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ADSORPTION OF CHROMIUM (VI) ONTO ZnO: MODELLING, OPTIMIZATION AND ISOTHERM STUDIES

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Abstract: The effects of pH, initial concentration of Cr(VI) and ZnO dosage on Cr(VI) adsorption onto ZnO were studied using the central composite design (CCD). A quadratic model equation was developed for the adsorption of Cr(VI) onto ZnO. The suitability of the model quadratic equation was ascertained using the analysis of variance (ANOVA). Perturbation and 3D response surface plots were used to explain the effects of the three studied parameters on the adsorption process. Adsorption of Cr(VI) onto ZnO is more sensitive to ZnO dosage followed by pH and then initial concentration of Cr(VI). pH and initial concentration of Cr(VI) have overall negative effect on the adsorption process. There is an optimum ZnO dosage, above which the percentage adsorption decreases. The optimization results predicted 45.91 % adsorption of Cr(VI) onto ZnO at a pH of 2.60, initial Cr(VI) concentration of 26.38 mg/L and ZnO dosage of 8.82 g/L. The model predicted maximum adsorption of Cr(VI) onto ZnO (45.91 %) was very close to the experimental value (42.40%). The adsorption equilibrium data was fitted to Langmuir, Freundlich and Dubinin-Radushkevich isotherms. The adsorption equilibrium was best described by the Freundlich isotherm model.
Keywords: Chromium (VI), Adsorption, ZnO, Optimization, Isotherm

INTRODUCTION

Occurrence of heavy metals in surface and underground waters is a serious public health problem in many parts of the world. Heavy metals are not biodegradable and toxic to human beings and animals (Gautam et al., 2014). Most of the heavy metals have an infinite lifetime; thus, they may accumulate in tissues of animals causing chronic health problems. Chromium is a heavy metal used in the production of ferrous and non-ferrous alloys, pigments, leather, catalysts etc (Dhal et al., 2013). Chromium mostly exists in the hexavalent chromium and trivalent chromium states in aqueous medium. Cr(VI) is much more mobile and toxic than Cr(III) (Bachate et al., 2013). The World Health Organization (WHO) limit of Cr(VI) in potable water is 0.05 mg/L (Mohod and Dhote, 2013).

Heavy metals can be removed from contaminated water via adsorption, ion-exchange, filtration, chemical precipitation, coagulation, flocculation, solvent extraction etc (Burakov et al., 2018, Fu and Wang, 2011). Compared to adsorption, some of the water treatment techniques are quite expensive because they require large amount of energy and chemicals. Adsorption has proven to be an attractive and economical method for the removal of various heavy metals from water (Uddin, 2017, Burakov et al., 2018). Indeed, adsorption process is characterized by low energy requirement and flexibility; hence, it can be used for various situations even with small equipment. Several adsorbents such as activated carbons, clays, ashes, crab shells, coconut shells, zeolites, metal oxides, rice husk, etc. have been applied for the removal of various heavy metals from water. However, most of the conventional adsorbents used in water treatment have certain problems such as high cost, slow rate of adsorption, etc (Afroze and Sen, 2018, Burakov et al., 2018).

Recently, there is a lot of research interest in developing metal oxide nanoparticles for water and wastewater treatment via adsorption. Metal oxide nanoparticles such as CeO_2 (Niu et al., 2018), ZnO (Olivera et al., 2018), Fe_3O_4 (Kumari et al., 2015), etc. usually have small particle size, large specific surface area, chemical and thermal stability, surface hydroxyl groups, ion exchange sites, high adsorption and regeneration efficiency for a wide variety of heavy metals in water (Kumari et al., 2015, Olivera et al., 2018, Niu et al., 2018). ZnO nanoparticles with varying shapes (nanoflowers, nanowires, nanorods, nanosheets. etc) can be readily prepared in large quantities using a wide variety of precursors (Lv et al., 2018, Kumar et al., 2013). ZnO nanoparticles are used in catalysis, gas sensing, solar cell technology, photocatalysis, antimicrobial formulations etc (Qi et al., 2017). ZnO nanoparticles are also used as adsorbents due to their favorable surface properties. Thus, ZnO nanoparticles have been applied for the adsorption of heavy metals in water (Sheela et al., 2012, Kumar et al., 2013). Kumar et. al. (2013) reported that the adsorption capacity of ZnO (9.38 mg/g) for Cr(VI) is three times higher than that of SnO_2 (3.09 mg/g) under similar experimental conditions even though the specific surface area of SnO_2 (24.48 m^2/g) is higher than that of ZnO (15.75 m_2/g).

In this paper, the effects of pH, initial concentration of Cr(VI) and adsorbent dosage on Cr(VI) adsorption have been studied using the response surface methodology (RSM) in order to develop model equation for the adsorption process and determine the optimum conditions for the adsorption of Cr(VI) onto ZnO. The adsorption were also studied under the optimum conditions of the process.

MATERIALS AND METHODS

The procedure for the synthesis of ZnO via thermal decomposition of $ZnCO_3$ has been described elsewhere (Alao, 2016, Shamsipur et al., 2013). The specific surface area and the average crystallite size pH at zero point charge of the ZnO are 55.0 m^2/g and 25 ± 5 nm, respectively.

– Adsorption experiments

Stock solution of Cr(VI) with a concentration of 1000 mg/L was prepared by dissolving $K_2Cr_2O_7$ in distilled water. The pH range of the Cr(VI) solutions was adjusted using either HCl or NaOH solution. The adsorption experiments were carried out in the dark in order to prevent photocatalytic reduction of Cr(VI) by ZnO. Adsorption experiments were performed by shaking 100 mL of Cr(VI) solution

of the desired concentration with the required amount of the adsorbent (ZnO). The flasks were continuously shaken for the desired contact time in a shaker. Thereafter, the adsorbent was separated. The concentration of the Cr(VI) in the filtrate was determined using an Atomic Absorption Spectrophotometer (AAS 500, England). Percentage adsorption of Cr(VI) and adsorption capacity (q_t) of ZnO for Cr(VI) were calculated using Eqs. 1 and 2, respectively.

$$\%\text{Adsorption} = \frac{C_o - C_t}{C_o} \times 100\% \quad (1)$$

$$q_t = \frac{(C_o - C_t)V}{V} \times 100\% \quad (2)$$

where C_o is the initial concentration (mg/L) of Cr(VI), C_t is the Cr(VI)concentration (mg/L) after a certain contact time, t, W and V are the weight of adsorbent and volume of the Cr(VI) solution, respectively.

– Design of adsorption experiments

The effects of three process parameters (pH, initial concentration of Cr(VI) and adsorbent dosage) on the adsorption of Cr(VI) onto ZnO were investigated using the central composite design as implemented in the Design Expert software version 6.0.6 (Stat-Ease Inc., Minneapolis, USA). The lowest and highest levels of each independent variable are given in Table 1. For the three variables, 20 experiments presented in Table 2 were designed conducted. In this work, the response is the percentage adsorption of Cr(VI) expressed by Eq. 1.

Table 1: Experimental ranges of the investigated independent variables

Independent variable	Code	Ranges	
		Low	High
pH	A	2	10
Initial concentration of Cr(VI) (mg/L)	B	25	100
Adsorbent dosage (g/L)	C	2	10

RESULTS AND DISCUSSION

– Adsorption of Cr(VI) onto ZnO

Figure 1 shows the effect of contact time on percentage adsorption of Cr(VI) onto ZnO; from where it can be seen that the percentage adsorption of Cr(VI) on ZnO increases with increase in contact time up to 120 minutes.

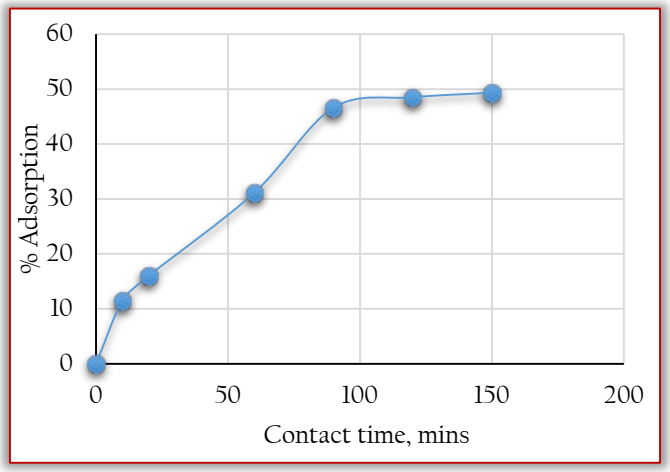


Figure 1: Effect of contact time on percentage adsorption of Cr(VI) onto ZnO

The adsorption is faster at shorter contact times due to the larger surface area of ZnO available at the beginning of the process. As the surface adsorption sites become saturated with increase in contact time, the adsorption is slowed down (Uddin, 2017). Thus, the adsorption-desorption equilibrium was achieved after contact time of 120 minutes. Therefore, all subsequent adsorption experiments aimed at studying the effects of the three process variables presented in Table 1 and adsorption isotherms (*vide infra*) were carried out for120 minutes.

– Modelling of Chromium (VI) Adsorption onto ZnO

The central composite design matrix and experimental responses are presented in Table 2. Based on experimental results obtained, an empirical relationship between the response and independent variables was fitted to second order polynomial using the Design Expert software. The experimental data was fitted to the model quadratic equation 3.

$$\%\text{Adsorption} = 37.52 - 3.01A - 6.12B + 5.24C - 1.01A^2 - 3.34B^2 - 6.40C^2 + 1.98AB - 0.20AC + 2.77BC \quad (3)$$

Table 2: Central composite design matrix and experimental values of the response for Cr(VI) adsorption using ZnO

Run	Independent variables			Response
	A	B	C	% Adsorption
1	1.00	25.00	10.00	45.80
2	5.50	62.50	6.00	37.50
3	5.50	62.50	12.73	31.50
4	1.00	100.00	2.00	20.30
5	5.50	62.50	6.00	38.10
6	5.50	62.50	6.00	37.60
7	5.50	62.50	0.73	10.50
8	10.00	100.00	2.00	15.40
9	13.07	62.50	6.00	20.40
10	5.50	125.57	6.00	32.30
11	5.50	62.50	6.00	35.70
12	10.00	25.00	2.00	19.30
13	5.50	62.50	6.00	38.60
14	10.00	25.00	10.00	21.90
15	10.00	100.00	10.00	19.80
16	2.07	62.50	6.00	38.90
17	1.00	100.00	10.00	33.20
18	5.50	62.50	6.00	37.10
19	5.50	0.57	6.00	40.20
20	1.00	25.00	2.00	31.20

The suitability of the model quadratic equation was ascertained using the analysis of variance (ANOVA). The results of the ANOVA for the proposed model equation are presented in Table 3. Model parameters are significant if the probability value (p-value) is less than 0.05 at 95% confidence level (Montgomery et al., 2009). Thus, the model equation is significant. The insignificance of lack of fit with p–value of 0.192 showed that the developed model is valid. The good fitting of the experimental data to the model equation was also supported by the high values of the regression coefficients ($R^2 = 0.972$; $R^2_{adj} = 0.948$). The closeness in the values of R^2 and R^2_{adj} indicates good predictability of the model. The value of adequate precision ratio of 22.197 indicates an appropriate signal to noise ratio because the minimum desired ratio is 4.0; this indicates that the quadratic model can be used to find the optimum conditions of the adsorption process.

The plot of actual vs. predicted values presented in Figure 2a shows that the model equation adequately describes the experimental

ranges of the process variables investigated. As shown in Figure 2b, the residuals are scattered randomly in the range of -3.0 to +3; this reveals good fitting of the quadratic model equation with the experimental data (Sakkas et al., 2010, Montgomery et al., 2009).

Table 3: Results of ANOVA for Cr(VI) adsorption onto ZnO

Source	Sum of Squares	Degree of Freedom	Mean Squares	F - Value	p - value
Model	1799.48	9	199.94	39.15	<0.0001
A	123.61	1	123.61	24.20	0.0006
B	510.69	1	510.69	100.00	<0.0001
C	374.52	1	374.52	73.34	<0.0001
A^2	14.70	1	14.70	2.88	0.1206
B^2	161.09	1	161.09	31.54	0.0002
C^2	590.58	1	590.58	115.65	<0.0001
AB	31.20	1	31.20	6.11	0.0330
AC	0.32	1	0.32	0.063	0.8074
BC	61.60	1	61.60	12.06	0.0060
Lack of Fit	46.11	5	9.22	9.31	0.192

$R^2 = 0.972$; R^2 adj = 0.948; Adq. Prec. ratio = 22.197

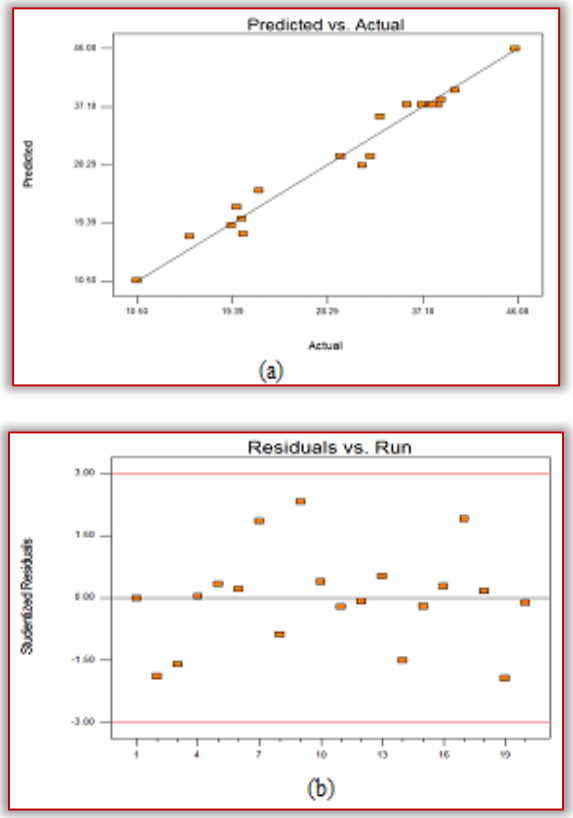


Figure 2: Plots of (a) the predicted against the actual experimental values and (b) the Studentized residuals against predicted values for Cr(VI) adsorption using ZnO

Perturbation is the deviation of the response (percentage adsorption) from the reference points (middle values of the independent variables). Herein, the reference points are: pH of 5, Cr(VI) concentration of 70.0 mg/l and adsorbent dosage of 5.0 g/l. The perturbation plots displayed in Figure 3 show the effect of each of the three studied independent variables on the response. Based on the slopes and curvature of the plots, it can be concluded that the percentage adsorption is more sensitive to adsorbent dosage (C) followed by pH (A) and then initial concentration of (B). The plots show that pH and initial concentration of Cr(VI) have overall negative effect on the adsorption process. Hence, highest adsorption is achieved at the lowest pH and the lowest initial concentration of Cr(VI). On the other hand, the percentage adsorption increases with increase in the adsorbent dosage. However, there is an optimum adsorbent dosage, above which the percentage adsorption decreases. The negative coefficients of quadratic terms of the model equation (3) account for this observation.

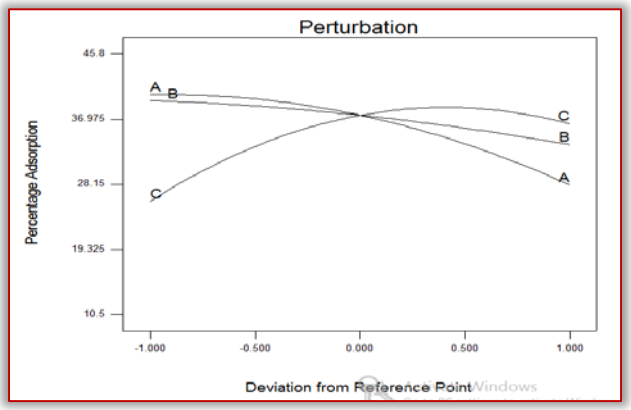
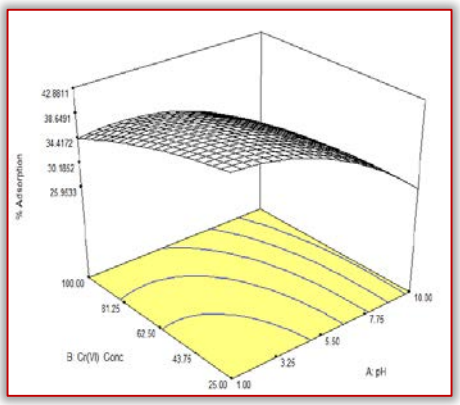
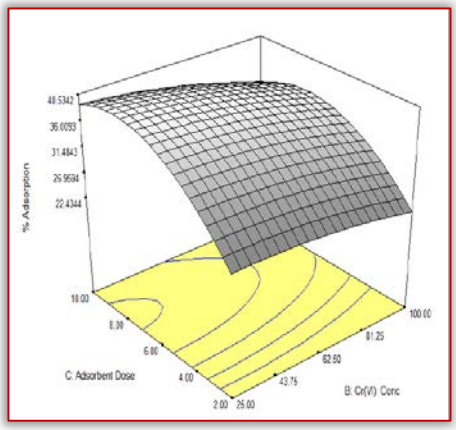


Figure 3: Perturbation plots for Cr(VI) adsorption onto ZnO



(a)



(b)

Figure 4: 3D response surface plots for Cr(VI) adsorption onto ZnO showing the simultaneous effects of (a) pH and initial concentration of Cr(VI), and (b) adsorbent dosage and initial concentration of Cr(VI)

So far, each of the three independent variables has been studied individually. As shown in Table 3, the interactions between pH and initial concentration of Cr(VI) as well as between initial concentration of Cr(VI) and adsorbent dosage are significant with p-values of 0.033 and 0.006, respectively. Whereas, the interactions between pH and adsorbent dosage are non-significant with p-

value of 0.8074. The interactions between the independent variables can be explained using the 3D response surface plots presented in Figures 4 and 5.

Figure 4a depicts the effects of pH and initial concentration of Cr(VI) on its adsorption. Cr(VI) adsorption onto ZnO decreases as the initial Cr(VI) concentration is increased. The decrease in Cr(VI) adsorption can be attributed to the fact that adsorbents have a limited number of active binding sites and at a certain concentration of an adsorbate the active sites become saturated (Khosravi et al., 2018, Bhatti et al., 2017). At low initial concentrations of Cr(VI), the available adsorption sites of ZnO were easily occupied by chromium ions resulting in higher percentage adsorption. However, as the initial concentration of Cr(VI) is increased, most of the available adsorption sites became occupied, leading to a decrease in the percentage adsorption (Mondal et al., 2018).

Depending on solution pH, Cr(VI) exists in various forms. The dominant specie is chromic acid (H_2CrO_4) at pH lower than 1.0 and $HCrO_4^-$ at pH between 1.0 and 6.5. At pH higher than 6.5, only CrO_4^{2-} is stable (Igberase et al., 2017). The pH of point zero charge of ZnO is around 9 (Omar et al., 2014) depending on the method of production. At a pH below the pH of point zero charge, the surface of ZnO is positively charged and above pH at point zero charge, the surface of the ZnO is negatively charged. The observed high adsorption of Cr(VI) at low pH can be attributed to availability of Cr(VI) in anionic forms ($HCrO_4^-$ and $Cr_2O_7^{2-}$) and the net positive charge of ZnO (Igberase et al., 2017). At low pH, the surface of ZnO is also protonated (Ballerini et al., 2007). This facilitates adsorption of Cr(VI) onto ZnO. As the pH is increased, the degree of protonation of the surface decreases leading to low adsorption of Cr(VI). Furthermore, at high pH, there is competition between OH^- and CrO_4^{2-} ions (Pradhan et al., 1999). The reduction in net positive charge of ZnO at high pH weakens the electrostatic forces between the ZnO and Cr(VI) and this leads to lower percentage adsorption.

Figure 4b shows that the number of surface sites for adsorption of Cr(VI) increases up to about 8 g/l. Thereafter, further increase in the adsorbent dosage lead to slight decrease in Cr(VI) adsorption. This observation can be attributed to overlap of surface active sites due to saturation of adsorbent particles and decrease in the charge of the dense outer layer of the cells, thereby blocking the active sites of ZnO from Cr(VI) (Igberase et al., 2017, Bhatti et al., 2017).

– Optimization of hexavalent chromium removal onto ZnO

The optimization was targeted at maximizing the percentage adsorption by setting the process variables (pH, initial concentration of Cr(VI) and adsorbent dosage) to be within the studied ranges presented in Table 1, whereas and the percentage adsorption was set to be maximum. The optimization results predicted 45.91 % adsorption of Cr(VI) onto ZnO at a pH of 2.60, initial concentration of Cr(VI) of 26.38 mg/L and adsorbent dosage of 8.82 g/L. In order to verify the optimization results, an experiment was performed under predicted optimum conditions. The experimental value obtained under the predicted optimum conditions was 42.40% which is very close to the predicted value of 45.91 %.

– Adsorption isotherms

Adsorption isotherm explains the interaction between the adsorbate and the adsorbent. In this work, Langmuir, Freundlich and Dubinin-Radushkevich isotherms were applied to investigate adsorption of Cr(VI) onto ZnO. The linearized forms of the Langmuir, Freundlich and Dubinin-Radushkevich isotherms are given by equations 4, 5 and 6, respectively (Kataria and Garg, 2018, Fida et al., 2015).

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

$$\ln q_e = \ln Q_S - K_D \varepsilon^2 \quad (6)$$

where C_e is the equilibrium concentration of the Cr(VI) ions in solution, q_{max} is the Langmuir maximum adsorption capacity of mk, K_L is the Langmuir constant that is related to the energy of adsorption, respectively. K_F and n are the Freundlich adsorption isotherm constants which determine the extent of the adsorption process, and the degree of nonlinearity between solution concentration and adsorption, respectively. Q_s is the Dubinin-Radushkevich maximum adsorption capacity, K_D is the activity coefficient which indicates the mean adsorption energy (E). ε is the Polanyi potential which is calculated using Eq. 7.

$$\varepsilon = RT \ln(1 + 1/Ce) \quad (7)$$

The mean adsorption energy (E) is calculated using Eq. 8.

$$E = 1/\sqrt{2KD} \quad (8)$$

The linearized plots of the Langmuir, Freundlich and Dubinin-Radushkevich isotherms are shown in Figures 5, 6 and 7, respectively. The slopes and intercepts of the plots were used to derive isotherm parameters and correlation coefficients (R^2) that are reported in Table 4. Analysis of the values of regression coefficients (R^2) indicates that the Cr(VI) adsorption onto ZnO obeys Freundlich isotherm model due to highest R^2 value of 0.981. This indicates that the adsorption of Cr(VI) onto ZnO takes place on the heterogeneous surface sites of ZnO (Agarwal et al., 2006). Other researchers have also reported that adsorption of Cr(VI) is best described by the Freundlich isotherm model (Sarin and Pant, 2006, Agarwal et al., 2006). Moreover, the value of 1/n in the Freundlich model is 0.531, which further signifies favourability of the adsorption of Cr(VI) onto ZnO (Kataria and Garg, 2018).

Table 4 shows that the correlation coefficient (R^2) of the Langmuir isotherm model is lower than those of Freundlich and Dubinin-Radushkevich isotherm, indicating that Cr(VI) adsorption onto the developed adsorbents did not occur on homogeneous surface by monolayer adsorption. Based on the results obtained for Dubinin-Radushkevich isotherm, the mean free energy of the adsorption process is 5.47 kJ/mol as shown in Table 4.

Therefore, removal of Cr(VI) by ZnO is physical adsorption. This is because physical adsorption is characterized by a mean free energy in the range of 1 kJ/mol to 16 kJ/mol, while chemisorption prevails for mean free energy greater than 16 kJ/mol (Fida et al., 2015, Kataria and Garg, 2018).

Table: 4: Isotherm constants for Cr(VI) adsorption onto ZnO

Isotherm	Parameters	
Langmuir	q_{max} (mg/g)	9.49
	R^2	0.725
Frendliuch	K_F	0.119
	1/n	0.531
	R^2	0.981
Dubinin-Radushkevich	E (kJ/mol)	5.47
	Q_D (mg/g)	0.9011
	R^2	0.901

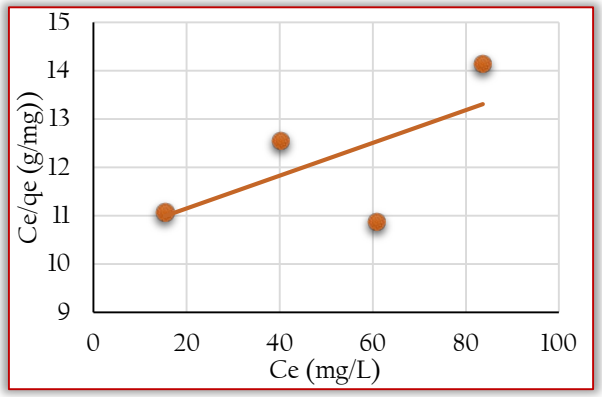


Figure 5: Langmuir isotherm plot for adsorption of Cr(VI) onto ZnO

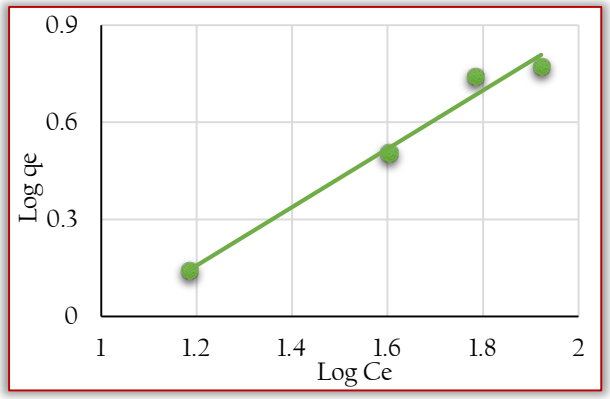


Figure 6: Freundlich isotherm plot for adsorption of Cr(VI) onto ZnO

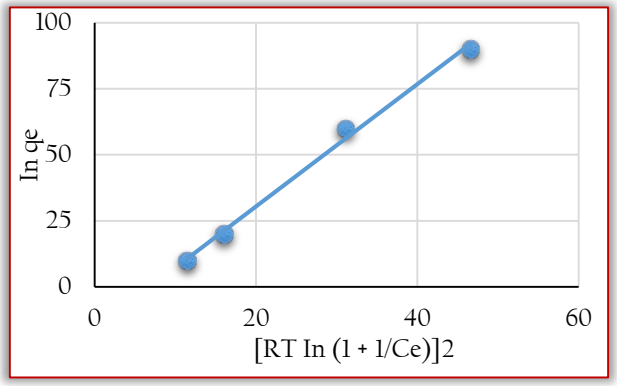


Figure 7: Dubinin–Radushkevich isotherm plot for adsorption of Cr(VI) onto ZnO

CONCLUSIONS

The adsorption-desorption equilibrium of Cr(VI) onto ZnO was achieved after a contact time of 120 minutes. A quadratic model equation was developed for the adsorption of Cr(VI) onto ZnO. Adsorption of Cr(VI) onto ZnO is more sensitive to adsorbent dosage followed by pH and then initial concentration of of Cr(VI). pH and initial concentration of Cr(VI) have overall negative effect on the adsorption process. There is an optimum adsorbent dosage, above which the percentage adsorption decreases. The optimization results predicted 45.91 % adsorption of Cr(VI) onto ZnO at a pH of 2.60, initial concentration of Cr(VI) of 26.38 mg/L and adsorbent dosage of 8.82 g/L. The model predicted maximum adsorption of Cr(VI) onto ZnO (45.91 %) was very close to the experimental value (42.40%). The adsorption equilibrium was best described by the Freundlich isotherm model. Removal of Cr(VI) by ZnO is physical adsorption mean free energy of 5.47 kJ/mol.

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