Adsorptive removal of Cr (VI) from aqueous solution using laboratory prepared ZnO nanoparticles

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Abstract: Nano sized zinc oxide (ZnO) been successfully prepared in laboratory by precipitation technique. As prepared ZnO materials were characterized by XRD and SEM analyses. The XRD pattern showed the crystallinity of the material and average crystallite size was found to be 16.61 nm. The SEM images of ZnO nanoparticle revealed that it was flakes like structure having smooth texture. Batch adsorption experiments were performed to investigate the percentage removal of Cr (VI) from aqueous solution. The effects of Cr (VI) concentration, pH of solution, adsorbent dose and contact time variations were studied in order to have adsorptive efficiency of as prepared ZnO nanoparticles. The optimum contact time for maximum adsorption was found to be 90 minutes. The optimum pH was found to be 2.0 at an initial concentration of 20 mg/L. Similarly, the optimum dose of ZnO for the adsorption of Cr (VI) was found to be 0.4 g. The adsorption properties of ZnO were then evaluated by using Langmuir, Freundlich and Temkin isotherm models. The maximum adsorption capacity (Q_m) was found to be 3.43 mg/g which is in good agreement with literature value. The correlation value showed that Langmuir isotherm model was found to be more favorable than Freundlich and Temkin adsorption isotherm model, indicating the presence of homogeneous equivalent active sites in ZnO with monolayer adsorption.

Key words: ZnO Nanoparticles; Cr (VI); Langmuir adsorption Isotherm.

Introduction

Chromium is an element that occurs naturally in rocks, plants, soils and volcanic dust. It exists in two stable oxidation states: Cr (III) and Cr (VI). It has beneficial as well as detrimental properties. The Cr (III) found naturally in vegetables, fruits, meat, yeasts and grains which is biologically essential trace element for human being. In contrast, Cr (VI) is hazardous which is carcinogenic[1,2,3] and mutagenic[4] to humans and animals. The Cr(III) is insoluble in ambient condition while the Cr (VI) compounds are highly soluble and mobile in water. Hence, Cr(VI) can easily enters into the living cells and shows toxic behavior. The most soluble, mobile and toxic forms of Cr (VI) in soils are chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$)[5] which are generally released from industries like leather tanning, metal plating, mining operations, manufacture of paints, alloys, batteries, explosive, ceramics and photography, pesticides and refining of ores.

The tolerance limit for Cr (VI) for discharge into land surface water is 0.1mg/L and in potable water is 0.05 mg/L[6]. Excess release of Cr (VI), makes environment pollution hence removal of Cr (VI) from waste water is of particular concern.

Several methods have been developed to remove chromium from the aqueous solution like solvent extraction, ion exchange, evaporation, filtration, chemical precipitation, membrane separation, reverse osmosis and adsorption[7].

However, these methods can proved to be too costly, impractical to apply over large scales, or unable to remove trace quantities of the metals. To overcome these drawbacks, adsorption is an alternative process to remove heavy metal ions from aqueous solution.

Adsorption is a well-established and powerful technique for the removal of chromium from waste water because it is a simple, cost effective, more readily available, having high efficiency, easy handling and environment friendly[8]. So far, most attention has been devoted to the study of different types of low cost and high removal efficiency materials to remove the pollutants from aqueous solution. The removal of Cr (VI) has been studied using sugarcane bagasse[9], coconut waste[10], banana peel[11], rice husk[12],

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hazelnut shell[13] etc. Up to date, different materials such as activated carbon[14], silica-gel[15], zeolites[16], and resins[17] have been used to adsorb contaminant from waste water.

In these days, nanoparticles become so popular to treat various organic and inorganic water contaminants, for the reduction or treatment of industrial wastes and non-point sources pollution control that involves controlling water pollution problems[18]. Different types of metals, metal oxides and alloy nanoparticles are available[19] that has been used as adsorbents, due to their large surface areas and small size[20]. Large number of scientists and researchers are working on metal oxides such as Titanium dioxide (TiO_2), Zinc Oxide (ZnO) and Iron Oxide (Fe_3O_4). Among them the attention has also given to Zinc Oxide (ZnO) materials which possesses variety of nanostructures for plenty of applications[21]. Although ZnO occurs naturally as the mineral zincite, most zinc oxide has been produced synthetically[22]. Crystralline ZnO has wurtzite crystal structure in ambient conditions.

In the present research work, ZnO was prepared by precipitation technique and used as an adsorbent for the removal of Cr (VI) from aqueous solution. The shape, size and structure of ZnO were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) analysis.

Materials and methods

Instruments

The X-Ray Diffractometer (D2-Phaser, Bruker, Germany) was used to study the phase state of as prepared ZnO material. It was operated at an accelerating voltage of 40 KV and current 40 mA with Cu-Kα radiation (λ=1.5418A°) in the diffraction angle of 10 to 50 degrees. Likewise, the surface morphology of prepared ZnO material was studied by Field Emission Scanning Electron Microscope (FE-SEM), Hitachi S-7400, Japan. The spectrophotometric analysis was carried out by using 2306 visible Spectrophotometer, (AB1211010, Electronics India) and with the help of deluxe pH meter (Max Electronics, India) pH of solution was measured.

Reagents

Analar grade (AR) reagents such as potassium dichromate, 0.25% 1,5-diphenyl carbazide (DPC) in acetone solution, HCl, H_2SO_4, HNO_3, NaOH and methylene blue were procured from Merck Company India.

Preparation of adsorbent:

The (ZnO) nano particles were prepared by precipitation method. The 5.95g of zinc nitrate was dissolved in 50 mL distilled water. An appropriate volume of ammonia solution was added into the solution until the pH reached to 7.0. The products were collected by centrifugation after thorough washing by distilled water. Then it was finally dried at 60 °C in an oven.

Batch adsorption study

The batch adsorption study was used to absorb pollutant from liquid solution. The samples were transferred into the adsorption bottle and a definite amount of adsorbent was added to the sample. The pH of the sample solution was adjusted by dilute HCl solution and NaOH solution. The sample solution was shaken for definite period of time in a shaker to attain adsorption equilibrium. The adsorption of adsorbate onto adsorbents may be affected by different parameters such as contact time, pH, initial concentration and amount of adsorbent used. The amount of adsorbate or loading was be calculated by following equation:

$$q = \frac{C_i - C_e}{W} \times V \ldots\ldots\ldots\ldots\ldots (1)$$

where, C_i and C_e are the initial and final or equilibrium concentrations of the adsorbate in mg/L respectively, V is the volume of solution taken in liter and W is weight of adsorbent in gram.

The removal percentage is defined as the ratio of decrease in adsorbate (Cr) ion concentration before and after adsorption to the initial concentration of metal in aqueous solution. Then the percentage removal is determined by the following equation:

$$Removal\ (\%) = \frac{C_i - C_e}{C_i}\ 100\% \ldots\ldots (2)$$

Results and Discussion

Characterization of adsorbent

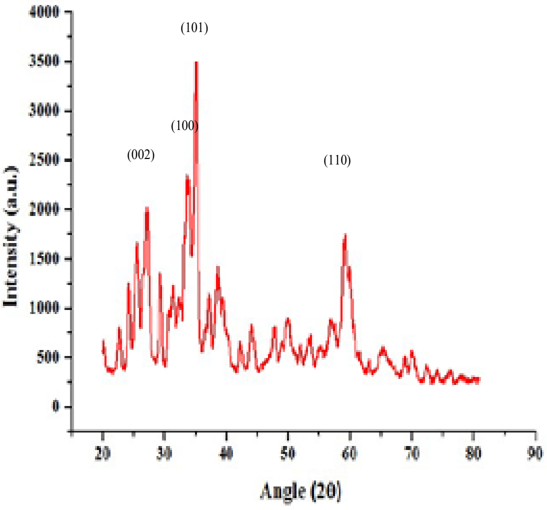

Figure 1: XRD pattern of ZnO.

Fig. 1 shows the XRD pattern of as prepared ZnO material. In the pattern, sharp intense peaks are clearly seen.

The major peaks are observed at 34° (002), 35° (101) and 59° (110) of 2θ degrees. According to JCPDS card (No-75-0576), these peaks were assigned to ZnO. This revealed that the resultant materials were of pure zinc oxide. There is no peak for impurities. The strong and sharp diffraction peaks are the indication of good crystallinity.

Similarly, the average crystallite size of the material has also been calculated using Scherer's equation (3).

$$D = \frac{K\lambda}{\beta \cos\theta} \dots\dots\dots\dots\dots (3)$$

Where, K is a constant which is equal to 0.94, λ is the wavelength of X-ray (0.154 nm), β is the full width at half-maximum height, θ is the diffraction angle and D is the particle size. Thus, the average crystallite size of zinc oxide material was found to be 16.61 nm. Hence, one can say that as prepared ZnO materials are found to be in nano form.

Scanning Electron Microscopy (SEM)

Surface morphology was studied by Scanning Electron Microscopy (SEM). The SEM image of as prepared ZnO nanoparticle is shown in Fig. 2. The surface was found to be smooth. The pores are not observed on the surface of ZnO nanoparticles. It looks like flakes. Such a smooth texture having flakes like structure was also reported[23].

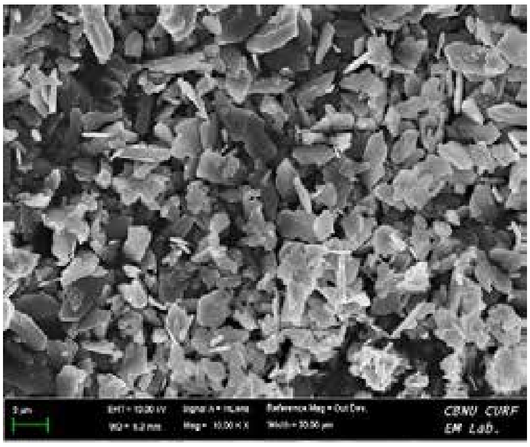

Figure 2: SEM images of ZnO.

Adsorption study on ZnO adsorbent

Prior to adsorption studies, different operational parameters such as pH, adsorbent dose, contact time, initial Cr (VI) concentration were investigated and results are presented below.

Effect of pH

The pH of solution is the most important parameter that affect the adsorption process of heavy metals in water samples. To evaluate the influence of pH on the adsorption process, first experiment was carried out at different initial pH values of 1, 2, 3, 4, 5, 6, 7 and 8 by keeping other parameters constant. Here 0.3 g of adsorbent (ZnO) dose was taken. The initial concentration of the adsorbant (Cr) 20 mg/L was maintained. The agitation speed 180 rpm for 2 hours was maintained. The adsorption of Cr (VI) on ZnO at different pH are shown in Fig. 3.

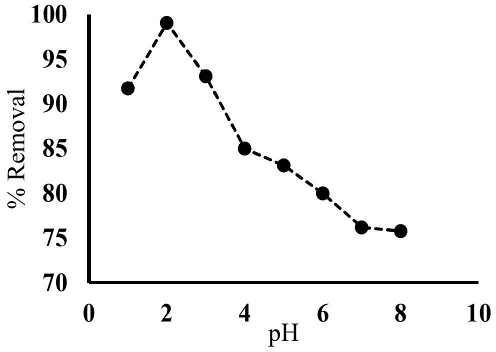

Figure 3: Effect of pH on the adsorption of Cr (VI) onto ZnO.

In Fig. 3, the adsorption of Cr(VI) on ZnO was obvious in all pH range. However, in lower pH range i.e. at pH 2, a clear peak could be seen which indicates the maximum adsorption of Cr(VI). The 99% of Cr(VI) was found to be removed. Then after pH 2 it was found to be decreasing continuously upto 75%. Hence, pH 2 was found to be optimum pH for Cr (VI) adsorption.

Here, two mechanisms are elucidated, for the adsorption of Cr (VI) from ZnO adsorbent: one may be electrostatic attraction mechanism and other may be ion exchange mechanism as described in literature[24]. In acidic medium, Cr (VI) may exist in the form of oxyanions such as $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}. Similarly, at pH ~ 2, the surface of ZnO adsorbent remains protonated to a higher extent suh as Zn^{2+}, $Zn\,(OH)^+$ [25]. As a consequence, a strong electrostatic force of attraction may exist between oxyanions of Cr (VI) and positively charged surface of the adsorbent i.e. (Zn^{2+}, $Zn\,(OH)^+$). Then removal of Cr (VI) from aqueous solution was obtained. Hence, adsorption of Cr (VI) can be illustrated as electrostatic mechanism [24,25].

On the other hand, at pH >4 ($HCrO_4^-$) species may shift to two different anionic forms $(CrO_4)^-$ and $(Cr_2O_7)^-$. At pH>4, there is a possibility of ion exchange between anions $(CrO_4)^-$ and $(OH)^-$ in reaction system that will prevent Cr ions to approach to the binding sites of the adsorbent, as a result removal of Cr ions get reduced. It may be due to negatively charged adsorbent surface thereby causing hindrance in the adsorption of oxyanions of Cr (VI) or small repulsion may occur between them. Hence, the adsorption of Cr (VI) in these pH range can said to be anion exchange mechanism[24,26]. The details of mechanisms are described in section 1 and 2.

Electrostatic attraction mechanism

Under acidic conditions, ZnO reacts with protons on the basis of the reactivity of the bulk material. Then the series of reactions occur as in reaction 4-10 [27,26]. There is a predominance of Zn^{2+}. It was also suggested that, the surface of ZnO may get hydrolyzed to form a layer of hydroxide i.e. $Zn\,(OH)^+$. Such reactions are also reported in literature[25,26].

$$ZnO_{(s)} + 2H^+_{(aq)} \longleftrightarrow Zn^{2+}_{(aq)} + H_2O_{(l)} \;\ldots\ldots(4)$$

$$ZnO_{(s)} + H^+_{(aq)} \longleftrightarrow Zn\,(OH)^+_{(aq)} \;\ldots\ldots\ldots\ldots(5)$$

$$Zn\,(OH)_{2\,(s)} \longleftrightarrow Zn\,(OH)_{2\,(aq)} \;\ldots\ldots\ldots\ldots(6)$$

$$Zn\,(OH)_{2\,(s)} \longleftrightarrow Zn^{2+}_{(aq)} + 2OH^-_{(aq)} \;\ldots\ldots\ldots\ldots\ldots(7)$$

$$Zn\,(OH)_{2\,(s)} \longleftrightarrow Zn\,(OH)^+_{(aq)} + OH^-_{(aq)} \;\ldots\ldots\ldots\;(8)$$

In such condition, the adsorption of Cr may be due to electrostatic attraction. Here $HCrO_4^-$, $Cr_2O_7^{2-,}$ CrO_4^{2-} get attracted on positive surface of ZnO matrix i.e. Zn^{2+} and $Zn(OH)^+$.

Ion exchange mechanism

Under alkaline conditions, ZnO reacts with hydroxide ions on the basis of the reactivity of the bulk material. In pH>4, following reactions (9-10) are expected[27]. In this condition ZnO surface remains negatively charged i.e. $Zn\,(OH)_3^-$ and $Zn\,(OH)_4^{2-}$.

$$ZnO_{(s)} + OH^-_{(aq)} + H_2O_{(l)} \longleftrightarrow Zn\,(OH)_3^-{}_{(aq)} \;\ldots..\;(9)$$

$$ZnO_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longleftrightarrow Zn\,(OH)_4^{2-}{}_{(aq)} \;\ldots\ldots\ldots(10)$$

In such condition, the adsorption of Cr may be due to anion exchange mechanism i.e. exchange of OH^- and $Cr_2O_7^{2-,}$ $CrO_4^{2-.}$

Effect of adsorbent dose

To evaluate the effect of adsorbent dose on the adsorption efficiency of Cr (VI) by ZnO, the adsorbent amounts were varied from 0.1-0.8 g. With reference to result obtained from graph (Fig. 3), pH was maintained to 2. In this study, 20 mg/L initial concentration of Cr (VI) was taken. The agitation speed 180 rpm and contact time 2 hours were maintained. Thus obtained % removal results were plotted as a function of adsorbent dose which is shown in Fig. 4.

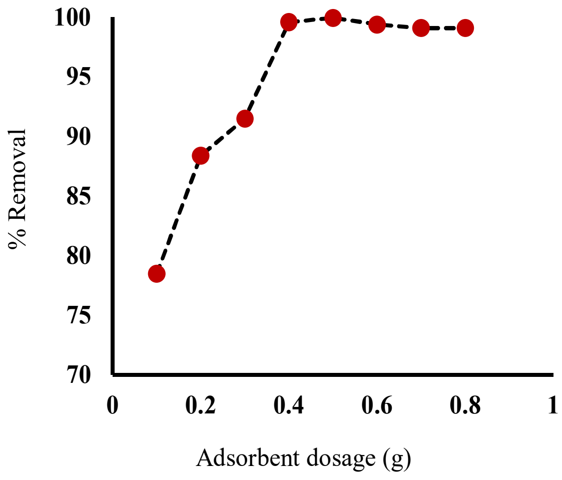

Figure 4: Effect of adsorbent dose for adsorption of Cr (VI) onto ZnO.

In Fig. 4, it was observed that the adsorption of Cr (VI) increases with increasing the adsorbent dose and the adsorption became almost constant after adsorbent dose 0.4 g. The initial increment in adsorption capacity may be due to increase in adsorbent dose and thus more surface binding sites were available for Cr (VI) adsorption or greater number of exchangeable sites available for Cr (VI) ions[28]. Therefore, the optimum adsorption efficiency for Cr (VI) was obtained at an adsorbent dose of 0.4 g.

Effect of contact time

To evaluate the effect of contact time on batch adsorption another experiment was carried out. Here, pH 2 was maintained and adsorbent dose 0.4 g . The initial Cr (VI) concentration was 20 mg/L. Then the solution was agitated at 180 rpm and contact time was varied from 1 to 150 minutes. Then the % removal of Cr were obtained at different time. Thus, obtained results were plotted as a function of contact time in minute which is shown in Fig. 5.

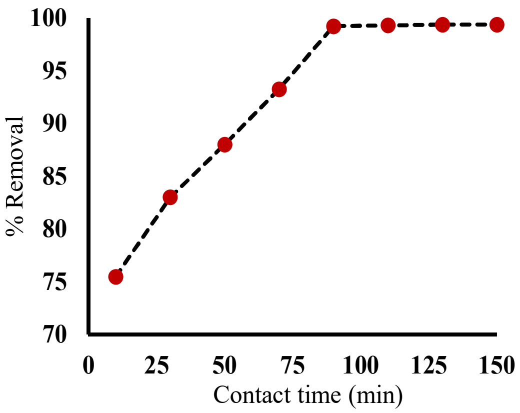

Figure 5: Effect of contact time for the adsorption of Cr (VI) onto ZnO.

In Fig. 5, it was observed that the adsorption rate was rapid till it attained equilibrium at a particular time after which there was no increase in adsorption. The plateau could be seen after 90 minutes. The equilibrium time was found to be 90 minutes. Thus the rapid adsorption is due to the presence of large number of adsorption sites and the plateau of graph is due to saturation in active adsorption sites in the adsorbent[29]. Though 90 minutes was found to be sufficient, the further work has been carried out maintaining 2 hours to attain equilibrium.

Effect of initial concentration of Cr (VI) ion

The effect of Cr (VI) concentration is shown in Fig. 6. The initial concentration of Cr (VI) ions were varied from 10-70 mg/L and keeping other parameters constant pH 2, dose 0.4 g, agitation speed 180 rpm and time 2 hours.

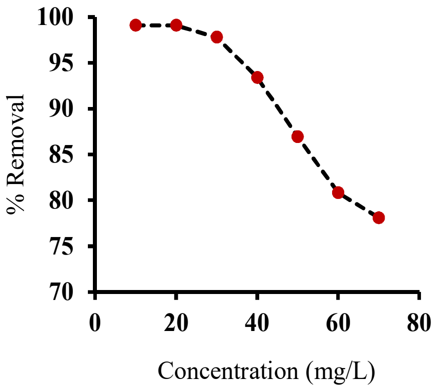

Figure 6: Effect of initial concentration for Cr (VI) onto ZnO.

In Fig. 6, it was found that the removal of Cr (VI) ions decreased as the concentration of Cr (VI) ions was increased. At lower concentration, the ratio of initial number of moles of metal ions to the available area is larger and subsequently the fractional adsorption becomes independent of its minimum concentration[30]. However, at higher concentration most of the adsorption sites present in the ZnO particle could be occupied by Cr ions and later on no free sites are available to adsorb. It clearly showed that a decrease in percentage removal of the Cr ions corresponding to an increase of initial Cr ion concentration. Therefore, the maximum adsorption of Cr (VI) ions was observed upto 20 mg/L initial concentration of Cr (VI).

Adsorption Isotherm Studies

Chromium adsorption isotherm studies were carried out to determine the of adsorption capacity of ZnO using adsorbent doses of 0.4 g at initial concentration of 20 mg/L, time of 2 hour pH of 2 and agitation speed of 180 rpm.

Here, three different isotherm models Langmuir, Freundlich and Temkin have been tested. The linearized Langmuir, Freundlich and Temkin plots are given in Fig. 7, 8 and 9. The slopes and intercepts of linearized Langmuir, Freundlich and Temkin plots were used to calculate the adsorption constants which were tabulated in Table 1, 2 & 3 respectively.

Langmuir isotherm model

It is widely applied model to describe experimental adsorption data based on the assumption that maximum adsorption corresponding to saturated monolayer of adsorbate molecule on adsorbent surface with a constant energy and no further adsorption.

The Langmuir adsorption equation can be represented as;

$Q_e = Q_m b C_e / 1 + bC_e$ ………….(11)

linear form of Langmuir expression is expressed as;

$1/Q_e = 1/ Q_m b C_e + 1 / Q_m$…………(12)

Where, Q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent; Ce (mg/L) is the equilibrium concentration of the adsorbate in solution after adsorption;

Qm (mg/g) is the maximum adsorption capacity corresponding to monolayer coverage of adsorbents and b (L/ mg) is the adsorption equilibrium constant. Here, the value of Q_m and b are presented in Table 1 which was calculated from the slope and intercept of the C_e/Q_e versus C_e plot.

Fig. 7 shows the Langmuir adsorption isotherm, a straight-line graph was obtained having a slope ($1/q_m$) of 0.2914 and intercept ($1/bq_m$) of 0.2637. Then Langmuir constants q_m and b were calculated. The maximum (q_m) of ZnO was found to be 3.43 mg/g and adsorption constant value (b) was found to be 1.1 mg/L. The correlation coefficient (R^2) obtained from the Langmuir equation was 0.988. The dimensionless separation factor (K_L) was measured using eq^n^ (13)

$K_L = 1/1 + bC_i$………………(13)

Where, C_i is the initial concentration of the adsorbate (mg/L) and K_L is the Langmuir equilibrium parameter and was found to be 0.04. This value lies between 0 and 1 which indicates the favorability of adsorption. Langmuir adsorption model indicated that there is homogeneous equivalent active sites with monolayer adsorption.

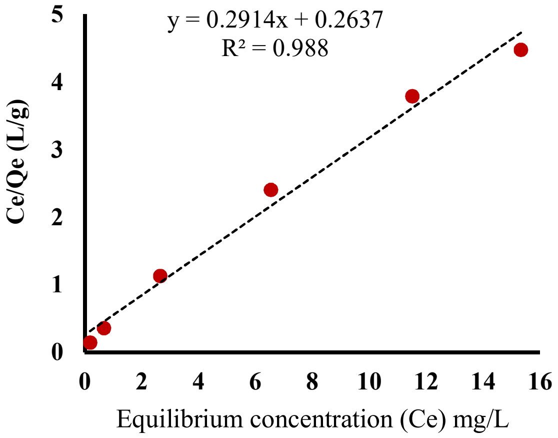

Figure 7: Langmuir adsorption isotherms for chromium adsorption.

All the results were also tabulated in Table 1.

Table 1: Langmuir constants for the plot.

Langmuir isotherm Parameters	
Langmuir constant b (L/mg)	1.1
Maximum loading Q_m (mg/g)	3.43
Correlation coefficient (R^2)	0.988
Separation factor (K_L)	0.04

Freundlich isotherm model

Freundlich isotherm is shown in Fig. 8. The adsorption capacity (K_F), adsorption intensity (n) were obtained using equation [$\log Qe = \log K_F + 1/n \log Ce$]. The K_F was calculated from intercept, whereas n was calculated from slope. The results are presented in Table 2. Here correlation coefficient value (R^2) was found to be 0.985 which was lower than correlation coefficient value (R^2) obtained from Langmuir model. Hence, Freundlich adsorption model is not favorable.

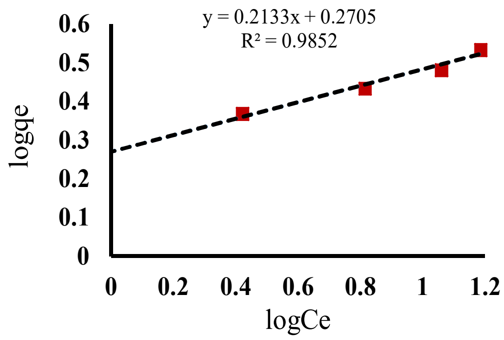

Figure 8: Freundlich adsorption isotherm for Cr (VI) adsorption.

Table 2: Freundlich constants for the adsorption of Cr (VI) by ZnO.

Freundlich isotherm parameters	
Adsorption capacity (K_F) (mg/g)	1.86
Adsorption intensity (n)	4.69
Correlation coefficient (R^2)	0.985

Temkin isotherm model

Temkin model gives the information of the constant K_T related to the Temkin isotherm equilibrium binding constant (L/g) which corresponds to maximum binding energy and B related to heat of sorption (J/mol). Temkin isotherm model where equilibrium loading qe was plotted against lnCe using Tempkin equation [$Qe = B\ln K_T + B\ln Ce$]. From the Temkin model, heat of sorption (B) and maximum binding energy (K_T) were calculated which are tabulated in Table 3. Here, correlation coefficient (R^2) value was found to be lower than langmuir adsorption model. Hence, this model is also not fitted.

Table 3: Temkin constants for the adsorption of Cr VI) by ZnO.

Temkin isotherm parameters	
Equilibrium binding energy (K_T) (L/g)	78.41
Heat of sorption (B) (J/mol)	0.45
Correlation coefficient (R^2)	0.979

Comparative study for adsorption capacities

The maximum loading (Q_m) of ZnO for Cr (VI) was compared with earlier investigation carried out in different adsorbents which are tabulated in Table 4.

Table 4: Comparison of adsorption capacities of ZnO with other adsorbents.

Adsorbents	**Adsorption loading Q_m (mg/g)**	**References**
ZnO	7.7	31
Coconut tree sawdust	3.46	32
Raw rice bran	0.15	33
Jatropha oil cake	0.82	34
Carbon nanotubes	9.0	35
Wheat bran	4.53	36
Modified banana peel	6.17	37
Nano sized Cellulose fibres	3.76	38
Fe_3O_4	3.55	39
ZnO	3.43	Present work

The results revealed that the adsorption capacity of prepared ZnO was 3.43 mg/g which was found to be in agreement with coconut saw dust, wheat bran, nanosized cellulose fibres and Fe_3O_4. However, it was less than carbon nanotubes, modified banana peel and ZnO used in literature review[31]. It could be due to the difference in amount of adsorbent dose and initial concentration taken. The 4 g of adsorbent dose (ZnO) at initial concentration of 9 mg/L was taken in the literature[31], while in present work only 0.4 g of ZnO was taken at initial Cr concentration of 20 mg/L at same conditions i.e. pH 2 and contact time 90 min.

Conclusions

Nanosized ZnO particles can be prepared by simple precipitation technique. The XRD analysis clearly showed the crystalline nature of ZnO and SEM image showed smooth flakes like structure. Adsorption of Cr(VI) on ZnO was promising at pH 2. The adsorption was fitted on Langmuir adsorption isotherm model which indicated the presence of homogeneous equivalent active sites on ZnO and adsorption was monolayer type. The maximum adsorption loading (Q m) was found to be 3.43 mg/g.

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