

MALEIC ANHYDRIDE FUNCTIONALIZED TiO₂ (TiOMA) NANOPARTICLES FOR DECONTAMINATION OF Cu (II) FROM WATER

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ABSTRACT

Functionalization of titanium dioxide (TiO₂) nanoparticles was done using maleic anhydride (MA) and adsorption of copper (II) on MA functionalized TiO₂ nanoparticles (TiOMA) was studied. Percentage adsorption of Cu (II) on TiOMA was determined with respect to pH, contact time and adsorbent dose. The study revealed that the removal of Cu (II) was best achieved at pH range from 7.0 to 9.0. The initial 15 mg/L Cu (II) concentration came down to less than 0.53 mg/L at contact time 180 min with adsorbent dose of 0.6 g/50 mL. The adsorption was studied for Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The Langmuir isotherm model was found to be best fitted. During the study, the thermodynamic parameters like enthalpy change (ΔH°), free energy change (ΔG°), entropy change (ΔS°) and activation energy (E_a) were determined for the better understanding of the adsorption process. The adsorption was found to be kinetically pseudo-second order controlled process.

KEY WORDS: Copper, Maleic anhydride, Titanium dioxide, Nanoparticles, Adsorption, Kinetics.

INTRODUCTION

Reliable access to clean and affordable water is one of the major global challenges for the 21st century. Water contamination is one of the most critical issues the world is facing due to the increase in population growth and has become a serious threat to environmental and human health. Though some of the heavy metals are essential in trace amounts, at higher concentrations they are highly lethal as they cause some incurable diseases. In the recent decade, the removal of toxic heavy metal contaminants from polluted water is one of the most important environmental issues being researched. The toxicity and poisoning by heavy metals like iron, arsenic, copper, lead, chromium etc. and other contaminants like fluoride are well documented (Al'Abri *et al.*, 2019; Joseph *et al.*, 2019; Khan *et al.*, 2008; Ning *et al.*, 2002; Saikia *et al.*, 2017; Singh *et al.*, 2010; Theivarasu *et al.*, 2012; Yang *et al.*, 2019).

Copper contamination of water is mainly occurring due to industrialization, since copper is broadly used in various industries like electrical, wood manufacturing, electroplating, paint etc. The heavy metal contaminants including Cu (II) are non-biodegradable, due to which they exist in the natural environment for a long time. The presence of Cu (II) in drinking water above the permissible limit leads to serious environmental as well as health problems. Excessive intake of Cu by human leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression (Dogan *et al.*, 2009; Masih *et al.*, 2018). Therefore, it is necessary to remove excessive Cu (II) from water prior to its use for drinking purpose.

Many methods have been used to remove heavy metals including copper from water and wastewater; mainly by adsorption, chemical

precipitation, flocculation, membrane separation, ionic exchange, bio-sorption and so on (Das *et al.*, 2017; Fu and Wang, 2011; Jegadeesan *et al.*, 2005; Kurniawan *et al.*, 2006; Mishra *et al.*, 2018; O'Connell *et al.*, 2008; Remoudaki *et al.*, 2003; Yan *et al.*, 2001; Yousefzadeh *et al.*, 2018). Among these techniques, adsorption can be accepted as one of the most suitable techniques for decontamination of drinking water, especially after precipitation/coagulation process. Till date, many adsorbents have been developed for purification of water including nanomaterials (Deedar *et al.*, 2009; Sadegh *et al.*, 2017), activated charcoal (Zhu *et al.*, 2009), synthetic porous inorganic materials (Yin *et al.*, 2009), carbon nanotubes (Rao *et al.*, 2007), chitosan (Chen *et al.*, 2008), lignocelluloses (Shukla *et al.*, 2009), natural inorganic minerals (Ren *et al.*, 2016; Yavuz *et al.*, 2008), zero-valent iron (Rangsivek *et al.*, 2005) functionalized polymers (Turkmen *et al.*, 2009; Zhou *et al.*, 2009) etc. But, the adsorption capacities of most of these adsorbents are not satisfactory due to lack of adequate active sites on the surface, diffusion limitation, high cost, difficulties in separation and regeneration of adsorbents. Therefore, necessity has arrived to develop novel adsorbents with large surface area with maximum active sites for adsorption with minimal diffusion resistance.

Recently progress in nano scale science and engineering suggests that many of the current problems involving water quality could be greatly diminished by using nanoparticles (Guo *et al.*, 2018; Qu *et al.*, 2013; Sousa *et al.*, 2017; Tiwari *et al.*, 2008). Due to high surface to volume ratio and greater active sites for interaction with metallic species, nanoparticles exhibit good adsorption efficiency near neutral values. Various nano-adsorbents have been exploited to remove heavy metal ions from aqueous solution. Nano-alumina (Pacheco *et al.*, 2001), nanomagnets coated by EDTA (Koehler *et al.*, 2009), carbon nanotube (Li *et al.*, 2003), hydroxyapatite nanoparticle (Wang *et al.*, 2009) etc. have been used as adsorbent for Cu (II) removal. It is important to note that nanoparticles, functionalized with various functional groups, are more effective since the free functional groups present on the surface provide large number of active sites as well as aqueous stability, which is necessary for the successful adsorption of toxic metal ions. In this direction, various nanoparticles have been functionalized and used as effective adsorbents for removal of heavy metals including Cu (II) from contaminated water (Abu-Dief *et al.*,

2016; Del Castillo *et al.*, 2014; Hao *et al.*, 2010; Singh *et al.*, 2011; Verma *et al.*, 2017; Wang *et al.*, 2006). However, some of these studies are not economic or require the control of various parameters to achieve the optimum Cu (II) removal. Therefore, a more effective and economical technique would be highly desirable.

Keeping these in mind, in the present study, TiO₂ nanoparticles were surface modified by functionalization using maleic anhydride (MA) and adsorption experiments were carried out to evaluate the performance of functionalized TiO₂ nanoparticles for removal of Cu (II) from water. The process parameters such as effect of adsorbent dose, pH, initial ion concentration and contact time were studied. Isotherms like Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models were studied. Various thermodynamic parameters were also calculated for the process to complete the investigation for efficacy of functionalized TiO₂ nanoparticles in adsorption of Cu (II) from contaminated water. The process was also analysed for kinetic models like pseudo first order, pseudo second order, Elovich and Intra-particle diffusion models at different experimental conditions.

MATERIALS AND METHODS

The titanium dioxide (TiO₂) nanoparticles (~ 7 nm, TiO₂- Anatase, 95%) were from SRL and used as such. The maleic anhydride (MA) was from Fluka (99% pure). The toluene used was from Pallav™ (99.5% pure). The copper (II) chloride dihydrated (99% pure) from Merck was used for the preparation of the stock solution. All the equipments used during the experiments were calibrated as per standard procedure. The initial pH of the Cu (II) solutions was adjusted using NaOH (0.1 M) and/or HCl (0.1 M) solutions as and when necessary and analysed by Cyber scan pH 510 (Eutech) instrument. The determination of concentration of Cu (II) was done using Atomic Absorption Spectrophotometer (Thermo scientific, iCE 3000 AA) having detection limit 5 µg/L. Bruker Optic (model-ALPHA-T) FTIR instrument have been used for FTIR spectra. SEM images were taken using a Zeiss Sigma 300 scanning electron microscope.

TiO₂ nanoparticles have been functionalized using maleic anhydride (MA) using polar protic (ethanol) and non polar (toluene) solvents (Del Castillo *et al.*, 2014). In a typical procedure, 5 g of TiO₂ was added to 400 mL of ethanol/toluene and

then heated up to 55 °C/80 °C depending on solvent used. Then, 12.33 g of MA was dissolved in 100 mL of solvent and added slowly to the reaction mixture. The reaction was maintained in constant reflux condition for 5 h. The functionalized TiO₂ nanoparticles (TiOMA) was recovered from solvent by centrifugation and then washed with water and dried in oven.

Adsorption study

The batch adsorption experiments were carried out to obtain the rate and equilibrium data. Parallel two experiments were conducted using control TiO₂ nanoparticles and MA functionalized TiO₂ nanoparticles (TiOMA) separately to compare the other parameters. The reaction mixtures consisting of 50 mL known concentration of Cu (II) solutions and known quantities of adsorbents were shaken in a temperature controlled orbital shaker with shaking speed of 175 rpm at three different temperatures of 298, 303 and 308 K. The effect of adsorbent dose on adsorption was studied by varying the adsorbent dose from 0.15 to 0.6 g/50 mL and maintaining pH of the solution at 7.5 with a constant contact time of 180 min. In this study, the Cu (II) concentration in spiked water was fixed at 5 mg/L. The study of the effect of initial pH of the solutions on Cu (II) adsorption by the TiOMA was done by using 15 mg/L of the adsorbent at varying pH of the solutions. The effect of contact time was studied with varying contact time from 60 to 360 min keeping pH of the solutions and dose of the adsorbent constant. The effect of initial Cu (II) concentration in feed water was studied with various adsorbent doses with varying initial Cu (II) concentration from 5 to 25 mg/L maintaining pH of the solution at 7.5 with a constant contact time of 180 min. The adsorption isotherm was also

performed by using 0.45 g of TiOMA with 50 mL spiked water at different initial concentrations of Cu (II). The kinetic and thermodynamic parameters for Cu (II) adsorption on TiOMA were established by conducting the experiments at different contact times and at three different temperatures respectively.

Desorption experiments

The adsorption/desorption cycles were carried out to understand the reusability of the TiOMA. The saturated TiOMA was prepared by treating 0.45 g of TiOMA with 50 mL of 25 mg/L Cu (II) solution under agitation for about 5 h at shaking speed of 175 rpm. Then filtered the Cu (II) saturated TiOMA and dried in oven 100 °C. The Cu (II) saturated TiOMA (0.15 g) was agitated for about 3 h at shaking speed of 175 rpm with 50 mL of NaOH solution (0.1, 0.3 and 0.5 M solution were used separately). The aqueous phases were then separated and concentrations of Cu (II) in that phase were determined.

RESULTS AND DISCUSSION

Characterization of TiOMA nanoparticles

The functionalized nanoparticles have been characterized using SEM, EDX and FTIR. The SEM image along with EDX pattern of synthesized TiOMA is shown in Fig. 1.

The SEM image of TiOMA with smooth edges implies the surface modification of TiO₂ nanoparticles and the particle sizes in the range of 16-26 nm. The EDX analysis confirms the presence of Ti, C and O in TiOMA sample, which implies the surface modification with maleic anhydride (MA). In the FTIR spectra (figure not shown), the peak

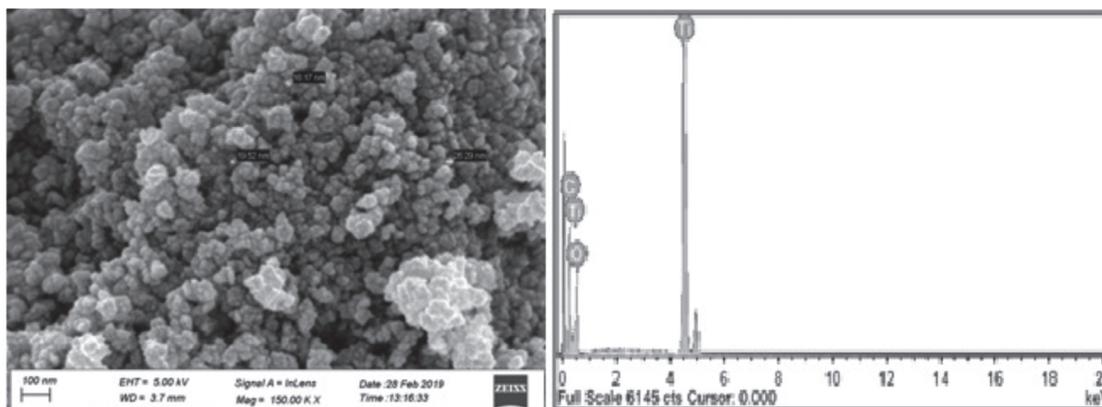


Fig. 1. FE-SEM and EDX pattern of TiOMA

near 3400 cm⁻¹ corresponds to the stretching vibration bands of -OH of adsorbed water molecule. The peak at 1629 cm⁻¹ is for the bending mode of Ti-OH. The peak at 1185 cm⁻¹ is due to the bands of C-O-Ti. The peaks at 1392-1300 cm⁻¹ are attributed to the bands of C-H vibrations.

Effect of adsorbent dose

The effect of adsorbent dose on adsorption of Cu (II) on TiOMA is shown in Fig. 2a. From this figure, it is observed that adsorption efficiency of Cu (II) from the solution increases rapidly with increase in adsorbent dose from 0.15-0.45 g/50 mL. A marginal increase is observed on further increase in the adsorbent dose for both TiO₂ and TiOMA. The increase in the removal efficiency may be attributed to the fact that with the increase in adsorbent dose, available surface for adsorption increases for the solute to be adsorbed. The removal of the Cu (II) is more effective in case of TiOMA compared to TiO₂.

Effect of pH

The effect of pH on adsorption of Cu (II) on TiOMA is observed in the pH range of 5 to 11 by plotting the

pH *vs* % removal of Cu (II), which is shown in Fig. 2b. It suggests that efficiency of Cu (II) removal increases with increasing pH from 5 to 8 and after that either marginal increase or decrease was observed. In the study, highest Cu (II) removal 90.1% (for TiOMA) and 65.2% (for TiO₂) was achieved at pH 8 with feed water conc. 15 mg/L using 0.45 g adsorbent. The results suggested that both at lower and higher pH value than that, the removal efficiency of TiOMA and TiO₂ were found to decrease. This may be due to the fact that extreme high and low protonated surfaces of TiOMA and TiO₂ are not favourable for Cu (II) adsorption.

Effect of initial Cu (II) Concentration

To know the effect of initial ion concentration on adsorption of Cu (II) on TiOMA, the initial ion concentration was plotted against the % removal of Cu (II) as presented in Fig. 2c. From this figure, it is obvious that adsorption efficiency is higher at lower initial Cu (II) concentration (5 mg/L) and a slow decrease in Cu (II) adsorption by TiOMA as well as TiO₂ were observed with increasing initial Cu (II) concentration. The decrease in Cu (II) removal

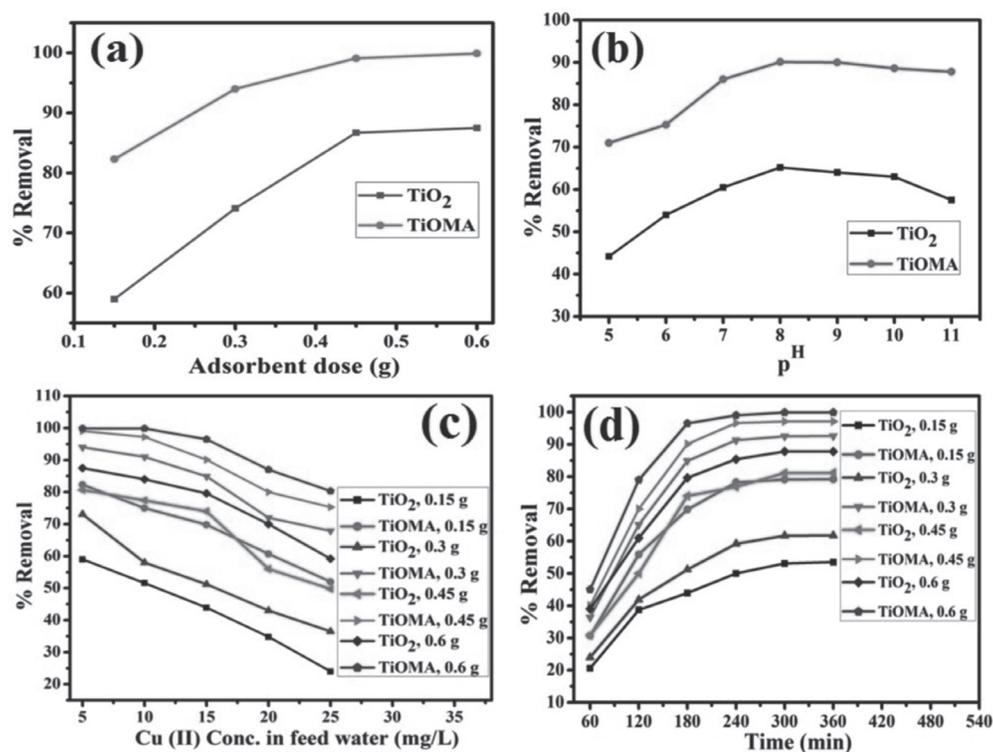


Fig. 2. (a) Effect of adsorbent dose of functionalized TiO₂ nanoparticles on adsorption. Graph showing the variation of adsorbent dose *vs* % removal of Cu (II), (b) Effect of pH on adsorption. Graph representing the variation of pH *vs* % removal of Cu (II), (c) Effect of initial ion concentration on adsorption. Graph illustrating the variation of conc. *vs* % removal of Cu (II), and (d) Effect of contact time on adsorption. Graph demonstrating the variation of time *vs* % removal of Cu (II)

efficiency at higher initial concentration may be due to saturation of the active sites of the adsorbent by the Cu (II) and hence, further increase in the Cu (II) concentration is not leading to the increase in absorption significantly.

Effect of contact time

The effect of contact time on adsorption of Cu (II) on TiOMA was studied by varying the agitation time using feed water containing 15 mg/L of Cu (II) and is illustrated in Fig. 2d. From the plot it is observed that adsorption efficiency increases with increasing the contact time and reaches nearly maximum removal at contact time of 180 min. After 180 min removal becomes nearly constant for both the cases of TiOMA and TiO₂. This may be due to the saturation of the adsorption site of the adsorbent. The feed water containing 15 mg/L of Cu (II) reduced by 96.5% at contact time 180 min with adsorbent dose of 0.6 g/50 mL.

Desorption Study

The experimental results (Table 1) from the desorption study revealed that trend of desorption percentage at different concentration of NaOH is in the order 0.1 M < 0.3 M < 0.5 M. The maximum desorption of Cu (II) was found to be 74.5% with 0.5 M NaOH solution. From the study it is revealed that the used TiOMA can be regenerated satisfactorily for reuse.

Kinetic study for the adsorption of Cu (II) on TiOMA

The adsorption mechanism of Cu (II) on TiOMA was investigated by studying the pseudo first order, pseudo second order, Elovich and Intra-particle diffusion kinetic models at different experimental conditions.

Pseudo first order kinetic model

The linear form of pseudo first order kinetic model (Lagergren *et al.*, 1898) is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad \dots (1)$$

Where; K_1 (1/min) = rate constant
 q_e (mg/g) = the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium
 q_t (mg/g) = the amount of adsorbate adsorbed per unit mass of adsorbent at time t
 t (min) = time

The $\log(q_e - q_t)$ vs t for various initial Cu (II) concentrations was plotted to understand the fitness of the adsorption kinetic with pseudo first order kinetic model shown in Fig. 3a. The values of K_1 at five different initial Cu concentrations were calculated from slopes of the respective linear plots and also the correlation coefficient (R^2) was computed and the values are given in Table 2. The correlation coefficient (R^2) values of the above plot reveals that the adsorption is not better fitted to Pseudo first order kinetic model.

Pseudo second order kinetic model

The linear form of equation of pseudo second order kinetic model (Ho *et al.*, 2006) is expressed as:

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

Where; K_2 (g/mg min.) = rate constant
 q_e (mg/g) = the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium
 q_t (mg/g) = the amount of adsorbate adsorbed per unit mass of adsorbent at time t
 t (min) = time

From the plot of $\frac{t}{q_t}$ vs t (Fig. 3b) for Cu (II) on TiOMA at different initial Cu (II) concentration at 303 K, the experimental value of q_e and K_2 of the pseudo second order equation were obtained. The plot (Fig. 3b) gives a straight line with higher correlation coefficient, R^2 values, which was higher than that observed for pseudo first order model. It indicates the better fitness of the pseudo second order model. The values of q_e , K_2 and R^2 are shown in Table 2. The value of q_e increases with the increase in initial Cu (II) concentration; this is due to

Table 1. Desorption study of TiOMA

Adsorbate adsorbed by adsorbent at saturated point (mg g ⁻¹)	Eluent used	Conc. of eluent (M)	Adsorbate eluted from adsorbent (mg g ⁻¹)	Regeneracy of adsorbent (%)
1.45	NaOH	0.1	0.51	35
1.45	NaOH	0.3	0.62	42.8
1.45	NaOH	0.5	1.08	74.5

the higher availability of Cu (II) to adsorb at higher initial Cu concentration. The values of rate constant, K_2 decreases with increase in initial Cu (II) concentration which indicates the saturation of the TiOMA with Cu (II) at higher initial Cu concentration.

Elovich kinetic model

The equation of the Elovich model is expressed (Chien *et al.*, 1980; Ho *et al.*, 2002) as below:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad \dots (3)$$

Where; α (mg/g min) = Elovich coefficients represents initial adsorption rate

β (g/mg) = the adsorption coefficient

Assuming $\alpha\beta t \gg 1$, $q_t = 0$, $t = 0$ and $q_t = q_t$ at $t = t$

$$q_t = \beta \log(\alpha\beta) + \beta \log t \quad \dots (4)$$

The value of $\log t$ vs q_t was plotted to understand the fitness of the adsorption kinetic with Elovich kinetic model, which is well displayed in

Fig. 3c. From the slopes and intercepts of the plots, the constant β and the initial adsorption rate α were calculated. The results with the correlation coefficients are shown in Table 2. The comparatively low correlation coefficients (R^2) for the Elovich kinetic model suggest that this adsorption system is not acceptable for this system.

Intra-particle diffusion model

The intra-particle diffusion is another kinetic model which is expressed (Demirbas *et al.*, 2002; Weber *et al.*, 1963) as:

$$q_t = K_{id}t^{1/2} + I \quad \dots (5)$$

Where; q_t (mg/g) = the amount of adsorbate adsorbed per unit mass of adsorbent at time t

K_{id} (mg/(g min^{1/2})) = rate constant of Intra-Particle diffusion model

t (min) = time

I = constant related to boundary layer thickness

The values of $t^{1/2}$ were plotted against q_t (Fig. 3d) to understand the fitness of the adsorption kinetic with Intra-particle diffusion model. Comparatively

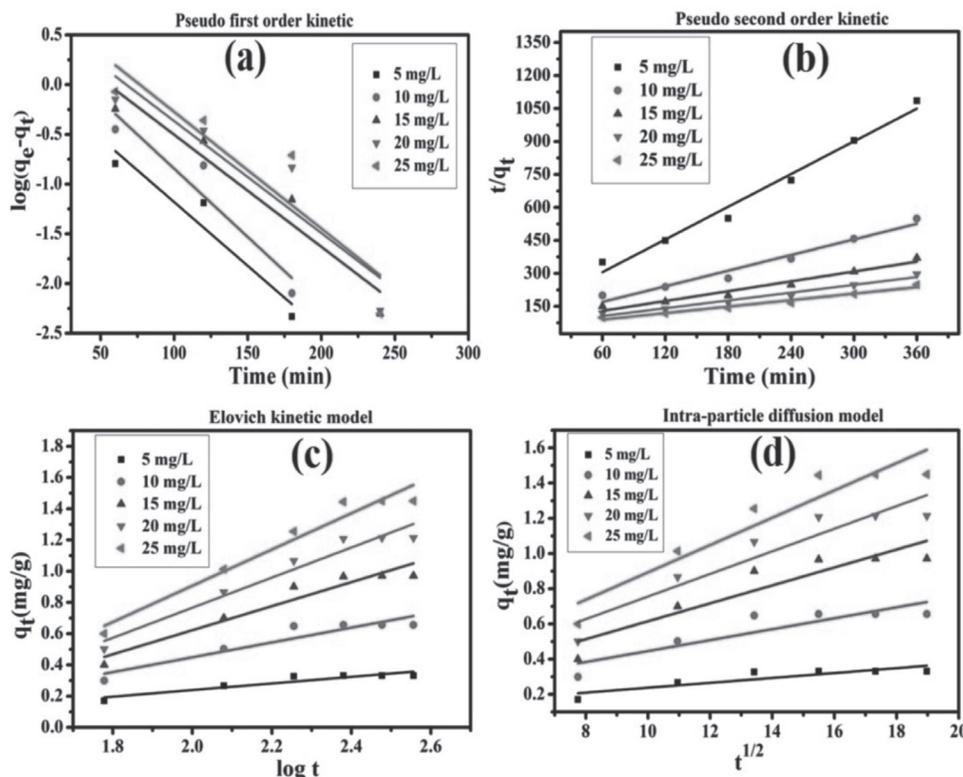


Fig. 3. (a) Pseudo first order kinetic model for adsorption kinetic study. Graph demonstrating the variation of $\log (q_e - q_t)$ vs time, (b) Pseudo second order kinetic model for adsorption kinetic study. Graph showing the plot between t/q_t vs time, (c) Elovich kinetic model for adsorption kinetic study. Graph showing the variation of $\log t$ vs q_t , and (d) Intra-particle diffusion model for adsorption kinetic study. Graph displaying the variation between $t^{1/2}$ vs q_t

low correlation coefficients (R^2) of the plot suggest that this adsorption system is not fit for this model. The rate parameters, together with R^2 are listed in Table 2.

Adsorption isotherm study of Cu (II) adsorption on TiOMA

Langmuir isotherm

The Langmuir isotherm is based on three assumptions (i) maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, (ii) the energy of adsorption is constant and (iii) there is no transmigration of adsorbate molecules in the plane of adsorbent surface.

The Langmuir adsorption isotherm (Chowdhury *et al.*, 2010) can be expressed as below:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad \dots (6)$$

$$\text{Or } \frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b}$$

Where; q_e (mg/g) = the amount of adsorbate adsorbed per unit mass of adsorbent

C_e (mg/L) = the unabsorbed adsorbent concentration in solution at equilibrium condition

q_m (mg/g) = the maximum amount of adsorbate adsorbed per unit mass of adsorbent to form a complete monolayer on the surface

b (L/mg) = Langmuir constant

In the Fig. 4a, the linear plot of C_e/q_e vs C_e with greater correlation coefficient (R^2) value indicates the monolayer adsorption of Cu (II) on TiOMA. The values of q_m and b were calculated from the slope and intercept respectively and are presented in Table 3. From the results, it was observed that the maximum Cu uptake (q_m) and the value of

Langmuir constant (b) related to the affinity of the binding sites were increased with the increase of temperature. Highest R^2 value suggested that the process preferably followed the Langmuir isotherm model.

Freundlich isotherm

The Freundlich isotherm is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent (Yang *et al.*, 1998). The isotherm is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption). The linear form of the Freundlich isotherm (Meenakshi *et al.*, 2008), equation is expressed as:

$$q_e = K_f C_e^{1/n} \quad \dots (7)$$

$$\text{Or } \log q_e = \log K_f + \frac{1}{n} \log C_e$$

Where; q_e (mg/g) = the amount of adsorbate adsorbed per unit mass of adsorbent

K_f [mg/g (L/mg) $^{1/n}$] = a constant, sorption capacity of the adsorbent

n = favourability of the adsorption process, constant related to energy of intensity of adsorption

The value of K_f and n (Table 3) were calculated from the linear plot of $\log q_e$ vs $\log C_e$ shown in Fig. 4b. From the plot it is observed that the values of n are lying between 1 and 10 which indicates the chemisorptions (Jiang *et al.*, 2002). Isotherms with $n > 1$ are classified as L-type isotherms reflecting a high affinity between adsorbate and adsorbent and is indicative of chemisorptions (Taha *et al.*, 2009). The Freundlich constant, K_f which is related to the adsorption capacity, increased with temperature, indicating that the adsorption process is endothermic.

Table 2. Kinetic parameters for the adsorption of Cu (II) on TiOMA

C_o (mg/L)	q_e (mg/g)	Pseudo first order kinetic model			Pseudo second order kinetic model			Elovich kinetic model			Intra-particle diffusion kinetic model		
		K_1 (1/min)	q_e (mg/g)	R^2	K_2 [g/(mg min)]	q_e (mg/g)	R^2	α [mg/(g min)]	β (g/mg)	R^2	K_{id} [mg/(g min $^{1/2}$)]	I (mg/g)	R^2
5	0.33	0.029	1.26	0.85	0.039	0.40	0.98	0.6261	0.21	0.85	0.014	0.10	0.73
10	0.66	0.032	3.38	0.81	0.012	0.84	0.96	0.1861	0.47	0.85	0.031	0.14	0.74
15	0.97	0.026	4.20	0.89	0.009	1.34	0.95	0.0836	0.77	0.91	0.051	0.11	0.81
20	1.21	0.026	5.74	0.79	0.008	1.69	0.97	0.0648	0.96	0.94	0.064	0.11	0.85
25	1.45	0.027	7.94	0.75	0.008	2.04	0.97	0.0521	1.16	0.95	0.078	0.12	0.87

Temkin isotherm

The Temkin isotherm model assumes that due to the adsorbent-adsorbate interactions the adsorption energy decreases linearly with the surface coverage. The linear form of Temkin isotherm model (Wang *et al.*, 2005) is given by the equation:

$$q_e = \left(\frac{RT}{b}\right) \log(AC_e) \quad .. (8)$$

Or $q_e = B \log A + B \log C_e$

Where; $B = \frac{RT}{b}$

b (J/mol) = Temkin constant, related to heat of sorption

A (L/g) = Temkin isotherm constant also, called equilibrium binding constant

R = gas constant (8.314 J/mol.k)

T (k) = absolute temperature

The value of correlation coefficients (R^2) >0.94 obtained from the linear plot of q_e vs $\log C_e$ (Fig. 4c) at different temperatures for Temkin adsorption

isotherm, which consider the chemisorptions of an adsorbate onto the adsorbent (Biswas *et al.*, 2007) revealed that adsorption process is fitted satisfactorily with the Temkin adsorption isotherm (Table 3). This supports the findings that the adsorption of Cu (II) onto TiOMA is a chemisorption process (Boparai *et al.*, 2011).

Dubinin-Radushkevich isotherm

Dubinin-Radushkevich (D-R) isotherm model is a semi-empirical equation where adsorption follows a pore filling mechanism. It assumes that the adsorption has a multilayer character, involves van der Waals forces and is applicable for physical adsorption processes (Hutson *et al.*, 1997). The linear form of D-R isotherm model is expressed as:

$$\log q_e = \log q_D - B_D \epsilon^2 \quad .. (9)$$

Where; $\epsilon = RT \log\left(1 + \frac{1}{C_e}\right)$

q_D (mg/g) = theoretical saturation capacity

B_D (mol²/kJ²) = constant related to adsorption energy

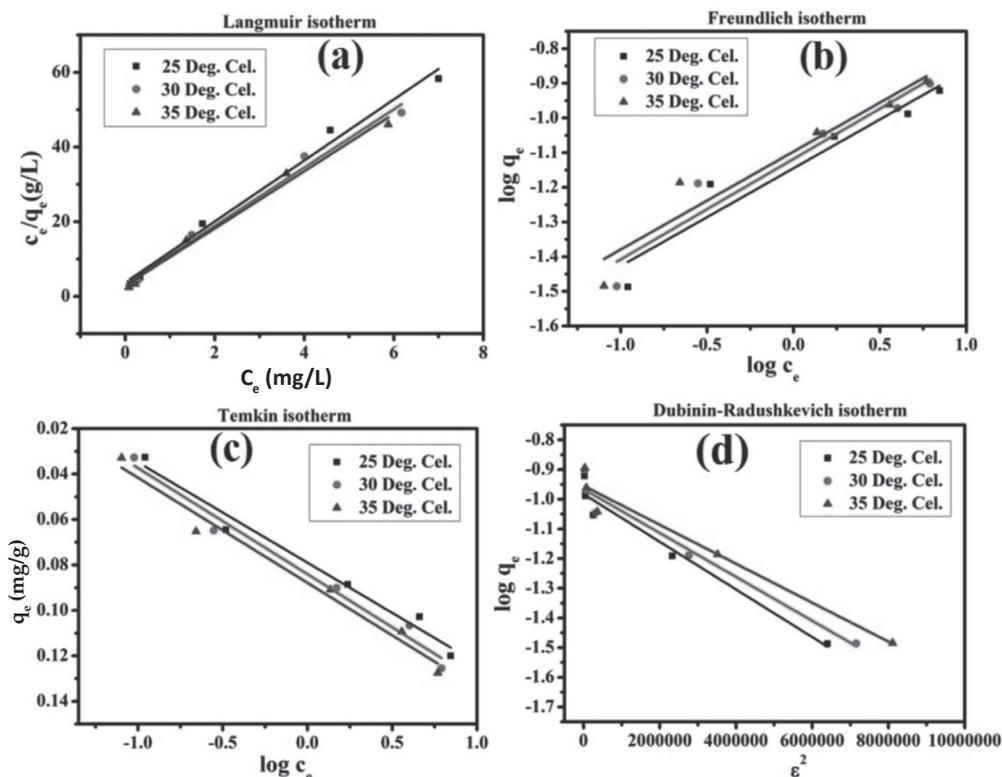


Fig. 4. (a) Langmuir isotherm model for adsorption study. Graph showing the plotting of C_e/q_e vs C_e , (b) Freundlich isotherm for adsorption study. Graph demonstrating the variation of $\log q_e$ vs $\log C_e$, (c) Temkin isotherm model showing the variation between q_e vs $\log C_e$ and (d) Dubinin-Radushkevich isotherm model for adsorption study. Graph displaying the variation between $\log q_e$ vs ϵ^2

R = gas constant (8.314 J/mol.K)

T (k) = absolute temperature

$$E_D = \frac{1}{\sqrt{2B_D}}$$

E_D (kJmol⁻¹) = the mean energy of sorption

The magnitude of E_D provides the information on the nature of sorption process i.e. physical/chemical.

In the Fig. 4d, the plot of $\log q_e$ vs ε^2 at different temperatures revealed that the values are not consistent with the q_m values previously determined for the Langmuir isotherm. The correlation coefficients for the D-R isotherm are the lowest compared to the values of the Langmuir isotherm models that suggests that the Cu (II) adsorption onto TiOMA is not a physical process only (Boparai *et al.*, 2011).

Thermodynamic Study of Cu (II) adsorption on TiOMA

The spontaneity of a process is determined from thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°), entropy change (ΔS°) and activation energy (E_a). If the value of ΔG° decreases with increasing temperature, the process will be spontaneous (Ngah *et al.*, 2008). The temperatures used in the thermodynamic study were 298, 303 and 308 K. The thermodynamic parameters were calculated based on the following equations:

$$\log b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} = -\frac{\Delta G^\circ}{RT}$$

$$\Delta G = \Delta H^\circ - T\Delta S^\circ \quad \dots (10)$$

Where, b is the equilibrium constant, R is the universal gas constant (8.314 J/mol K), and T is the temperature (K). The positive enthalpy change (from table 3), ($H^\circ = + 6.07005$ kJ/mol), implies the endothermic nature of the adsorption process. The positive entropy change, ($S^\circ = + 0.02318$ J/mol K), reveals that the randomness increases at the solid/liquid interface during the adsorption of Cu (II) onto the TiOMA. The negative value of free energy change (G°) which is decreasing with increasing temperature indicates that the process is favourable and spontaneous in nature.

The sticking probability, S^* of an adsorbate on adsorbent can be expressed by a modified Arrhenius type equation related to the surface coverage (θ). This is a function of the adsorbate/adsorbent system, which is the measure of the potential of an adsorbate to remain on the adsorbent indefinitely (Sundaram *et al.*, 2008) and it can be expressed as:

$$S^* = (1 - \theta) \exp\left(-\frac{E_a}{RT}\right)$$

$$\text{Or } \log(1 - \theta) = \log S^* + \frac{E_a}{RT} \quad \dots (11)$$

Where, θ is surface coverage, E_a is activation energy.

$$\theta = \left(1 - \frac{C_e}{C_o}\right)$$

Where, C_o and C_e are the initial and equilibrium Cu (II) concentrations respectively.

From the plot $\log(1-\theta)$ vs $1/T$ with intercept $\log S^*$ and slope E_a/R , the value of S^* and E_a were calculated (Table 4). The value of S^* was found to be 1.2794×10^{-7} which is very close to zero, indicating that the adsorption mechanism follows

Table 3. Parameters of adsorption isotherms for Cu (II) on TiOMA

		298 K	303 K	308 K
Adsorption isotherm	Adsorption parameters	Values		
Langmuir	q_m (mg/g)	0.1224	0.1283	0.13054
	b (L/mg)	2.1994	2.3491	2.6423
	R^2	0.9847	0.9865	0.9864
Freundlich	n	3.5474	3.4507	3.5398
	K_f [mg/g (L/mg) ^{1/n}]	0.07163	0.07623	0.08002
	R^2	0.9009	0.9087	0.9004
Temkin	B	0.0442	0.0467	0.0462
	A (L/g)	61.2816	63.2203	79.9039
	b (kJ/mol)	56.0537	53.943	55.4277
	R^2	0.9699	0.9720	0.9702
Dubinin-Radushkevich	q_D (mg/g)	0.10406	0.10817	0.11097
	B_D (mol ² /kJ ²)	8×10^{-8}	7.4×10^{-8}	6.6×10^{-8}
	E_D (kJ/mol)	2.5	2.5993	2.7524
	R^2	0.9528	0.9502	0.9522

chemisorption (Horsfall *et al.*, 2005) whereas the activation energy (E_a) for the process was found to be 13.419 kJ/mol.

The R_L and χ^2 values of Cu (II) adsorption onto TiOMA

The Langmuir isotherm constant parameter (R_L) also called dimensionless equilibrium parameter is essential characteristics of the Langmuir isotherm, which provides the valuable information on the adsorption efficiency of the isotherms process. The R_L can be related with Langmuir isotherm constant by the following equation (Wang *et al.*, 2005):

$$R_L = \frac{1}{1+bC_0} \quad \dots (12)$$

Where, b is the Langmuir isotherm constant
 C_0 is the initial Cu (II) concentration (mg/L).

The value of R_L indicates the shape of the isotherms. From the condition $0 < R_L < 1$, the Langmuir isotherm is favourable; $R_L = 0$ and $R_L = 1$ give irreversible and linear isotherm respectively; whereas $R_L > 1$ is unfavourable. R_L values at different temperatures studied were calculated (Table 5) and the values ranges from 0.0149 to 0.0834, which implies that the Langmuir isotherm is favourable.

The difference between the experimental and various models data can be measured with the help of Chi-square test analysis. Mathematically, this test statistic can be expressed as:

$$\chi^2 = \sum \left[\frac{(q_{e.exp} - q_{e.cal})^2}{q_{e.cal}} \right] \quad \dots (13)$$

Table 4. Values of thermodynamic parameters

Temp. (K)	Thermodynamic parameters				
	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	E_a (kJ/mol)	S^*
298	-0.8376	6.07005	0.02318	13.419	1.2794×10^{-7}
303	-0.9535				
308	-1.0694				

Table 5. Values of R_L and χ^2 values of Cu (II) adsorption onto TiOMA

Temp (°K)	R_L values					χ^2 values for Adsorption kinetics	
	5 mg/L	10 mg/L	15 mg/L	20 mg/L	25 mg/L	Pseudo first order	Pseudo second order
298	0.0834	0.0435	0.0294	0.0222	0.0179	14.2445	0.4634
303	0.0785	0.0408	0.0276	0.0208	0.0167		
308	0.0704	0.0365	0.0246	0.0186	0.149		

Where, $q_{e.exp}$ is experimental equilibrium capacity data and $q_{e.cal}$ is the equilibrium capacity from a model. If data from the model are similar to experimental data, χ^2 value will be small and if they differ, χ^2 will be large (Gandhi *et al.*, 2011).

The χ^2 values were calculated (Table 5) for Pseudo first and Pseudo second order kinetic models. The lower χ^2 value (0.4634) with respect to the pseudo-second order model revealed that Cu (II) adsorption onto TiOMA obeyed the pseudo-second order kinetics. The pseudo-first order model provided higher values (14.2445) suggesting poor pseudo-first order fit to the data for Cu (II) adsorption onto the TiOMA.

CONCLUSION

Titanium dioxide (TiO₂) nanoparticles have been functionalized using maleic anhydride (MA) and studied the adsorption of Cu (II) onto it. From the study it has been observed that the initial 15 mg/L Cu (II) concentration can be reduced up to less than 0.53 mg/L at contact time 180 min with adsorbent dose of 0.6 g/50 mL. Study indicated that the removal efficiency of Cu (II) from water is higher in case of MA functionalized TiO₂ nanoparticles than that of TiO₂. Also, it was found that the adsorption process followed the Langmuir isotherm model and the pseudo second order kinetic model was better fitted to the data for the adsorption. The study reveals that, the MA functionalized TiO₂ nanoparticles can be a useful adsorbent material for the removal of Cu (II) from water.

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