

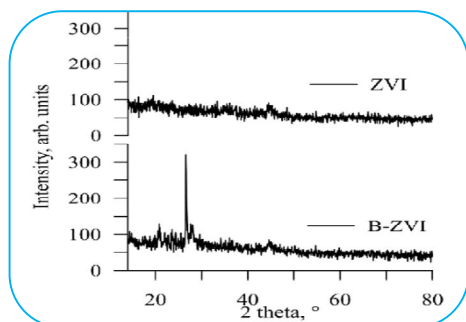


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KINETIC STUDIES OF SORPTION OF CR (VI) ON BENTONITE AT DIFFERENT PARAMETER

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ABSTRACT:

During investigation of the Sorption power of Bentonite clay for removal of Cr (VI) ions at different concentration, pH, Time and temperature from wastewater take place during investigate factor such as the concentration of Cr (VI) ion, adsorbent, fixed shaking speed, time, temperature and pH of solution on sorption process. Study sorption process interpreted to be Langmuir's pseudo second order kinetic equation, Langmuir's adsorption isotherm and

thermodynamic studies. Finally concluded that Bentonite was found to be more influence and usable for removal of Cr (VI) ion at wastewater.

KEYWORDS: Kinetic Studies, Thermodynamic Studies, Equilibrium Studies, Effective clay, Toxic Chromium ion.

INTRODUCTION:

The environmental pollution many heavy metal are responsible because heavy metal more toxic and carcinogenic. These are effect of plant speed germination, root and shoot length and other effect Hexavalent chromium sources rocks, animals, plants soils and industrial dusts and gases. Jindal steel power Limited raigarh Chhattisgarh and Monet steel power Limited Patrapali Chhattisgarh raigarh this industry in involve the use of Cr (VI) ion because it is the steel production. Electro plating energy power limited because

this industries protrude Cr (VI) ion occurs into our environment. Two most stable oxidation state of Chromium metal existing in Hexavalent and Trivalent in aqueous solution Cr (VI) is very toxic, carcinogenic and mutagenic nature. In the human body maximum quantity exist for Cr (VI) as more than 33µ/person.

The simple methods of Hexavalent chromium ions remove from aqueous solution are precipitation method, ion exchange methods, electro dialysis method, coagulation method and sorption method. Hexavalent chromium ions generally exists in the tape water as chromate ion (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and it is not precipitate easily precipitation, ion exchange, electro dialysis

method. A man all the methods described above the adsorption methods is specially preferred as an advance technique for the treatment of wastewater due to its high efficiency, easy handling less expensive. In this work adsorption Bentonite are uses in the removal of Cr (VI) from wastewater.

The project of the present study to the effect of concentration of Cr^{6+} ion adsorption on Bentonite clay at constant pH (2.0) constant temperature (30°C) and constant particle size. Parameter calculated the adsorption kinetic study, equilibrium and thermodynamic parameters and find out effect of adsorbent dose and initial and final concentration on the adsorption of Cr^{6+} to investigate the experimental data of adsorption

through Langmuir's pseudo second order kinetic equation, Langmuir's adsorption isotherm and thermodynamic to investigate adsorption preparation of Cr^{6+} and discuss it.

REGARDED REAGENT & METHODS

All chemical used our investigation of analytical reagent (A.R.) or laboratory reagent (L.R.) grade. Potassium Dichromate (99.5%) and sulphuric acid (98%w/w) supplied by molly chem. Limited Mumbai by help of Javed trading raigarh (C.G.), product code 17120, distilled water used in preparation of Bentonite supplied by titan biotech ltd. Bhiwadi.

Adsorbent analysis: - The particle size and surface area analysis for the adsorption Bentonite clenched recorded (table-1) element analysis for Bentonite uses evaluated IIT Bombay.

Constituent	Wt (%)
SiO_2	47.68
Al_2O_3	32.29
Fe_2O_3	1.25
MgO	0.31
CaO	0.42
Na_2O	0.23
TiO_2	2.11

Table-1 percentage of Constituents element in Clay

APPARATUS AND INSTRUMENTATION

Water bath shaker was used to shaking heavy metal ion solution with adsorbent Bentonite a use 20 ml volume of heavy metal ion solution of a known initial and final concentration was mixed with 1g of Bentonite clay for different time (20, 40, 60, 80, 100, 120, 140, 160 min.) at fixed temperature, fixed pH and fixed speed. The pH value of the solution initial and final were measurement by digital pH meter (model No. 110 BNR) and conductivity measured by digital conduct meter (model No.160 BNR) and metal ion concentration was using colour developed measured by help of Digital photoelectric colorimeter (model No. 112 systronic).

Experimental process

Prepared 1000ppm Cr (VI) ion concentration stock solution of potassium dichromate using distillate water and several solutions with different initial concentration of potassium dichromate (50, 100, 150, 200, 250 ppm) are prepared. The required 2 pH was adjusts by drop wise addition of 0.1N sulphuric acid depending on the acidic of the solution. All experiment cored at 30°C by adding 1g adsorbent to different concentration (50, 100, 150, 200, 250 ppm) of 20 ml of dichromate solution and the sacking residence time was (20, 40, 60, 80, 100, 120, 140 and 160 minute) take 20ml of dichromate solution and 1g of Bentonite absorbent were than separated from the dichromate solution by using batman filter paper No. 40 and residual Cr^{6+} ion concentration in the solution than determine by colorimeter. These process repeated by different concentration of dichromate solution.

Adsorbent	Bentonite
Surface area	1198
Particle size	45 μ

Table-2 surface area and particle size analysis of Bentonite

RESULT AND DISCUSSION

Characterisation of Bentonite: - Bentonite clay is a same basic element of the other clay but different chemical properties. Chemical composition of element in Bentonite obtained from XRF studies by help

of IIT Bombay are SiO_2 (47.68%) Al_2O_3 (32.29%) , Fe_2O_3 (1.25%), CaO (0.42%) and TiO_2 (2.11%) adsorption water molecule on the surface A peak around $1400\text{-}1600\text{cm}^{-1}$ is attributed to presence as carbonate. some small peaks addition peaks and vibration in vibrational frequency indicates that of Cr^{6+} ion taken place on Bentonite surface.

Effect of initial Cr (VI) ion concentration

The initial concentration ion is a most important parameter in adsorption since a certain amount of adsorbent can absorbed a certain amount of Cr^{6+} metal ion. The removal of Cr^{6+} ion percentage was investigate by different concentration from 100 mgL^{-1} - 250 mgL^{-1} with 50 gL^{-1} adsorbent dose of Bentonite with the same condition illustrated in figure-1 and 2.

The result represent in fig-1 showed that the % of Cr^{6+} ion adsorption was decreased with increase in initial concentration, the removal of Cr (VI) ion percentage decrease from 77.00% to 68.20%. But the actual amount of Cr^{6+} ion adsorbed per unit mass of the adsorbent was increased from 1.56 mgg^{-1} to 3.41 mgg^{-1} with increase of Cr^{6+} ion concentration in the test solution as illustrated in fig-2 at low.

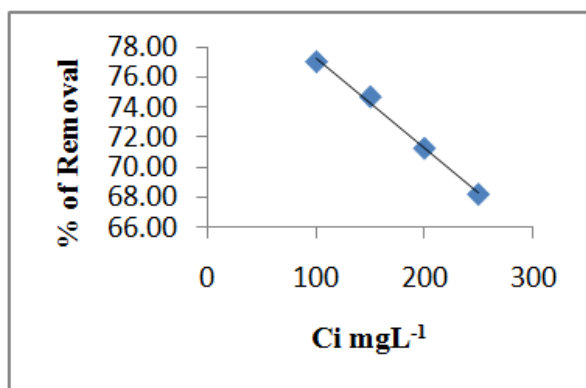


Fig-1 : effect of initial conc. on Cr(VI) adsorption

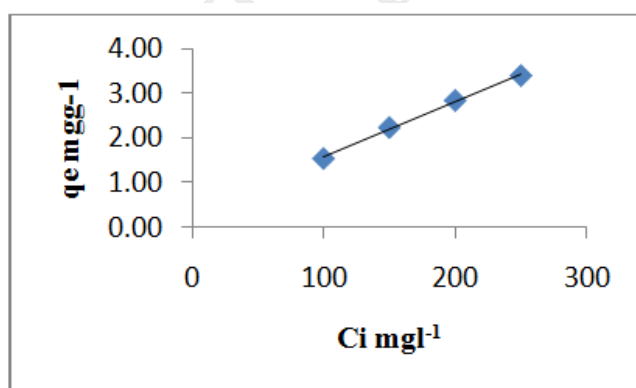


Fig-2 : effect of initial conc. on Cr(VI) adsorption

Effect of contact time

The result represent in fig-3 showed that the mgg^{-1} of Cr^{6+} ion adsorption on Bentonite was increased with increase in contact time at different initial concentration. Initially the rate of adsorption is fast slows the main reason more number of active particle are present in the Bentonite clay so adsorption is fast. Time increases number o active particle is decreases adsorption also decreases.

Effect of pH

Fig-4 represents effect of pH on adsorption. if pH increasing from 2.0 to 10.0 the absorption of Cr (VI) is decreases. Because increasing pH negative Cr (VI) ion absorption is difficult. The acidic medium association of negatively charged HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ resulting in high adsorption on strongly. Alkali mediums the adsorbent surface get deprotonated and become negatively charged. As a result adsorption of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ decreases.

Effect of temperature

Temperature effected adsorption of Cr (VI) from west water temperature increasing from 303K to 313K processor to endothermic amount of adsorption is also increases from 1.56 mgg^{-1} (78.00%) to 1.862 mgg^{-1} (93.10%) to the rate constant of adsorption are increases from 1.49×10^{-2} , 3.40×10^{-2} and 4.04×10^{-2} per min at 303K, 313K and 323K are increase temperature with respect indicate the amount of adsorption increases. Indicate figure 5.

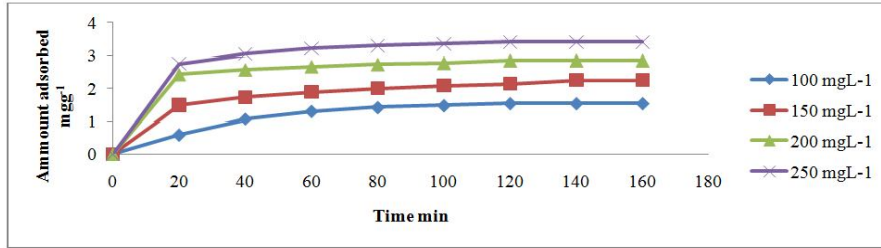


Figure- 3:- effect of contact time on adsorption of Cr (VI) on Bentonite

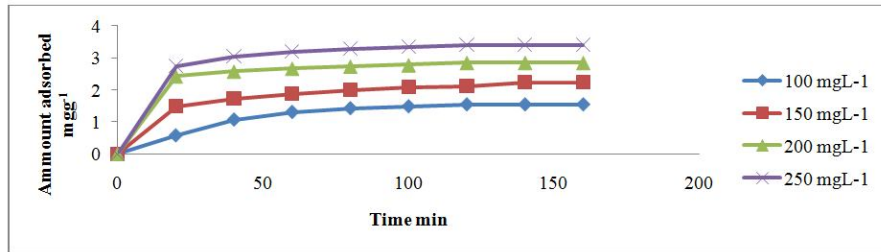


Figure- 4:- effect of pH on adsorption of Cr (VI) on Bentonite

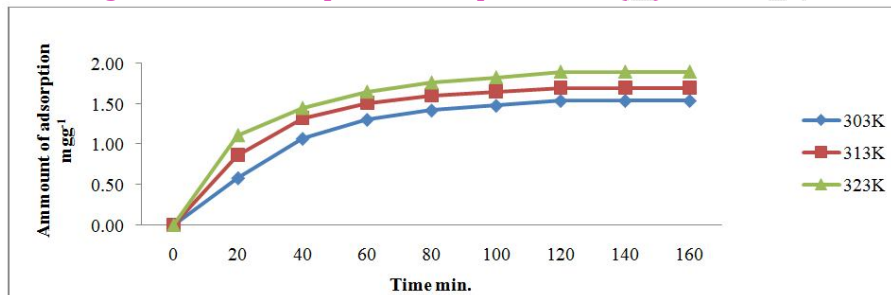


Figure-5:- effect of Temperature on adsorption of Cr (VI) on Bentonite

Kinetic studies

In order to clarify the adsorption kinetics, Lagergren’s pseudo-first-order and pseudo-second-order kinetic equation will be applied to the experimental data the linearized form of the well known Lagergren equation for adsorption kinetic at different concentration is as below:-

$$\text{Log} (q_e - q_t) = \text{log} q_e - \frac{t \cdot k_1}{2.303}$$

Where q_e and q are the amounts of the metals sorbent at equilibrium and time “t” respectively and k_1 is the rate constant of sorption. K_1 can be determined experimentally by plotting of $\text{log} (q_e - q_t)$ versus t.

The Lagergren’s pseudo-second-order kinetic equation is given as

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where k_2 is the rate constant of the second order equation, q the amount of adsorption after time t and q_e is the amount of adsorption at equilibrium k_2 can be determined experimentally by plotting of t/q versus t.

Equilibrium studies

Experimental equilibrium data obtained will be discussed using Langmuir adsorption isotherm which is as below-

$$\frac{C_e}{q_e} = \frac{1}{Q \cdot b} + \frac{C_e}{Q} \quad \text{or}$$

$$\frac{C_e}{q_e} = \frac{1}{Q} \cdot C_e + \frac{1}{Q \cdot b} \quad \text{or}$$

$$y = mx + c$$

Where q_e is the amount of Cr (VI) ion adsorbed per gram of the adsorbent at equilibrium, C_e (mgL^{-1}) is equilibrium concentration of Cr (VI) ion in the solution, Q and b are Langmuir constant indicating the sorption capacity and sorption energy respectively. fig-8 is indicate relation C_e/q_e Vs C_e . The structure is linear indicate the follow of Langmuir isotherm. Slope and intercept of the straight line obtained give the value of Q and b respectively.

Thermodynamic process

In order of determine the thermodynamic feasibility and the thermal effect of the adsorption. The Gibb's free energy (ΔG^0), the entropy (ΔS^0) and the enthalpy (ΔH^0) will be calculated for study different temperature from 303K to 313K using following equation

$$K_c = \frac{C_s}{C_e}, \Delta G^0 = -RT \ln K_c, \Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta H^0 - T\Delta S^0 = -RT \ln K_c$$

$$\Delta H^0 - T\Delta S^0 = -2.303RT \log K_c$$

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT}$$

Were C_s is the equilibrium concentration of adsorbent in mgL^{-1} , C_e is equilibrium concentration of adsorbate in solution in mgL^{-1} and K_c is the equilibrium constant. ΔG^0 has been calculated from the above equation. Plot graph between $\log K_c$ verses $\frac{1}{T}$ gives strait line. Slope and intercept of this line give the value of ΔH^0 and ΔS^0 . Figure 12 give various graphs between $\log K_c$ verses $\frac{1}{T}$ and show in fig-10. The value of ΔH^0 and ΔS^0 . All value listed table -4.

Table-3
Adsorption isotherm constant for adsorption of Cr (VI) ion on Bentonite clay

Langmuir isotherm result				Lagergren first order				Lagergren second order			
Temp. (K)	R^2	Q	b	Conc. mgL^{-1}	$K_1 \text{ min}^{-1}$	$q_{\text{cal}} \text{ mgg}^{-1}$	$q_{\text{exp}} \text{ mgg}^{-1}$	R^2	$K_2 \text{ g/mg/min}$	$q_{\text{cal}} \text{ mgg}^{-1}$	R^2
				100	3.45×10^{-2}	1.888	1.54	0.999	1.49×10^{-2}	1.919	0.983
303	0.998	5.59	1.85×10^{-2}	150	1.84×10^{-2}	1.074	2.24	0.999	2.56×10^{-2}	2.451	0.997
313	0.988	6.62	2.06×10^{-2}	200	2.07×10^{-2}	1.535	2.85	0.999	6.08×10^{-2}	2.958	0.999
323	0.980	7.94	4.29×10^{-2}	250	2.99×10^{-2}	1.208	3.41	0.999	4.52×10^{-2}	3.558	0.999

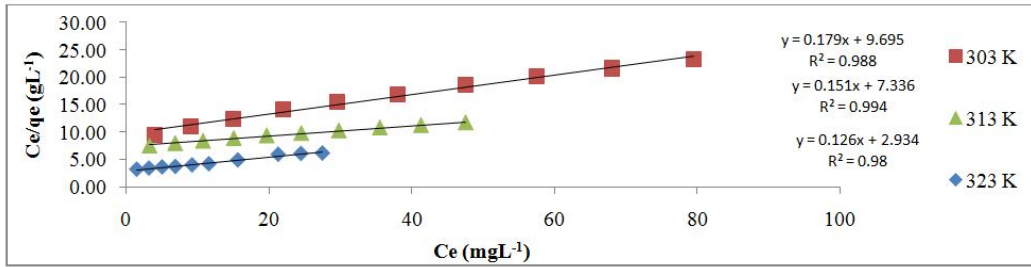


Fig 7:- Lagergren's adsorption isotherm for the adsorption of Cr (VI) ion on Bentonite

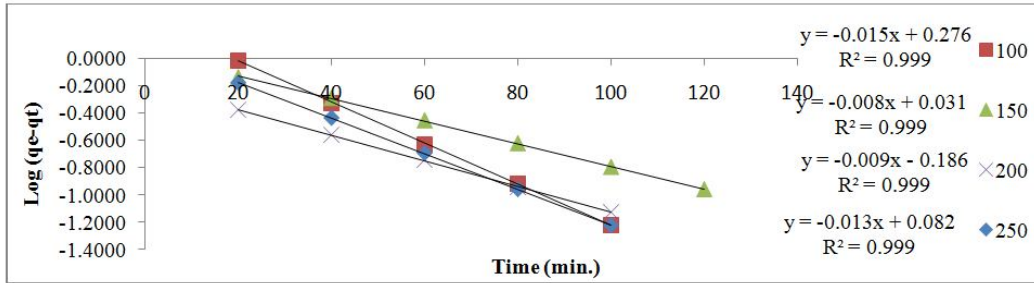


Fig-8 Lagergren's pseudo first-order kinetic adsorption of Cr (VI) ion on Bentonite

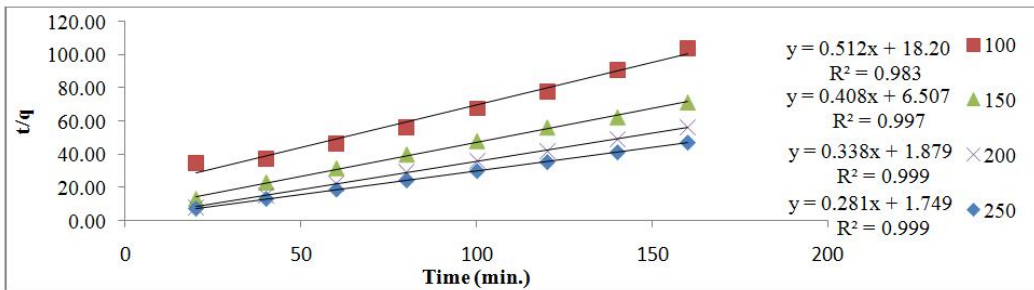
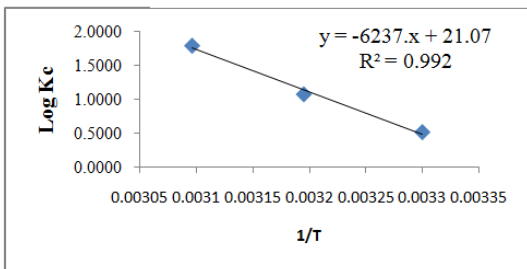


Fig-9 Lagergren's pseudo second-order kinetic adsorption of Cr (VI) ion on Bentonite



Temp. K	ΔG^0 kJ/mol	ΔH^0 kJ/mol	ΔS^0 J/mol	E_a kJ/mol
303	-3.044	119.420	48.52	61.749
313	-6.49			
323	-11.12			

Table-4 Thermodynamic study for adsorption of Cr (VI) ion on Bentonite

CONCLUSION

In the different parameter best evidence the initial concentration of Cr (VI) ion effect of adsorption on Bentonite clay are best adsorbent under specific condition.

Experimental equilibrium data Cr (VI) ion effect of pH, initial concentration, temperature and contact Time are best evidence by Langmuir adsorption isotherm, Lagergren first and pseudo second order tare equation thermodynamic parameter also favour the adsorption.

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