ADSORPTIVE REMOVAL OF HEXAVALENT CHROMIUM BY USING WOOD CHARCOAL AND MODIFIED WOOD CHARCOAL

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Abstract: The present work reported that the adsorption of Chromium(VI) from aqueous solution using locally available wood charcoal. It was found to be giving poor removal efficiency of Cr(VI) in water. Therefore, an attempt has been made to modify wood charcoal by oxidizing agent such as hydrochloric acid and also nanoparticles consisting of Iron oxide nanoparticles which were loaded on the treated wood charcoal for the preparation of a new nanosorbent, Fe_3O_4-TWC.

The treated WC and Fe_3O_4-TWC was characterized by SEM and XRD techniqes. Experimental data were exploited for equilibrium, kinetic and isothermal evaluations related to the adsorption processes. The Cr(VI) adsorption process was found to be favourable at pH 4.0 and it reached equilibrium time of 240 min for WC (15%), 100 min for TWC (82%) and 60 min (96%) for Fe_3O_4 –TWC. Kinetic studies show that the overall adsorption rate of Cr (VI) is illustrated well by Pseudo second order kinetics than the Pseudo first order kinetics. Isothermal studies were conducted at an initial chromium concentration in the range of 5.0 to 20.0 mg/L to assess its adsorption efficiency with respect to water. The equilibrium data were well fitted by Freundlich isotherm as R^2=0.997.

Keywords: locally available wood charcoal, Fe3O4 nanoparticles, kinetic study, isothermal study,desorption studies.

1 INTRODUCTION

Advances in science and technology have brought tremendous progress in many spheres of development, but in the process, also contributed to the degradation of environment all over the globe due to the very little attention paid to the treatment of industrial effluents. Industrial pollution continues to be a potential threat affecting the drinking water. Waste streams containing heavy metals such as Cu, Zn, Ni, Pb, Cd, Cr are often encountered in various chemical industries. The discharge of non-biodegradable heavy metals into water stream is hazardous because the consumption of polluted water causes various health problems[1].

The major environmental issue with Chromium is the release of contaminants from industrial wastewater containing this heavy metal. The total quantity released into the environment remains very high even though control technologies have been applied to many industrial and municipal sources[2].

Estimated global discharge of trace elements (1200 metric tonnes/ year), in which Chromium has a value of 142 in water, 30 in air and 896 in soil[3].Cr (VI) is highly toxic, carcinogenic and and is hence of grave concern. The entry routes of Chromium into the human body are inhalation, ingestion, and dermal adsorption. Occupational exposure generally occurs through inhalation and dermal contact, whereas the general population is exposed most often by ingestion through Chromium content in soil, food, and water[4].

Innovative processes for treating industrial wastewater containing heavy metals often involve technologies for reduction of toxicity in order to meet technology-based treatment standards. In order to detoxify heavy metals, various techniques like photocatalytic oxidation, chemical coagulants, electrochemical, bioremediation, ion-exchange resins, reverse osmosis, and adsorption has been employed. Most of these methods have some drawbacks such as low efficiency, high demand for energy, high cost, requiring special chemicals, and the problems related to the disposal of sludge.While the adsorption process due to its ease of operation, flexibility in design, low cost and high efficiency has been effectively applied to the removal of heavy metals including Cr(VI). In adsorption studies, various adsorbents such as granular

activated carbon (GAC), powder charcoal powder, mineral cartridge, biological and agricultural waste have been used for removal of Cr(VI) [5,6].

Wood charcoal powder due to its high porosity, large surface area and high efficiency has gained more interests than the others. However, the main problem concerning wood charcoal lies within its reusability and separation of it from aqueous solution. Among these nano-based adsorbents are the more convenient technologies for removal of heavy metals from the aqueous system. Thus, establishing the optimal conditions to facilitate the separation of wood charcoal from the solution after the adsorption process seems to be essential. This so-called method has been widely used for the last few years due to its simplicity and high-speed[7,8,9,10,11].

Application of iron oxide based nanomaterial is more attractive for removal of heavy metals contamination from the water because of their important features like small size, high surface area, fast kinetics and magnetic property[12]. For Fe_3O_4 nanoparticle, both physical and chemical adsorptions of heavy metal were reported [13]. Here in, we will put more emphasis on wood charcoal modified with (Fe_3O_4) based nanoparticles which have significant efficiency for the removal of Cr (VI) in the contaminant.

2 EXPERIMENTAL

2.1 Materials and Methods

2.1.1 Reagents

All glassware used were manufactured by M/s Borosil Glass Works Ltd., (Bombay, India) and marketed under the brand name ' Borosil'. All chemicals and reagents used were analytical reagent grade (AR). Working standards for calibration of Chromium were made using technical grade potassium dichromate of 98.7% purity. Instruments used for the present work include Evolution 201 model of UV-VIS Spectrophotometer for adsorbance readings.

2.1.2 Adsorbate

A stock solution of Chromium (VI) (1000 mg/L) was prepared by dissolving the required amount of potassium dichromate ($K_2Cr_2O_7$) in water and further diluted to prepare the solutions in the concentration range of 0.1-60 mg/L. The residual concentration of Cr (VI) measured using a UV–VIS spectrophotometer at 540 nm by diphenylcarbazide method [13,4].

2.1.3 Adsorbent

Adsorbent included is raw wood charcoal, and which was treated with hydrochloric acid. In addition, treated wood charcoal modified with iron oxide nanoparticles which can be synthesized by co-precipitation method[14].

2.1.4 Synthesis of iron oxide nanoparticles

Iron oxides (Fe_3O_4) are usually prepared by dissolving the stoichiometric mixture of ferric ($FeCl_3$) and ferrous ($FeCl_2$) salts in an aqueous medium with a ratio of 1:2 (Fe^{3+}/Fe^{2+}). 100 ml of 0.2 mol/L solution of $FeCl_3$ and 100 ml of 0.4 mol L^{-1} solution of $FeCl_2$ were mixed and dissolved in distilled water. Then concentrated ammonia solution (NH_3) was added into the above solution and the pH value was maintained between 10-12 with continuous stirring using a magnetic stirrer for 1 hour and a dark precipitation was formed. The produced precipitation was filtered & after drying at 60 °C for 10 hours the powder will be obtained [14, 15, 16]. Particles with sizes ranging from approximately ~26 nm will be obtained using this method. The chemical reaction of Fe_3O_4 formation may be written as

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$$

2.1.5 Preparation of wood charcoal modified by iron oxide nanoparticles

Wood powder in addition to Fe_3O_4 was prepared by the following procedure. The required amount of iron oxide nanoparticles was added to the above treated wood charcoal corresponding ratio (2:1). The mixture was stirred for 30 min in a polyethylene vessel. After collected, the final formed iron oxide impregnated wood charcoal washed thoroughly with ethanol which was dried at 60 °C for 10 hrs and was named as Fe_3O_4-TWC nanosorbent.

2.2 Experimental Procedure

Batch experiments were conducted for the development of adsorption kinetic profiles. A stock of Cr (VI) solution (1000 mg L^{-1}) was firstly prepared by dissolving $K_2Cr_2O_7$ in distilled water. All working solutions at the desired concentration were prepared from this stock solution by diluting with distilled water. Chromium spiked synthetic water samples (100 ml) of a particular concentration were taken in the bottles. The batch adsorption experiments were also conducted to determine the equilibrium time (10–330 min), initial metal concentrations (5.0–20.0 mg L^{-1}), and adsorbent dosages (2.0–8.0 g L^{-1}) to obtain the maximum adsorption capacity. The initial pH was adjusted with solutions of 0.1M NaOH/HCl. In the adsorption experiment, 2.0 g sorbents of WC, TWC, and Fe_3O_4-TWC in 50mL of the Cr (VI) metal ion solution (C_0=5,10,20 mg L^{-1}) at pH 4.0 in different conical flasks were used for the batch adsorption studies. The batch adsorption studies were carried out in a mechanical shaker at 200 rpm [17, 18]. After required contact time, the samples were withdrawn from the shaker and the adsorbent from the sample bottles was filtered and the filtrate was analyzed using spectrophotometry for the determination of adsorbed metal ion concentration for the analysis of chromium.

All the investigations were carried out in duplicate to avoid any discrepancy in experimental results.

3. RESULTS AND DISCUSSION

3.1 characterization of nanosorbents

The surface morphology of TWC and Fe3O4-TWC was investigated using a Scanning Electron Microscope and XRD.

SEM analysis was carried out and the SEM morphology of TWC and Fe_3O_4-TWC nanosorbents was shown in Figure 3.1(a) and 3.1(b). The surface morphology of wood charcoal adsorbent (Fig 3.1(a)), clearly states the porous structure of the wood charcoal and relatively smooth surface. There are holes and cave type openings on the surface of the specimen which enhances the adsorption capacity due to the larger surface area. The presence of functional groups in TWC is advantageous, because of functional groups, which are soft bases, have a chemical affinity towards Chromium. Thus the presence of –COOH, -OH in TWC qualifies it as a potential sorbent [19, 20].
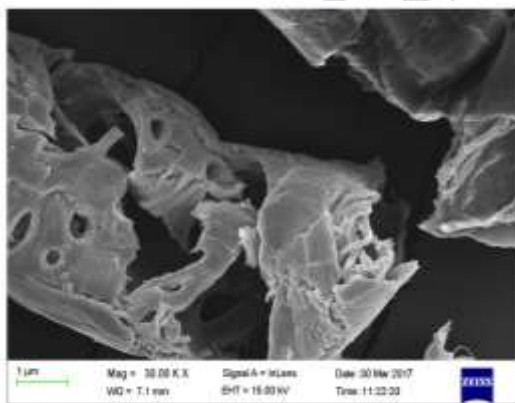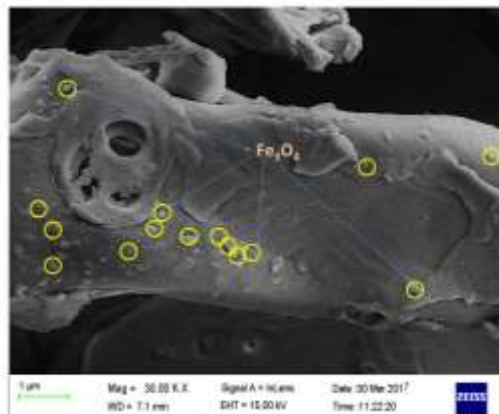

| **Figure 3.1 (a): SEM images of TWC** | **Figure 3.1(b): SEM images of Fe_3O_4-TWC nanosorbent** |

The bulk density of nanosorbents were found to be in the range 0.35~0.55 gmL^{-1} with 1.2~1.3% and 11.4~12.53% of the moisture and ash content, respectively, for both sorbents. The surface morphology of Fe_3O_4-TWC nanosorbent was shown in Figure 3.1(b). It can be found that there are few pores in wood charcoal and the small aggregates are observed from the general view of the composite, which appear brighter, supported on the darker surface of the wood charcoal. Based on the above results, the sorbents treated WC and Fe_3O_4–TWC are good and suitable for employing as a sorbent for metal removal.

To determine the the relative amounts of phases in a mixture by referencing the relative peak intensities using XRD. Figure 3.1(c) shows the XRD patterns of TWC. The diffraction peak of TWC only centres at around 23.8^0 which is attributed to the (002) plane reflection of amorphous carbon. The diffraction peaks of Fe_3O_4-TWC are at 23.8º, 30.6º, 35.6º, 43.2º, 55.6º, 62.9º are corresponding to their indices (002), (220),

(311), (400), (511), and (440) (JCPDS Card No. 75-0033) are formed. Bragg reflections in the X-ray diffraction patterns point crystalline structure of the end products[21,22].
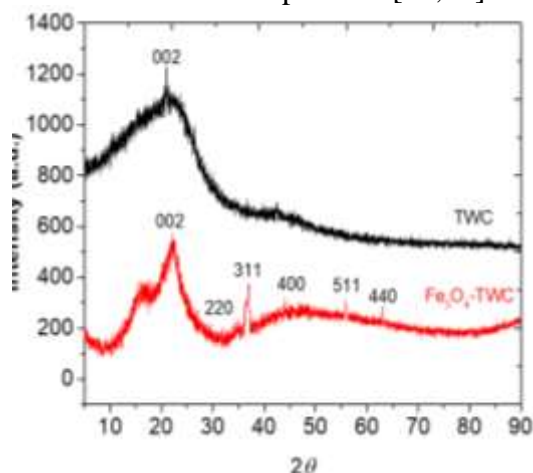

Fig 3.1(c): XRD spectrum of treated TWC and   Fe₃O₄-TWC

3.2 Influence of pH

The optimum pH for Cr(VI) adsorption was investigated by adding 2.0 g L^{-1} of adsorbent to aqueous metal solution (20 mg L^{-1}) and was adjusted to various pH values (2.0 to 12.0) using 0.1 moL L^{-1} NaOH/HCl. After adjusting the solution pH, flasks were shaken at respective contact times at 200 rpm at room temperature. As shown in Figure 3.2, the metal uptake increased with the increase of pH in the range of 2.0 to 4.0 and after above pH 4.0 at 200 rpm room temperature, it was slowly decreased to a lower value for the three sorbents. The plausible explanation for the lower adsorption capacity observed at lower pH is due to the fact that the concentrations of protons and hydronium (H_3O^+) ions were higher and this competes for the binding of active sites on the surface of the sorbent with metal ions. At acidic pH 4, the dominant form of Cr(VI) is $HCrO_4^-$, observed higher adsorption at lower pH can be attributed to strong electrostatic attraction between positively charged surface groups and $HCrO_4^-$ [23,24].
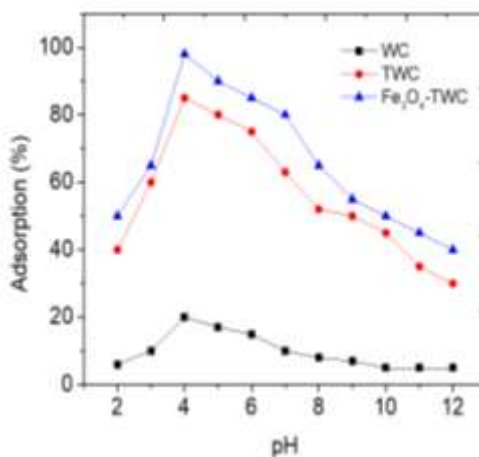

Figure 3.2: Evaluation of pH influence on adsorption of Cr (VI) onto WC, TWC and Fe₃O₄-TWC

3.3 Influence of Contact Time and Initial Metal Ion Concentration

The contact time was also evaluated as one of the most important factors affecting the adsorption efficiency. Figures 3.3(a), 3.3(b), 3.3(c) shows the adsorption efficiency of metal ions (initial concentration, 5.0–20.0 mg L^{-1}) by three sorbents (2.0 g L^{-1}) as a function of contact time (10 to 330 min) in a mechanical shaker. Initially, the adsorption was fast and as the time passes it no longer remains same. The amount of adsorption efficiency was found to be 0.4 mg/g to 1.5 mg/g with increase in initial concentration from 5.0 to 20.0 mg/L as shown in Fig 3.3(a).

From contact time data (Figure 3.3(a))**,** it may be seen that untreated wood charcoal showed an increase in removal efficiency as time increases and maximum removal sets in at 240 min.

As shown in Figure 3.3 (b), with the increase in an initial concentration of Cr (VI) from 5.0 to 20.0 mg L^{-1}, the absolute adsorption per unit mass of TWC sorbent increased from 2.4 mgg^{-1} to 8.2 mgg^{-1}. But in initial concentrations 10 mg L^{-1} and 20 mg L^{-1} the time to reach equilibrium became longer. This may be as a result of higher numbers of chromium ions creating high competition for available adsorbent sites and repulsive forces[25,26]. So the optimal contact time was taken as 100 min for Cr (VI) adsorption using treated wood charcoal.

As shown in Figure 3.3 (c), it has been observed that metal ion adsorption was rapid at an initial stage (within the first 20 min); after this it was relatively slow until it reaches the equilibrium. The plausible reason is that a large number of vacant surface sites are available at first, the bulk of adsorption takes place within the first few minutes. Based on the results 60min was fixed for further batch adsorption experiments.

The amount of sorption efficiency at this time increases from 2.5 mg/g to 9.4 mg/g as initial Cr (VI) concentration increases from 5 to 20 mg L^{-1} respectively.

However, the percentage of Cr (VI) adsorption decreases with increasing initial concentration. It may be due to the fact that the available active adsorption sites became fewer at higher initial concentration.
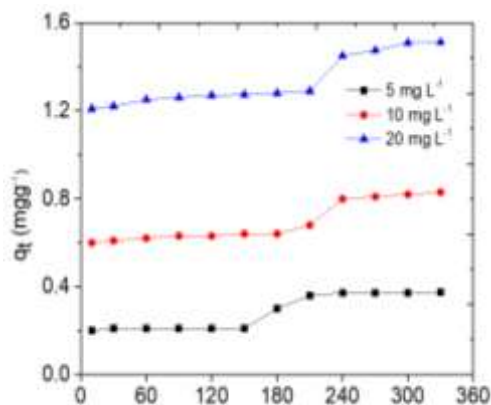

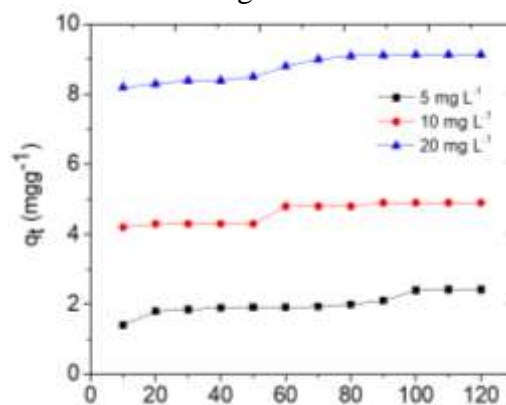**Fig 3.3(a): Evaluation of contact time influence on adsorption of Cr (VI) onto WC sorbent**

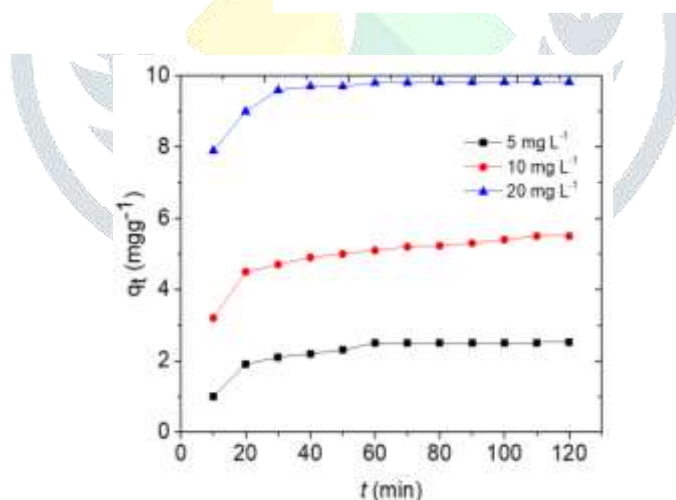**Fig 3.3(b): Evaluation of contact time influence on adsorption of Cr (VI) onto TWC sorbent**

Fig 3.3(c): Evaluation of contact time influence on adsorption of Cr (VI) onto Fe$_3$O$_4$-TWC nanosorbent

3.4 Influence of adsorbent dosage

The effect of the sorbent concentration (2.0–8.0 g L^{-1}) on the metal (20 mg L^{-1}) removal efficiency was studied at pH 4.0 in a mechanical shaker at respective equilibrium times for three types of adsorbents with 200 rpm and the results are shown in Fig 3.4(a), Fig 3.4(b)and Fig 3.4(c). The percentage of metal ions uptake was found to be increased with the increasing concentration of the adsorbent dose but the amount of metal adsorbed for unit mass was decreased considerably.

Jung et al [12, 27] reported that with an increase in the dosage of various adsorbents, the Cr (VI) removal was enhanced. However, a decrease in the adsorption capacity with an increase in the adsorbent dosage is probably due to insaturation of the active sites on the adsorbent surface during the adsorption process. This

phenomenon can also be due to the aggregation resulting from high adsorbate concentrations, leading to the decrease in the active surface area of the adsorbent.
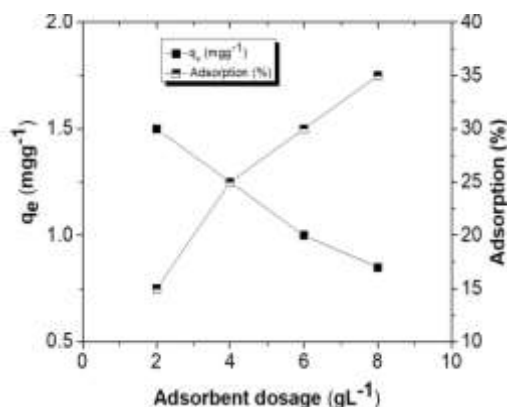

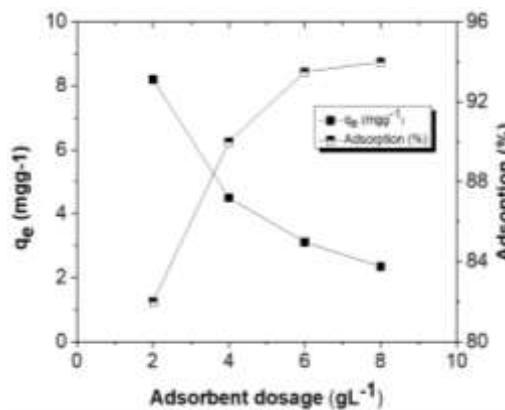**Fig 3.4(a): Evaluation of dosage influence on adsorption of Cr (VI) onto WC sorbent.**

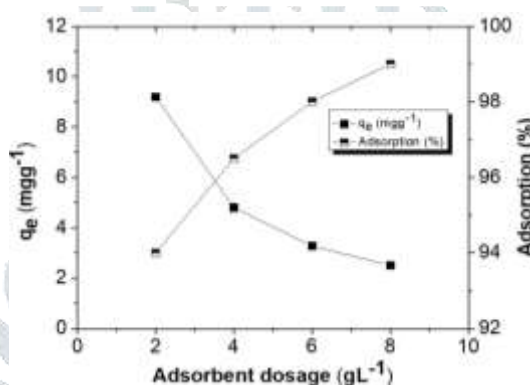**Fig 3.4(b): Evaluation of dosage influence on adsorption of Cr (VI) onto TWC sorbent**

Fig 3.4(c):Evaluation of dosage influence on adsorption of Cr (VI) onto Fe₃O₄-TWC

3.5 Adsorption Kinetics

In order to know the nature of adsorption process, two kinetic models including pseudo-first-order and pseudo-second-order models were used to fit the adsorption data of Cr (VI) onto TWC and Fe$_3$O$_4$-TWC. 50 mL samples containing 5.0–20 mg L^{-1} Cr (VI) metal ion solutions at optimum pH 4.0 was added to 2.0 g L^{-1} sorbent. Adsorption processes were carried out.

3.5.1 Pseudo first order reaction:

The pseudo-first-order describes the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time.The pseudo-first-order rate equation is given as

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{K_1}{2.303}\right)t$$

Linear plots were obtained by plotting log (q$_e$ –q$_t$) vs. *T* respectively at different concentrations as shown in Fig 3.5(a) and Fig 3.5(b). Values of K$_1$ was calculated from the slope and q$_e$ was obtained from intercept of the plots. The results in Table 3.1 show that the values of R^2 were low and the experimental q$_e$ value does not agree well with the calculated value. This shows that the adsorption of Cr (VI) is not fit for first-order kinetics for both sorbents of TWC and Fe$_3$O$_4$-TWC.

3.5.2 Pseudo-Second-Order reaction:

The pseudo-first-order model works effectively only in the region where adsorption process occurs rapidly. Therefore, the pseudo-second-order kinetic model is expressed as follows,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right)t,$$

Where q_t and q_e = the amount of metal adsorbed (mgg^{-1}) at time (*t*) and at equilibrium (mgg^{-1})

K_2 = the rate constant of pseudo-second-order kinetics adsorption (g mg^{-1} min^{-1}).

The values of K_2 and q_e were calculated from slope and intercept of the model curves t/q$_t$ versus t [3.6(a), 3.6(b)] obtained, and experimental data at equilibrium and correlation coefficient (R^2) for both sorbents was summarized in Table 3.1.

It was observed that pseudo-second-order kinetics model [Figure 3.6(a) and 3.6(b)] showed best fit with high correlation coefficient values range. Further low difference in equilibrium adsorption capacity qe (mg/g) values obtained by experimental data and model at equilibrium which indicates that the adsorption of Cr (VI) onto TWC and Fe$_3$O$_4$-TWC follows the pseudo-second-order kinetics. From comparison of the two models, it can be concluded that the adsorption of Cr (VI) onto TWC and Fe$_3$O$_4$-TWC follows the rate limiting pseudo-second-order kinetics may be chemical sorption or chemosorption involving valency forces through sharing or exchange of electron between adsorbent and adsorbate [28-31].
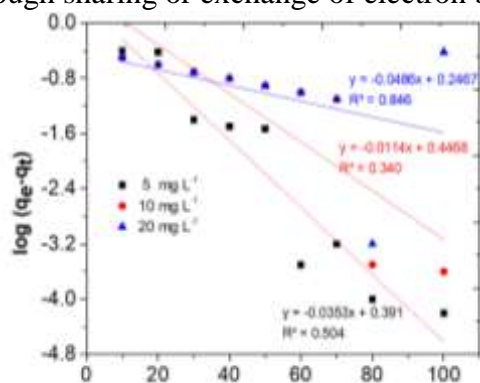

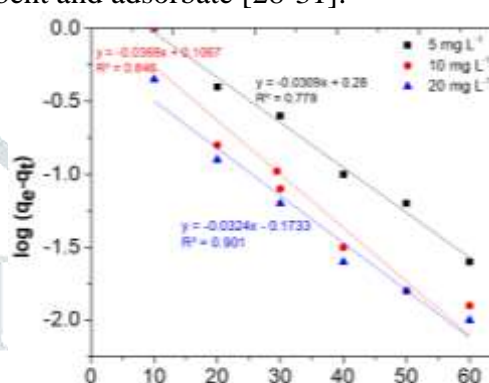**Fig 3.5(a): Pseudo-first order for Cr(VI) adsorption onto TWC**

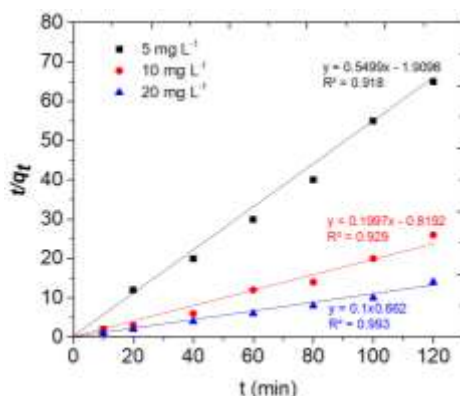**Fig 3.5(b): Pseudo-first order for Cr (VI) adsorption onto Fe$_3$O$_4$-TWC**

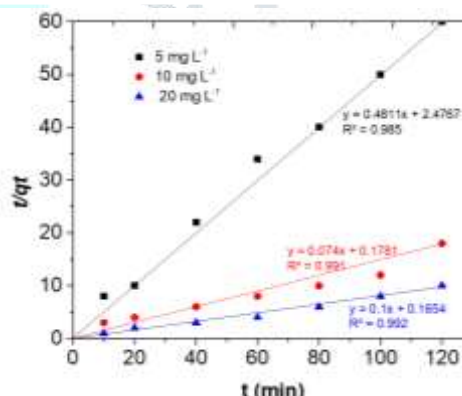**Fig 3.6(a): Pseudo-second order for Cr (VI) adsorption onto TWC sorbent**

Fig 3.6(b): Pseudo-second order for Cr (VI) adsorption onto Fe$_3$O$_4$-TWC

Adsorption isotherms are common models that compare adsorbent surface properties and their adsorption capacity of pollutants. In the present study, Langmuir and Freundlich were selected to fit experimental data.

3.6.1 Langmuir isotherm model :

The linear form of Langmuir's equation is commonly written as

$$\frac{C_e}{q_e} = \frac{1}{q_{max}(1/K_L)} + \frac{1}{q_{max}(C_e)}$$

Wher **q$_e$** is Mass of sorbate adsorbed per unit mass of sorbent (mg/g) and **C$_e$** is equilibrium concentration of sorbate in solution after adsorption (mg/L)

q_{max} and K_L indicate the maximum adsorption capacity of adsorbent and Langmuir equilibrium constant, respectively. These were obtained from the slope (1/q_{max}) and intercept (1/ q_{max} K_L) of the linear fit of the plot between Ce/qe versus Ce (Figure 3.7(a) and Fig.3.7 (b)) and were summarized in Table 3.2. The obtained results indicated that the adsorption of Cr (VI) onto TWC and Fe$_3$O$_4$-TWC showed good fit with

Langmuir isotherm model. The obtained results also concluded that the maximum adsorption capacity was increased.

For a Langmuir type adsorption process, the shape

of the isotherm indicates the nature of adsorption as favourable or unfavourable and may be classified by a term separation factor (R_L), a dimensionless constant given as

$$R_L = \frac{1}{(1 + K_L C_0)}$$

Where C is the highest initial concentration of adsorbate (mg L^{-1}),$_L$ (Lmg^{-1}) is the Langmuir constant.The separation factor (R_L) indicates the isotherm shape as Favourable ($0 < R_L < 1$), Linear ($R_L = 1$),Unfavourable ($R_L > 1$),Irreversible ($R_L = 0$)

The R_L values in the present investigations were found to be between 0.023 and 0.029 for the both the sorbent. These values were in the range of

$0 < R_L < 1$ indicating that the adsorption of Cr (VI) on TWC and Fe$_3$O$_4$-TWC nanosorbents are favourable.
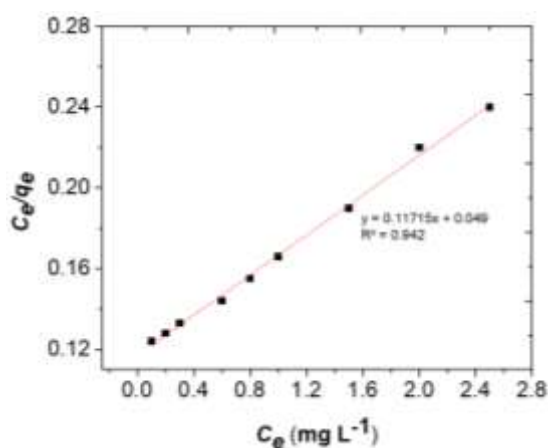

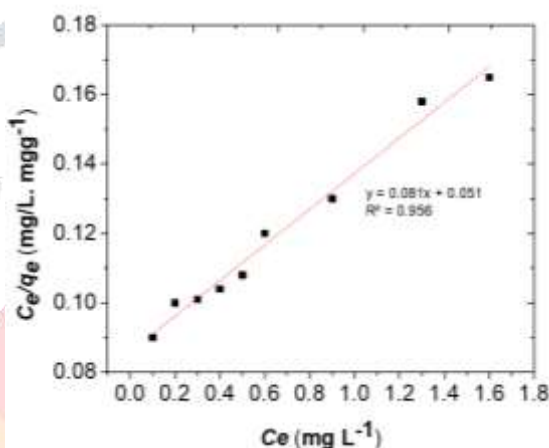**Fig 3.7(a): Langmuir Isotherms of Cr (VI) adsorption onto TWC**

Fig 3.7(b): Langmuir Isotherms of Cr (VI) adsorption onto Fe$_3$0$_4$-TWC

3.6.2 Freundlich isotherm model

The Freundlich isotherm model equation in the exponential expression can be expressed as

$$q_e = K_F C_e^{1/n}$$

The logarithmic form of the equation becomes

$$\text{Log } q_e = \log K_F + 1/n \log C_e$$

K_F = Freundlich constant that is taken as an indicator of adsorption capacity at given equilibrium concentration Ce

n = empirical constant which indicates the adsorption intensity.

q_e = mass of sorbate adsorbed per unit mass of sorbent (mg/g).

The Freundlich isotherm constants can be determined by plotting log Ce vs log qe which gives a straight line with slope of $(1/n)$ and intercept (log K_F) of the plot was shown in Figures 3.8(a) and 3.8(b) and were summarized in Table 3.2. Larger values of Freundlich constant K_F mean larger capacities of adsorption.

The constant 1/n is a function of the strength of adsorption. Larger values of 1/n mean the adsorption bond is weak. Smaller values of 1/n mean the adsorption bond is strong. As 1/n becomes very small, the isotherm plot approaches horizontal and the isotherm is termed irreversible. The coefficient of correlation indicates a strong linear relationship for values close to 1 and a weaker linear relationship for values closer to 0.

The correlation coefficients (R^2) of the curves were 0.994 and 0.997 for adsorption of Cr (VI) onto TWC and Fe$_3$O$_4$-TWC sorbents which indicates that the Freundlich isotherm model was well fitted.

The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to sorbate molecules interactions. It was not well fitted to the adsorption data of Cr(VI) onto both sorbents

were predicted by the R^2 values of this isotherm From Table 3.2, it was observed from both, Freundlich isotherm models were yielded best fit as indicated by the highest R^2 values at system temperature.
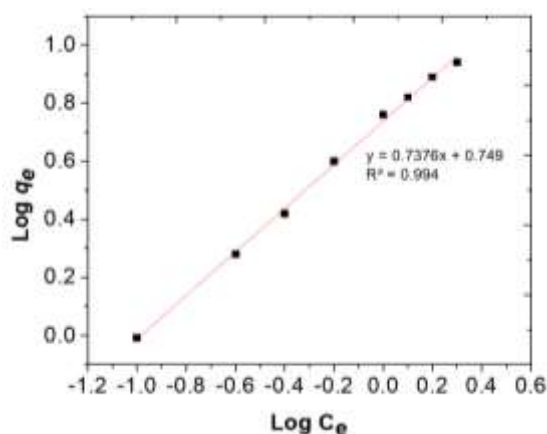

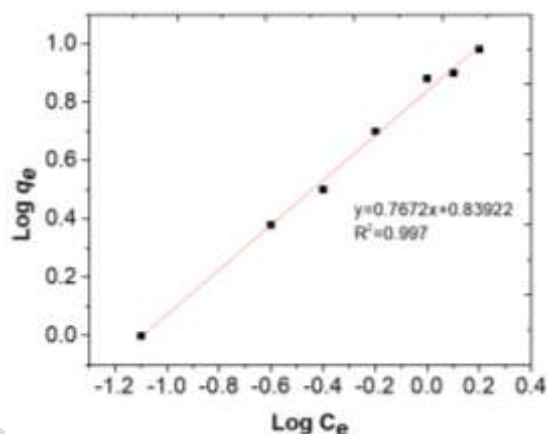**Fig 3.8(a):Freundlich Isotherm of Cr(VI) adsorption onto TWC adsorbent**

Fig 3.8(b):Freundlich Isotherm of Cr(VI) adsorption onto Fe₃O₄-TWC nanosorbent

The magnitude of the Freundlich constant gives a measure of favourability of adsorption. Values of 1/n close to 1 represent favourable adsorption process.

The order of isotherms models fitted to the Cr (VI) adsorption onto TWC and Fe₃O₄-TWC was as follows: Freundlich > Langmuir. Best fitting of the equilibrium data with Langmuir and Freundlich isotherms suggests that both adsorbent surface reaction is based on heterogenous adsorbent surfaces with different adsorption sites [32-34].

Table 3.1: Adsorption kinetics data for TWC sorbent and Fe₃O₄-TWC nanosorbent

Name of sorbent	Initial metal ion conc, mg L^{-1}	Pseudo-First-order			Pseudo-Second-order		
		q_{e1} (mgg^{-1})	K_1 (min^{-1})	R^2	q_{e2} (mgg^{-1})	K_2, (g mg^{-1}min^{-1})	R^2
TWC	5.0	0.876	0.131	0.846	1.993	0.129	0.918
	10.0	1.621	0.095	0.340	3.697	0.116	0.929
	20.0	6.001	0.156	0.504	9.337	0.109	0.993
Fe₃O₄-TWC	5.0	1.903	0.0761	0.779	2.094	0.129	0.985
	10.0	3.711	0.0641	0.846	3.714	0.117	0.991
	20.0	8.180	0.0405	0.901	9.426	0.101	0.992

Table 3.2: Adsorption constants of Langmuir isotherms for Cr (VI) onto TWC and   Fe₃O₄-TWC

Name of Sorbent	Langmuir isotherm parameters				Freundlich isotherm parameters		
	q_m,(mgg^{-1})	K_L,(Lmg^{-1})	R^2	R_L	K_f, mgg^{-1}(mg L^{-1})$^{-1/n}$	1/n	R^2
TWC	16.357	2.174	0.942	0.023	5.42	0.777	0.994
Fe₃O₄-TWC	17.953	1.681	0.956	0.029	6.917	0.777	0.997

4.   DESORPTION STUDIES OF ADSORPTION

Adsorption and desorption properties indicate reusability of the sorbent. It is important that the sorbent is easily regenerated and the desorbing agent is effective, cheap, non-polluting and non damaging the structure of the sorbent. The regeneration of the adsorbents was achieved by washing loaded sorbents with different desorbing agents: HNO_3, HCl and H_2SO_4 at different concentrations for desorption studies of Cr (VI) from two adsorbents. As the concentration of desorbing solutions increases, the desorption amount of Cr (VI) ions from loaded nanosorbents increases. The obtained results indicates that more than 90% of Cr (VI) ions were able to be desorbed from both sorbents using 0.03 mol L^{-1} hydrochloric acid, nitric acid, and H_2SO_4 solutions. Especially, > 90% recovery of Cr (VI) was achieved with 0.03 mol L^{-1} H_2SO_4 and nitric acid from the both sorbents, TWC and Fe_3O_4-TWC. However, 98.00% Cr (VI) desorption was achieved HCl from Fe_3O_4-TWC. The obtained results elucidate the adsorption and desorption behavior of Cr (VI) in aqueous solutions for recovery and recycling of sorbent at particular treatment of effluents. From the results, it was observed that maximum desorption efficiency loaded with metal for both sorbents at three different agents as shown in figure 3.9.
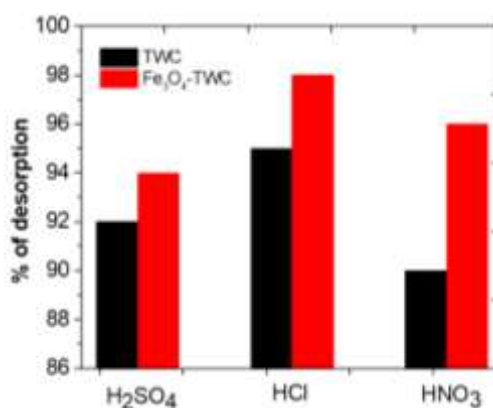

Fig 3.8: Maximum % of desorption efficiency loaded with metal adsorption for both adsorbents

5 CONCLUSIONS

This study shows successfully synthesized and characterized TWC and Fe_3O_4-TWC. Hence, TWC and Fe_3O_4-TWC obtained were a potential sorbents for Cr (VI) removal. Adsorption is affected by various parameters, such as nanosorbent concentration, pH, dosage, contact time. The effect of pH on Chromium removal was studied in the range of 2.0 to 12.

Maximum removal efficiency was observed at pH 4. Equilibrium time was achieved within 240 min for untreated WC, 100 minutes for TWC and 60 minutes for Fe_3O_4-TWC.

The influence of dosage on Cr (VI) adsorption was studied in the range of 2.0 to 8.0 g L^{-1}. Maximum adsorption was takes place at 2.0 gL^{-1} of both sorbents. The adsorption efficiency percentage was found to be 15% for WC, 82% for TWC, 94% for Fe_3O_4-TWC. The adsorption efficiency of three sorbents found to be increased with decreasing adsorbent dosage. The adsorption of Cr (VI) onto TWC and Fe_3O_4-TWC follows a Pseudo second order kinetics and shows good fit. It is found that the adsorption equilibrium correlated reasonably well with the Freundlich isotherm with R^2=0.994 for TWC and R^2=0.997 for Fe_3O_4-TWC. Desorption of metal ion was found to be increased with increase in the concentration of desorbing solution and maximum was 98% using HCl on Fe_3O_4-TWC which gives more compared to TWC was 95%.

The obtained results concluded that the tested sorbents could be reused without significant losses in its initial adsorption capacity. It is clear from the results that TWC and Fe_3O_4-TWC nanosorbent appear to be economic as well as efficient sorbents for the Cr (VI) removal from aqueous solutions.

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