upon their binding strength and reversibility. From the adsorption isotherm studies for removal of chromium by concrete powder, it is noted that lower temperatures is favourable, as plots of adsorption isotherms of Freundlich, Temkin and Langmuir are coinciding with each other at 30°C and 40°C. All the straight lines in plots were below the 0°C, which indicating the favourable conditions for physical adsorption, due to weak vander waal forces. From the effect of initial chromium concentration it is noted that concrete material introduced in chromium solution will already covered by at least one monolayer of adsorbed water and formation of

multi layers is possible due to the different physical forces such as diffusion, dispersion etc. as the Langmuir adsorption isotherm is not followed, the concrete powder is heterogeneous, with different type of materials on its surface, cleavages and change is the nature of active site.

Fourier Transform Infrared Spectroscopy:

The FTIR spectra of concrete powder before adsorption and after adsorption were shown in figure-4.3.16. The peak at 648.08 cm^{-1} , indicates the presence of Si-O-Si and Al-O-Si bonding, in the spectrum of concrete powder before adsorption. The same peaks were observed after adsorption indicating that these molecules are not participating in the binding of chromium molecules from the aqueous solution. Similarly the peaks around 420-460 cm^{-1} , 730 and 773 cm^{-1} , 1000-1150 cm^{-1} indicates asymmetric Si-O-Si vibrations and O-Si-O bonding before and after adsorption. Hence, it is concluded that the every substance surface has a tendency to take up the molecules which comes in contact of them. The stretching of peaks from 3410.15 cm^{-1} to 3431.36 cm^{-1} indicates the OH of $\text{Ca}(\text{OH})_2$ in the concrete powder and it have taken up the molecules of chromium from aqueous solution.

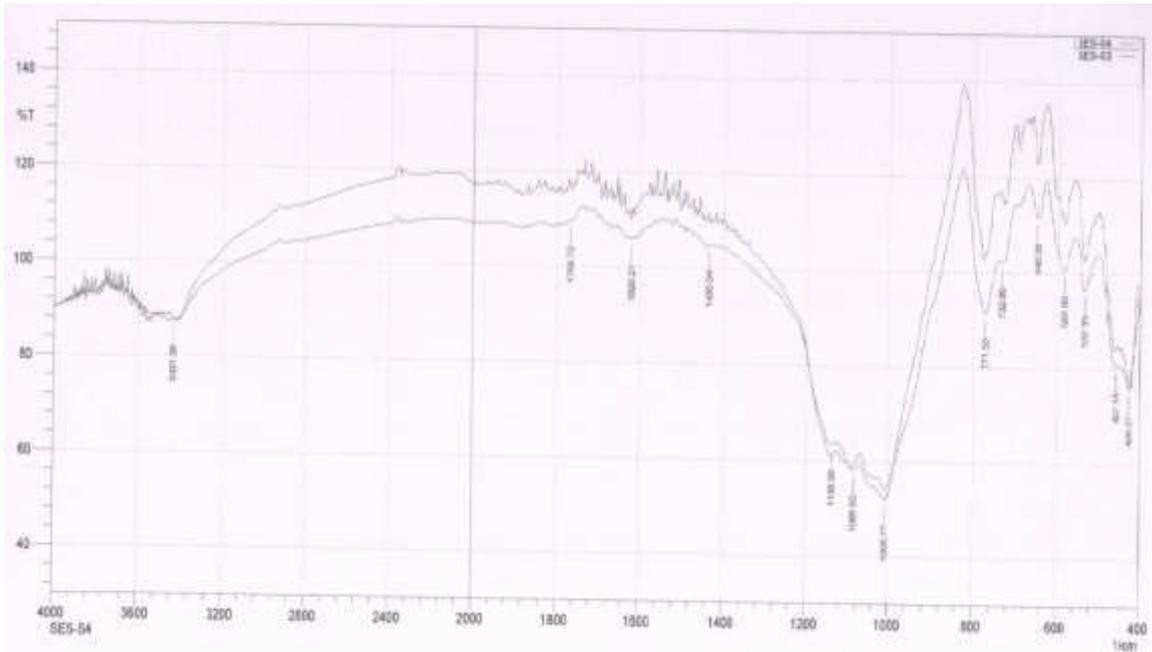


Figure-15: FTIR spectrum of concrete powder before and after adsorption of Chromium

Table-1: Isotherm kinetics for adsorption of Chromium (VI) by Concrete

| S.No | Parameters | Temperature °C | | | | | |
|---------------------------------------|--------------------|----------------|--------|---------|---------|---------|---------|
| | | 0 | 30 | 40 | 50 | 60 | 80 |
| Temkin Adsorption Isotherm | | | | | | | |
| 01 | R ² | 0.999 | 0.999 | 0.999 | 0.998 | 0.996 | 0.999 |
| | ASS | 0.628 | 1.015 | 4.208 | 6.782 | 14.45 | 0.680 |
| | a _T | -0.448 | -0.679 | -1.451 | -1.327 | -1.994 | -0.586 |
| | b _T | 0.967 | 0.967 | 0.973 | 0.965 | 0.987 | 0.967 |
| Langmuir Adsorption Isotherm | | | | | | | |
| 02 | R ² | 0.708 | 0.899 | 0.750 | 0.999 | 0.978 | 0.927 |
| | ASS | 0.002 | 0.000 | 0.017 | 0.000 | 0.000 | 0.004 |
| | Q ₀ | 1.147 | 1.161 | 1.352 | 1.234 | 1.331 | 1.389 |
| | b _L | -0.0015 | 0.0016 | -0.0040 | -0.0024 | -0.0036 | -0.0044 |
| Freundlich Adsorption Isotherm | | | | | | | |
| 03 | R ² | 0.999 | 0.999 | 0.999 | 0.999 | 0.999 | 0.999 |
| | ASS | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.058 |
| | Log k _f | -0.116 | -0.118 | -0.274 | -0.162 | -0.214 | -0.116 |
| | 1/n | 1.054 | 1.053 | 1.139 | 1.072 | 1.116 | 1.054 |

Table-2: Kinetic parameters for adsorption of Chromium by Concrete

| 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 | 0.959 | 0.998 | 0.987 |
| | ASS | 0.010 | 0.055 | 0.011 |
| | K ₁ | 0.050 | 0.046 | 0.093 |
| Pseudo Second order kinetic model | | | | |
| 02 | R ² | 0.956 | 0.996 | 0.984 |
| | ASS | 0.752 | 0.007 | 0.006 |
| | K ₂ | 4.487 x 10 ⁻³ | 6.758 x 10 ⁻³ | 1.894 x 10 ⁻³ |
| Elovich model | | | | |
| 03 | R ² | 0.968 | 0.939 | 0.884 |
| | ASS | 2.367 | 26.91 | 378.8 |
| | α | 1.046 | 7.167 | 17.85 |
| | β | 0.355 | 0.147 | 0.056 |
| Intraparticle diffusion model | | | | |
| 04 | R ² | 0.694 | 0.612 | 0.535 |
| | ASS | 22.82 | 172.8 | 1527 |
| | k _{id} | 0.3885 | 0.8911 | 2.264 |
| | I | 3.019 | 17.34 | 34.47 |

Table-3: Thermodynamic parameters of Chromium adsorption by Concrete

| S. No | Temperature | ΔG° (KJ/ mol) | ΔS° (KJ/ mol) | ΔH° (KJ/ mol) |
|-------|-------------|---------------|----------------|---------------|
| 01 | 273 | - 1107.31 | 4.340 | 77.54 |
| 02 | 303 | -1229.08 | | |
| 03 | 313 | -1269.65 | | |
| 04 | 323 | -1310.21 | | |
| 05 | 333 | -1350.78 | | |
| 06 | 353 | -1431.90 | | |

Table-4: Equilibrium parameter RL 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 | 0.1001 | 0.0286 | 0.0117 |
| 02 | 30 | 0.1001 | 0.0286 | 0.0117 |
| 03 | 40 | 0.1004 | 0.0286 | 0.0118 |
| 04 | 50 | 0.1002 | 0.0286 | 0.0117 |
| 05 | 60 | 0.1003 | 0.0286 | 0.0118 |
| 06 | 80 | 0.1004 | 0.0286 | 0.0118 |

REFERENCE

- 1) N. Gandhi, D. Sirisha, K.B. Chandra Shekar, Adsorption of Chromium (VI) from aqueous solution by using brick powder. *Asian Academic Research Journal of Multidisciplinary*, 1(15), 112-137, (2013).
- 2) N. Gandhi, D. Sirisha, K.B. Chandra Shekar, 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), 253-272, (2014).
- 3) H.Y Liu, V. Badarinarayana, D.C. Audino, J. Rappsilber, M. Mann, C.L. Denis, *The NOT proteins are part of the CCR4 transcriptional complex and affect gene expression both positively and negatively. EMBO J* 17(4), 1096-106, (1998).
- 4) K. Ganesan, Y. Alias, Synthesis and Characterization of Novel Dimeric Ionic Liquids by Conventional Approaches, *Int. J. Mol. Sci.* 9(7), 1207-1213, (2008).
- 5) J.W. Patterson, *Industrial Wastewater Treatment Technology*, 2nd edition, Butterworth Publishers, Stoneham, Ma, (1985).
- 6) N. Gandhi, D. Sirisha, K.B. Chandra Shekar, Adsorption of Fluoride from aqueous solution by using chalk powder. *World Journal of Pharmacy and Pharmaceutical Sciences*, 2(5), 3897-3914, (2013).
- 7) N. Gandhi, D. Sirisha, M. Hasheena, 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), 1253-1262, (2014).
- 8) D Sirisha, K. Mukkanti, N. Gandhi, "Adsorption Studies on Alum Sludge", *Advances in Applied Science Research*, 3(5), 3362-3366, (2012).
 - 9) A. Manjusha, N. Gandhi, 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), 1-6, (2012).
 - 10) A. Manjusha, N. Gandhi, D. Sirisha, "Adsorption of Chromium (VI) from aqueous solution by using mangifera indica bark dust". *Universal Journal of Environmental Research and Technology*. 2(1), 1-4, (2012).
 - 11) M.I. Temkin, V. Pyzhev, *Kinetic of Ammonia Synthesis on Promoted Iron Catalyst*, *Acta Phy. Chem, URSS*, 12, 327 – 356 (1940).
 - 12) Y.S. Ho, J.F. Porter, 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, 1 – 33 (2002).
 - 13) Z. Chen, W. Ma, M. Han, *Biosorption of Nickel and Copper onto Treated Alga (Undriapinnarlifida). Application of Isotherm and Kinetic Models*, *J. Hazar. Mater.* 155, 327 – 333 (2008).
 - 14) P. Brow, I. Jetcoat, I. Parrisha, D. Gilla, E. Grahams, *Evaluation of the Adsorptive Capacity of Peanut hull Pellets for Heavy Metals in Solution*, *Advanc. Envir. Res.* 4, 19 – 29, (2008).
 - 15) E.S. Cossich, C.R.G. Tavares, T.M.K. Ravagnani, *Biosorption of Chromium (III) by Sargassum Sp. Biomass*, *Elctro. J. Biotech.* 5, 133 – 140, (2002).
 - 16) I. Langmuir, *The Adsorption of Gases on Plane Surfaces of Glass Mic and Platinum*. *J. American Chem. Soci.*, 40, 1361 – 1403, (1918).
 - 17) A.R. Tembhurkar, D. Shipa, *Studies on Fluoride Removal using Adsorption Process*, *J. Envir. Sci. Eng.* 48, 151 – 156, (2006).
 - 18) M. Dakiky, M. Khamis, A. Manasra, Mereb, *Selective Adsorption of Chromium (VI) in Industrial Wastewater using Low – Cost Abundantly Available Adsorbents*, *Advanc. Envir. Res.* 6, 533 – 543 (2002).
 - 19) H.M.F. Freundlich, *Over the Adsorption in Solution*, *J. Phy. Chem.* 57, 385 – 470 (1906).
 - 20) E. Demirbas, M. Kobya, E. Sentark, T. Ozkan, *Adsorption Kinetics for the Removal of Chromium (VI) from Aqueous Solution on the Activated Carbons Prepared from Agricultural Waste*, *Water SA*, 30, 533 – 539 (2004).
 - 21) S. Lagergren, *About the Theory of so Called Adsorption of Soluble Substances*, *Kunliga Svenska Vetenskapsakademiens Handlingar*, 24, 1 – 39, (1898).
 - 22) L. Deng, Y. Su, H. Su, X. Wang, X. Zhu, *Sorption and Desorption of Lead (II) from Wastewater by Green Algae (Cladophora fascicularis)*, *J. Hazar. Mater.*, 143, 220 – 225 (2007).
 - 23) S. Doyurum, A. Celik, *Pb (II) and Cd (II) Removal from Aqueous Solution by Olive Cakes*, *J. Hazar. Mater. B.* 138, 22 – 28, (2006).
 - 24) G. Suresh, 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, 352 – 365, (2009).
 - 25) Y.S. Ho, *Adsorption of Heavy Metals from Waste Streams by Peat*, Ph.D. Thesis, University of Birmingham, Birmingham UK, (1995).
 - 26) H. Elifantz, E. Telor, *Heavy Metal Biosorption by Plant Biomass of the Macrophyte (Ludwigia stolonifera)*, *Water Air and Soil Pollution*, 141, 207 – 218, (2002).
 - 27) Y.S. Ho, G. Mcay, *Study of the Sorption of Divalent Metal ions to Peat*. *Adsorption Sci. Technol.*, 18, 639 – 650, (2008).
 - 28) S.M. Yakout, 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, 144 – 153, (2010).
 - 29) D.L. Sparks, *Kinetics of Soil Chemical Process*, Academic Press, New York, (1989).
 - 30) J. Zhang, R. Stan forth, *Slow Adsorption Reaction between Arsenic Species and Geothite. Diffusion or Heterogeneous Surface Reaction Control*, *Langmuir*, 21, 2895 – 2901, (2005).
 - 31) M.J.D. Low, *Kinetics of Chemisorption of Gases on Solids*, *Chem. Rev.* 60, 267 – 312, (1960).
 - 32) S.H. Chien, W.R. Clayton, *Application of Elovich Equation to the Kinetics of Phosphate Release and Sorption on Soils*, *Soil Sci. Soci. American J.* 44, 265 – 268 (1980).
 - 33) D.L. Sparks, *Kinetics of Reaction in Pure and Mixed Systems in Soil Physical Chemistry*, CRC Press, Boca Raton, (1986).
 - 34) W.J. Weber, J.C Morris, *Kinetics of Adsorption on Carbon from Solution*, *J. Sanitary Eng. Div. American Soci. Chem. Eng.* 89, 31 – 39, (1963).
 - 35) F. Wu, R. Tseng, R. Juang, *Initial behaviour of Intraparticle Diffusion Model used in the Description of Adsorption Kinetics*, *Chem. Eng. J.* 153, 1 – 8 (2009).
 - 36) A.A. Khan, R.P. Singh, *Adsorption Thermodynamics of Carbofuran on Sn (IV) Arseno silicate in H⁺, Na⁺ and Ca⁺² forms*, *Colloids. Surface*, 24, 33 – 42, (1987).
 - 37) H. Uslu, I. Inci, *Adsorption Equilibria of L – (+) – Tartaric Acid onto Alumina*. *J. Chem. Eng. Data*, 54, 1997 – 2001, (2009).
 - 38) P.N. Palanisamy, P. Sivakumar, *Adsorption Studies of Basic red 29 by a Non _Conventional Activated Carbon Prepared from Euphorbia Antiquorum L. Inter. J. Chemtech. Res.* 1, 502 – 506, (2009).
 - 39) M. Karthikeyan, K.P. Elongo, *Removal of Fluoride from Aqueous Solution using Graphite. A Kinetic and thermodynamic Study*, *Indian J. Chem. Technol.* 15, 525 – 532, (2008).

- 40) N Gandhi; D Sirisha; Smita Asthana, Bio adsorption of Alizarin red dye using immobilized *Saccharomyces cerevisiae*. *International Research Journal of Natural and Applied Sciences*, 2(3), 1-17, (2015).
- 41) D. Sirisha, Smita Asthana, N. Gandhi, M. Hasheena, Adsorptive removal of aqueous SO_2 by using Orange Peel Powder. *Indian Journal of Science-Discovery*. 12(34), 39-51, (2015).
- 42) M.P. Koivula, K. Kujala, H. Ronkkomaki, M. Makela, Sorption of Pb (II), Cr (III), Cu (II), As (III) to peat and Utilization of the Sorption Properties in Industrial Waste Landfill Hydraulic barrier Layers. *J. Hazard. Mater.* 164, 345 – 352, (2009).
- 43) M. Yurtsever, I.A. Sengil, Biosorption of Pb (II) ions by Modified Quebracho tannin resin, *J. Hazard. Mater.* 163, 38 – 64, (2009).