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Adsorptive Removal of Chromium (VI) from Synthetic Wastewater by Using Chalk powder as Cost –Effective Adsorbent

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Abstract— **In this study, a series of batch laboratory experiments were conducted in order to investigate the feasibility of chalk powder as cost effective adsorbent for the removal of chromium from aqueous solution by the adsorption process. Investigation was carried out by studying the influence of initial solution pH, adsorbent dosage, contact time and initial concentration of chromium. The particle size of chalk powder used was 250 mic. All batch experiments were carried out at a constant temperature of 30°C (±2°C) using mechanical shaker that operated at 100 rpm. The single component equilibrium data was analyzed using Langmuir, Freundlich and Temkin adsorption isotherms.**

Index Terms— **Chromium (VI), Batch Adsorption, Adsorption Isotherms, Adsorption Kinetics, Chalk powder, Thermodynamics.**

I. INTRODUCTION

The international standard for drinking water states that water intended for human consumption must be free from organisms and chemical substances that which are hazardous to health [1]. The water used for drinking, irrigation and for agricultural use should be free from chromium.

The heavy metal chromium is a carcinogenic, tasteless and odorless chemical found in industrial effluents and is highly toxic to living organisms. Aerosol from chromium refining plants affects human life by causing cancer and chromates act as irritants to eyes. Chromium exposure causes damage to liver and kidney. It also causes chromosome abnormalities [2]. Over exposure of industrial labors to dust and mists of chromium species lead to lung carcinoma. Its ingestion leads to nausea and hemorrhage. Chromium is reported to cause skin dermatitis, nasal membrane, inflammation, ulceration and liver damage. When adsorbed into the body, they severely irritate gastrointestinal tract, leading to circulatory shock and renal damage. Numerous techniques have been employed for the removal of heavy metal ions such as chromium. These include chemical precipitation, co-precipitation, coagulation, evaporator recovery process, reverse osmosis, electrolytic recovery, and adsorption [3].

Recently attention has been drawn towards the development of alternative methods like adsorption which uses low cost and waste materials as adsorbents. Adsorption plays an important role in elimination of metal ions from aqueous solutions in water pollution control [4].

II. METHODS & MATERIALS

Selection of Adsorbent

Chalk powder is the waste material collected from classrooms. Chalk is the form of Calcium carbonate with minor amount of silt and clay. As Calcium carbonate decomposes only at 900^0C, the adsorption taking place in the present study is physical adsorption. Chalk powder due to certain porosity adsorbs chromium from aqueous solution of chromium. Taking all these factors into consideration chalk powder is selected as an adsorbent [5]. The present work, examines the possibility of using a well-known physicochemical method like adsorption for the removal of chromium from water. The initial screening studies have been carried out by introducing a known amount of adsorbent into the aqueous solution of chromium.

Table-1: Characterization of Adsorbent

S. No.	Parameter	Result
01	Surface area	34.72
02	Particle size	250 µm
30	Particle density	0.31
04	Moisture content	9%
05	Porosity & void ratio	66
06	Apparent density	0.29
07	Real density	0.83

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 [6].

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 ($25 \pm 2^{\circ}$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 [7].

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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 ± 2°C) and contact time of 60 minutes. The filtered solutions were analyzed for residual and removal of chromium concentrations respectively [8].

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 is selected as the optimum pH [9].

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.

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 [10]. 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 [11 - 13]. The assumptions made by Temkin are

- ✓ Heat of adsorption decreases with surface coverage due to the interactions between adsorbent and adsorbate [14].
- ✓ 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 [15 – 16]

$$q_e = B_T \ln K_T C_e \text{ ……(i)}$$

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

$$q_e = B_T \ln K_T + B_T \ln C_e \text{ ….(ii)}$$

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 [17] 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:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \text{…….(iii)}$$

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 [18]. This is commonly used to describe the adsorption characteristics for the heterogeneous surface [19]. The data often fit the empirical equation proposed by Freundlich.

$$q_e = k_f C_e^{1/n} \text{ …..(iv)}$$

The linear form of Freundlich equation is as follows [20]

$$\log q_e = \log k_f + 1/n (\log C_e) \text{ …..(v)}$$

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 [21].

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

$$dq_t/dt = k_1 (q_e - q_t) \text{ …..(vi)}$$

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

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} X\, t \text{ …..(vii)}$$

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 [25].

(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, [26]. The pseudo second order kinetic order equation expressed as

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

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) [27]. The plot of t/qt 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 [28].

(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 [29-30]. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation [31]. The Elovich or Roginsky–Zeldovich equation is generally expressed as follows [32 -34, 13]

$$\frac{dq_t}{d_t} = \alpha \exp(-\beta\, q_t) \text{.......(ix)}$$

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/β) and an intercept of 1/β In (αβ).

(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 [35].

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

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 qt 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) qt 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 [36]. 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, at different temperature by using following equation.

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

K_c (L/g) values were obtained using the Khan and Sing method [37] 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 [38].

$$\Delta G^{o} = - RT \ln K_c \text{....(xii)}$$

The changes in enthalpy (ΔH^o) and entropy (ΔS^o) for chromium and chromium adsorption were calculated from the slope and intercept of the plot of ln Kc against 1/T according to the van’t Hoff equation [39].

$$\ln K_c = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{RT} \text{..... (xiii)}$$

Where ΔS^o is change in entropy, ΔH^o is change in enthalpy ΔG^o is change in free energy. Plotting ln K_c versus $1/T$ shows straight lines. From their slope and intercept, ΔH^o and ΔS^o are determined. The negative values of ΔG^o 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 [10, 41].

$$R_L = \frac{1}{1 + bC_o} \quad \text{....(xiv)}$$

Where C_o = 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.

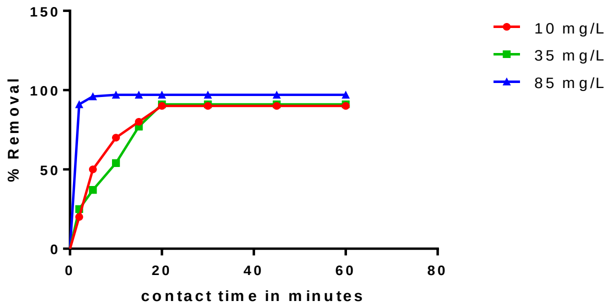
Non-linear regression analysis

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.

III. RESULTS & DISCUSSION

Effect of Contact time between Chromium and Chalk Powder

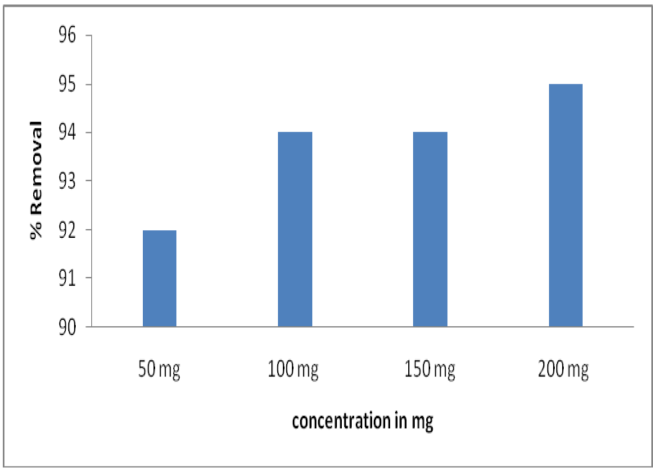
The experimental run measured the effect of contact time on the batch adsorption of Cr (VI) and at initial concentration of 10 mg/L, 35 mg/L and 85 mg/L. The results indicated that increase in contact time from 1 to 20 minute enhanced the percent removal of Cr (VI) significantly. The initial rapid adsorption gives away a very slow approach to equilibrium at lower concentration. The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium. For Chalk powder optimum contact time is 20 minutes. Results are given in figure- 1. This difference in chalk powder behavior in very dilute solution can be explained by Debye-Hukel theory, which states that the contact time of adsorption of opposite ionic molecule in a medium depends on the dilution of the medium. At lower concentration, due to the dilution the mobility of chromium metal ions increases and they are free to move in entire region of solvent media. They have to cross the relaxation effect and electrophoretic effect. Thus to reach equilibrium stage, it needs certain amount of time.



Figure–1: Variation of contact time between Chromium and Chalk powder

Effect of Initial Chromium Concentration on Chalk Powder

The adsorption of Chromium (VI) onto Chalk powder was studied by varying initial Chromium (VI) concentration using 1.0 gm/L, chalk powder at room temperature (25± 2°C) and contact time of 60 minutes. The results are represented in the graphical form as percentage removal versus initial chromium concentration (Figure-2). The initial chromium concentration is increased from 50 mg/L to 200 mg/L and the corresponding removal gradually increases from 92% to 95%. From the figure-2, it is well known fact that by increasing the concentration of metal, the adsorbed amount increases. Availability of free adsorbent sites increases which increases the adsorption process. From these experiment it can be concluded that chalk powder can be use to remove chromium from industrial wastewater even at higher concentrations.



Figure–2: Variation of initial concentration of Chromium

Effect of Chalk Powder Dosages

The effect of adsorbent dose on the removal of Cr (VI), is studied in neutral condition (pH 7), at ambient temperature (25± 2°C) and contact time of 60 minutes for initial chromium concentration of 85 mg/L. The added amount of adsorbent was varied from (0.2 g – 1.4 g). The results are presented in figure-3. It is evident from figure-3 that the removal of chromium increases from 94% to 96% for 0.2 gm-1.4 g/L of Chalk powder. It is observed that after dosage of 0.6 g/L, there is no significant percentage removal of chromium (VI). It may be due to the overlapping of active sites at higher dosage [5].

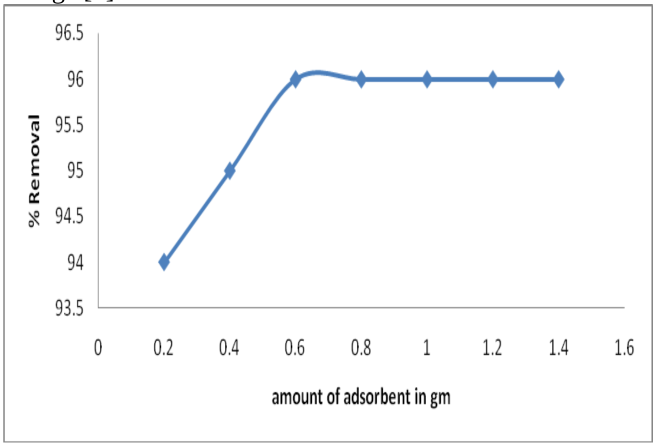


Figure – 3: Variation of Chalk powder dosages on adsorption of chromium

Effect of pH:

Percentage removal of Chromium (VI), at different pH is studied in batch adsorption experiments using 1.0 gm of chalk powder in 1000 ml of synthetic solution which is having the chromium concentration 85 mg/L. The experiments are carried out at room temperature (25± 2°C) and contact time of 60 minutes to maintain equilibrium conditions. After 60 minutes the samples were checked for chromium removal and the results are presented in the graph form shown in figure- 4. It is evident from the graph that the chromium adsorption was constant at pH 6.5 – 7.5. The lowest chromium adsorption was recorded at pH 2. The equilibrium adsorption (*qe*) was found to increase with increasing pH [6]. The percentage removal was decreased in alkaline condition due to competition for active sites by excessive amounts of hydroxyl ions [5]. Chalk powder is a form of $CaCO_3$ with a minor amount of slit and clay. Chalk powder has variable surface charge characteristics and leads to surface charge that is pH dependent. The pH of the medium in which chalk powder is suspended affects the magnitude of the surface charge and also metal hydrolysis. As the pH increases, divalent metal retention on the surfaces via adsorption inner surface complexation and precipitation increases. When the pH of the adsorbing medium is increased there was a corresponding increase in deprotonation of the surface leading to decrease in H^+ ions on the surfaces. 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 positive sites on the surface. But at alkaline medium competition may occur between chromium (VI) and hydroxyl ions for positive sites on the surface.

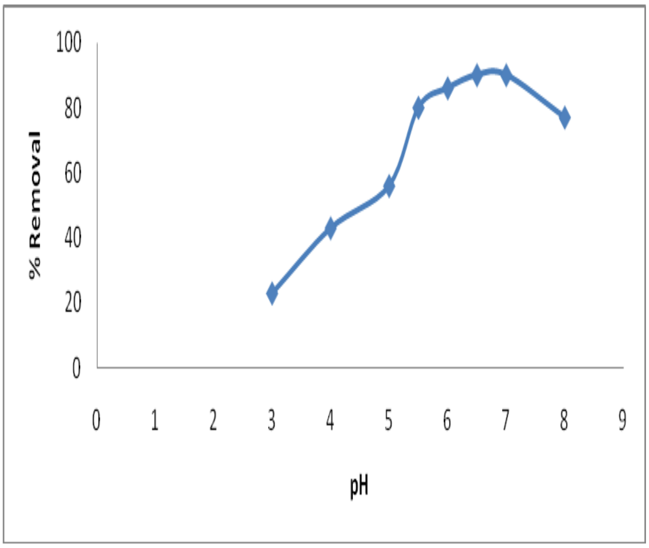


Figure-4: Effect of pH on adsorption of chromium

Effect of Temperature:

The effect of temperature on the adsorption of chromium (VI), with initial concentrations of 10 mg/L, 35 mg/L, and 85 mg/L is studied by using 1.0 gm of adsorbent. The results are represented as percentage removal of chromium (VI) versus temperature (Figure-5). The percentage removal of chromium (VI) with initial concentration 10 mg/L decreased from 82 – 48%, for 35 mg/L decreased from 94 -85% and for 85 mg/L decreased from 96 - 84% for 0 – 80°C temperature respectively. It can be clearly seen from the figure-5, that at the temperature 0°C, the percentage removal was high and with increase in temperature the percentage removal is decreased. The continuous decrease in Percentage removal indicated that the adsorption process is exothermic in nature.

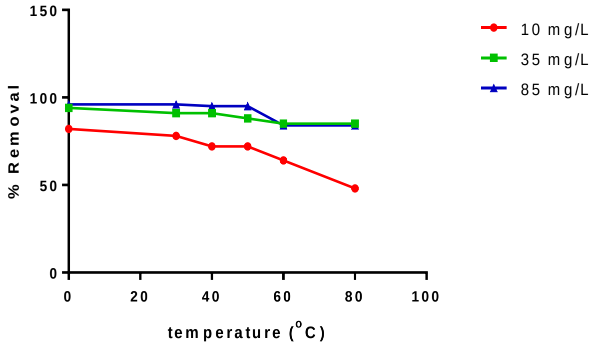


Figure-5: Plots for removal of chromium (VI), at different temperatures.

Temkin Adsorption Isotherm:

The present study on removal of chromium by chalk powder at different temperature shows a linear relationship and the correlation coefficient values are high compared to Langmuir and Freundlich adsorption isotherm models, the results are shown in figure- 6 (a) & (b) and the calculated values were listed in table-1.

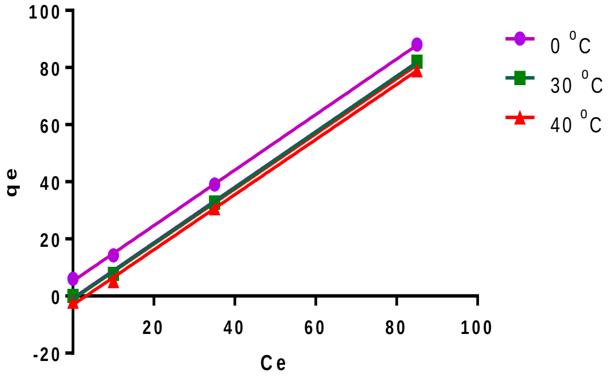


Figure-6 (a): Temkin adsorption isotherm plots at 0, 30 and 40°C.

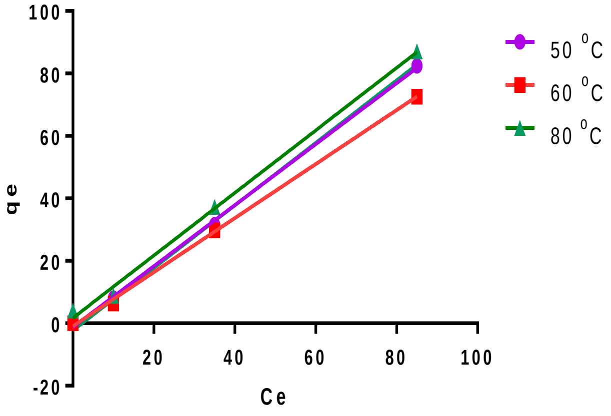


Figure-6 (b): Temkin adsorption isotherm at 50, 60 and 80°C.

Freundlich Adsorption Isotherm:

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 if adsorption process follows freundlich adsorption model. From the figure-7, it is evident that the adsorptive removal of chromium by chalk powder at different temperatures is following freundlich model. The R^2 values are comparatively higher than the Langmuir model and lower than Temkin adsorption isotherm model. The R^2 values, 1/n values and log K_f values are listed in table-1.

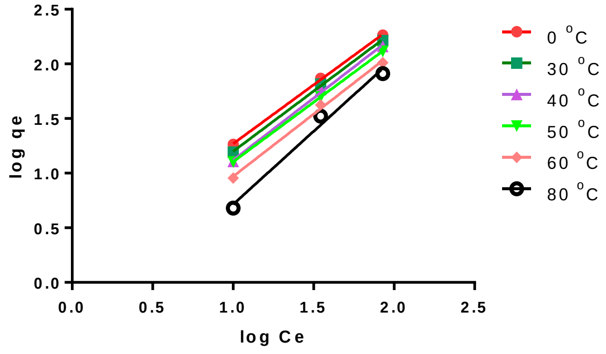


Figure-7: Plots for Freundlich adsorption isotherm at different temperatures

Langmuir Adsorption Isotherm:

The figure-8 shows the plot of C_e/q_e against C_e. Values of Q_0 and b_L are calculated from the slope and intercept of the plot and listed in table-1. From the figure-8 and table-1 it is observed that the R^2 values were in between 0.571 to 0.850 at different concentration of chromium, which were lesser R^2 values of Temkin and Freundlich isotherm studies. These results concluding that removal of chromium adsorption by chalk powder cannot describe by Langmuir adsorption isotherm.

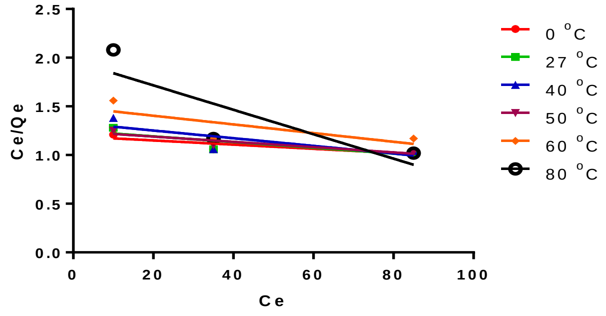


Figure-8: Plots for Langmuir Adsorption isotherm at different temperatures

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 [11].

Pseudo first order equation:

The plots of log $(q_e - q_t)$ versus t at different time intervals are represented in figure-9. From the figure-.9 it was observed that the relationship is non linear and R^2 values are very low (0.044 – 0.952) compare to pseudo second order kinetics. The graph indicating that adsorption process is not validity of Lagergren rate equation of first order kinetics. The adsorption rate value k_1 is calculated from the slope and listed in table-2.

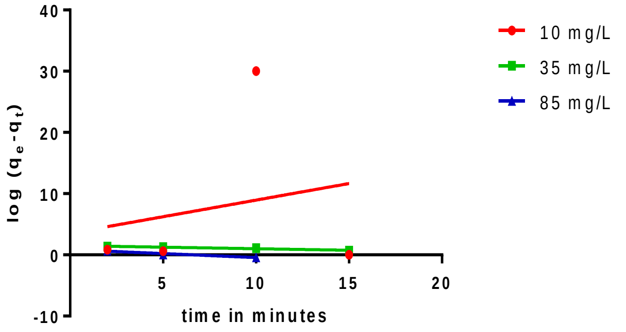


Figure-9: Pseudo first order kinetic model for removal of chromium

Pseudo Second order equation:

The plots of t/q_t versus t at different time intervals are represented in figure-10. From the figure-10 it is observed that the relationship is linear and R^2 values (0.999) are very high compared to pseudo first order kinetics. The graph indicating that adsorption process is following pseudo second order kinetics. The adsorption rate constant K_2 is calculated from the slope and shown in table-2.

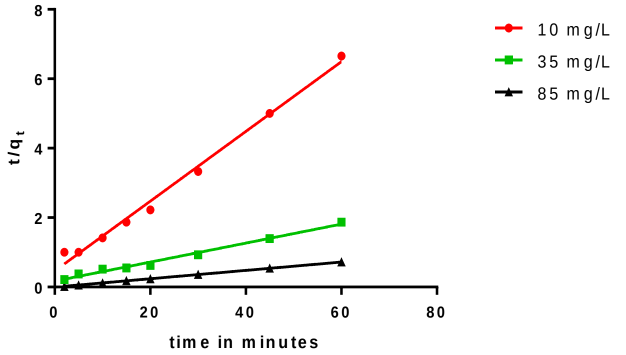


Figure-10: Pseudo Second order kinetic model for removal of chromium

Elovich Model:

If the adsorption of aqueous Chromium solution by Chalk 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 at different initial chromium concentrations represented in figure-11. It was evident from the figure-11, the R^2 values were very low (0.685 – 0.898) which concluding the adsorption process does not fit for Elovich model. The R^2 and ASS (Absolute Sum of Squares) values are given in table-2.

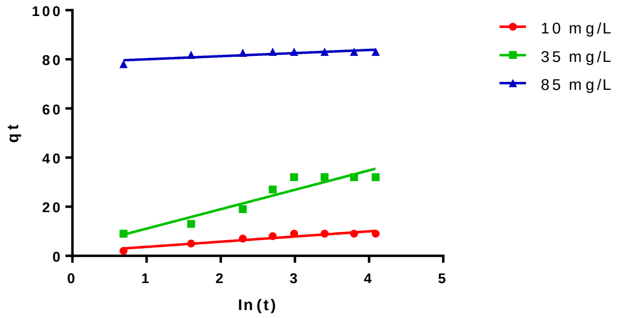


Figure-11: Elovich model for removal of Chromium

Intra particle diffusion model analysis

Figure-12 represents the plots of q_t versus $t^{1/2}$ for adsorption of Chromium solution by Chalk powder at various initial Chromium concentrations. From the figure-12 and table-2 it can be concluded that the adsorption mechanism could not be explained by intra particle diffusion model.

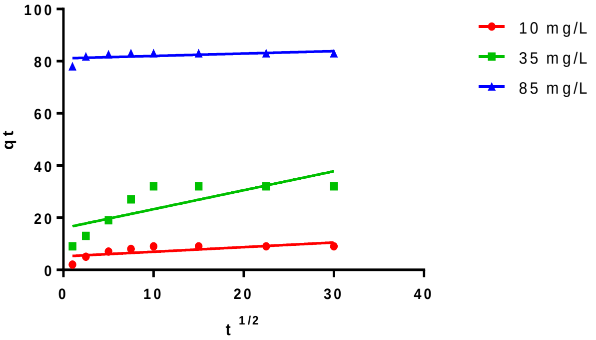


Figure-12: Plots for Intra particle diffusion model of removal of Chromium by Chalk powder

Equilibrium parameter:

R_L, of different temperatures are calculated for the initial concentrations of Chromium (VI) and are given in table-3. The observed R_L values for Chromium (VI) are between 0 to 1 and it indicative of the favourable adsorption.

Thermodynamic parameter calculation:

Figure-4.1.13 showing intercept of straight line with vertical axis gives the values of K_c. The changes in enthalpy (ΔH^o) and entropy (ΔS^o) for Chromium adsorption were calculated from the slope and intercept of the plot of ln Kc against $1/T$ (table-4) according to the van't Hoff equation (figure-14).

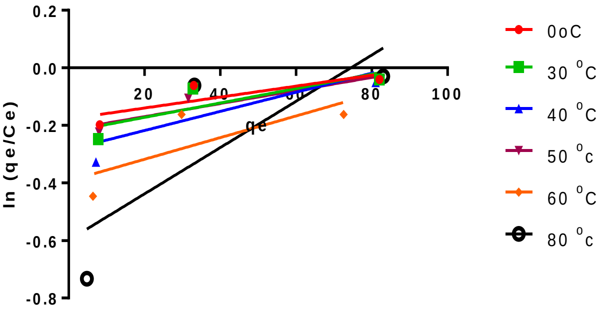


Figure-13: Relationship between ln(q_e/C_e) and q_e at different temperatures.

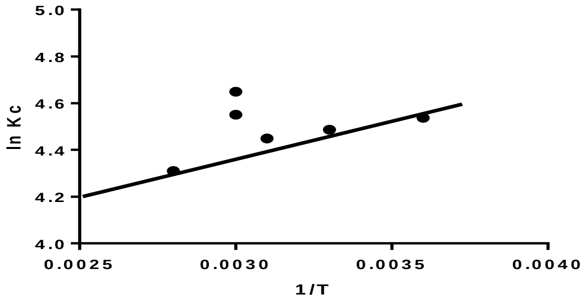


Figure-14: plots of ln K_c and 1/T of chromium adsorption at different temperature

Removal efficiency of Chalk powder on other physico - chemical parameters of industrial wastewater

To find out removal efficiency of chalk powder on physico chemical parameters of industrial wastewater, the adsorption experiment were carried out with paint manufacturing industry waste water with a optimum adsorbent dosage (0.6 gm/L). After equilibrium contact time the water sample were checked for pH, Electro Conductivity, Salinity, Turbidity, Total Dissolve Solids, Acidity, Alkalinity and total hardness of water [21-29]. The results of paint manufacturing industry waste water before adsorption and after adsorption were shown in figure- 15 (a) & (b). From the figure- 15 (a) & (b), it was concluded that chalk powder not only having removal capacity of chromium (VI), it can removes Acidity, Alkalinity, Turbidity and Total Hardness of water [29-31].

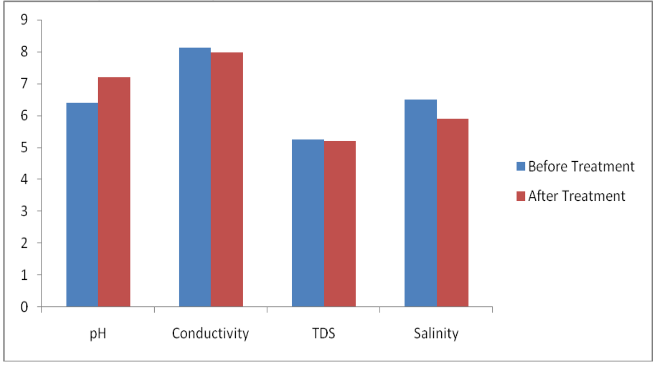


Figure-15 (a): Change in pH, EC, TDS and Salinity of paint manufacturing industry waste water after adsorption

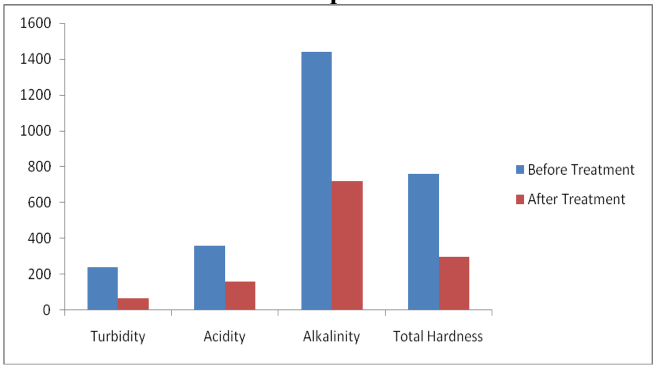


Figure-15 (b): Change in Turbidity, Acidity, Alkalinity and Total Hardness of paint manufacturing industry waste water after adsorption

Fourier Transform Infrared Spectroscopy:

The FTIR spectra of chalk powder before adsorption and after adsorption were shown in figure-16.

S.No	Peaks of Chalk powder before adsorption	Peaks of Chalk powder after adsorption	Comment
01	3562.52 cm^{-1}, 3404.36 cm^{-1}, 3242.34 cm^{-1},	3562.52 cm^{-1}, 3404.36 cm^{-1}, 3242.34 cm^{-1},	Results indicating that there is no involvement of –OH groups in adsorption mechanism
02	2351.23 cm^{-1}, 2241.28 cm^{-1}, 2113.98 cm^{-1}	2241.26 cm^{-1}, 2115.91 cm^{-1}	There is a slight change in peaks before and after adsorption

The change in peaks at 700 cm^{-1} to 1000 cm^{-1} indicating adsorption of Cr (VI) by chalk powder is due to quartz minerals, carbonates ions along with the available surface, density and porosity of chalk powder.

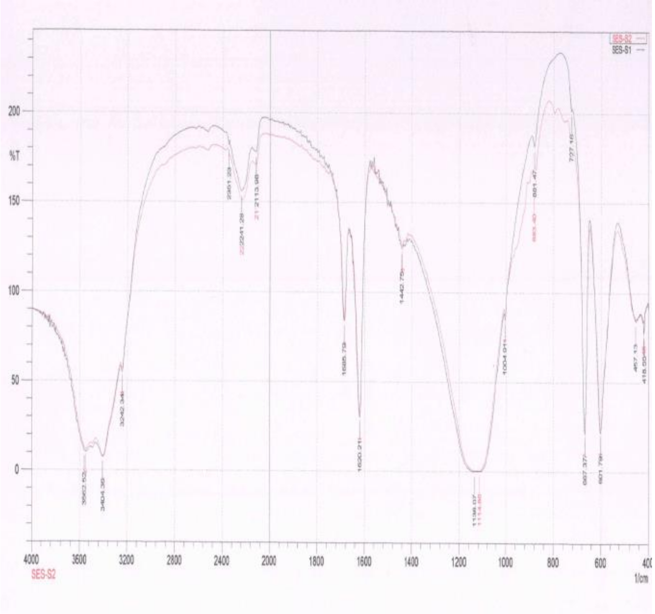


Figure-16: FTIR spectrum of Chalk powder before and after adsorption

Conclusions:

Chalk powder can be used as adsorbent for removal of Cr (VI), from industrial waste water. The high porosity, non hazardous nature of chalk powder leads to eco friendly and lowcost physical adsorption technology for removal of Cr (VI) from industrial waste water. Removal at low pH should be avoided. It is always better to maintain a pH range of 6.5 – 7.5. the results showed that waste water quality is improved and study demonstrated that the treated waste water can be sucessfully utilized for agriculture and aqua culture. The results of investigation are quite useful in developing an appropriate technology for designing a waste water treatment plant for removal of Cr (VI).

Table-4.1.1: Isotherm kinetics for adsorption of Chromium by Chalk powder

S.No	Parameters	Temperature ^{o}C					
		0	30	40	50	60	80
	Temkin Adsorption Isotherm						
01	R^2	0.999	0.999	0.999	0.999	0.999	0.996
	ASS	1.239	2.011	3.053	4.008	2.813	14.02
	a_T	-0.783	-0.997	-1.104	-1.240	-0.910	-2.300
	b_T	0.971	0.973	0.964	0.976	0.865	1.002
	Langmuir Adsorption Isotherm						
02	R^2	0.720	0.677	0.622	0.850	0.571	0.697
	ASS	0.0052	0.0120	0.0270	0.0037	0.0430	0.1990
	Q_0	1.193	1.251	1.331	1.244	1.493	1.967
	b_L	-0.0021	-0.002	-0.003	-0.002	0.0044	-0.012
	Freundlich Adsorption Isotherm						
03	R^2	0.999	0.999	0.997	0.999	0.997	0.987
	ASS	0.0002	0.0004	0.0012	0.0227	0.0016	0.0095
	Log k_f	-0.159	-0.203	-0.267	-0.186	-0.321	-0.623
	1/n	1.078	1.103	1.136	1.090	1.141	1.337

Table-4.1.2: Kinetic parameters for adsorption of Chromium by Chalk 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	0.044	0.933	0.952
	ASS	625.1	0.017	0.027
	K_1	-1.249	0.115	0.299
	Pseudo Second order kinetic model			
02	R^2	0.991	0.987	0.999
	ASS	0.240	0.028	0.0077
	K_2	0.463	0.171	0.0011
	Elovich model			
03	R^2	0.889	0.898	0.685
	ASS	5.033	64.31	6.65
	α	4.438	11.85	1.702×10^{27}
	β	0.474	0.126	0.793
	Intraparticle diffusion model			
04	R^2	0.504	0.605	0.293
	ASS	22.56	250.1	14.95
	k_{id}	0.177	0.726	0.092
	I	5.174	16.01	81.10

Table-4.1.3: Equilibrium parameter R_L values at different concentration and different temperatures

S.No	Temperature (^oC)	Concentration of Chiromium (mg/L) and R_L values		
		10 mg/L	35 mg/L	85 mg/L
01	0	0.1002	0.0286	0.0117
02	30	0.1002	0.0286	0.0117
03	40	0.1003	0.0286	0.0118
04	50	0.1002	0.0286	0.0118
05	60	0.1004	0.0286	0.0118
06	80	0.1010	0.0289	0.0119

Table-4.1.4: Thermodynamic parameters of Chromium adsorption by Chalk powder

S. No	Temperature	ΔG^o (KJ/ mol)	ΔS^o (KJ/ mol)	ΔH^o (KJ/ mol)
01	273	-10.297 x 10^3	4.071	135.8
02	303	-11.300 x 10^3		
03	313	-11.577 x 10^3		
04	323	-12.218 x 10^3		
05	333	-12.862 x 10^3		
06	353	-12.649 x 10^3		

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