Micro-Plasma Assisted Synthesis of ZnO Nanosheets for the Efficient Removal of Cr\textsuperscript{6+} from the Aqueous Solution

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Abstract: Herein, we report a micro-plasma assisted solvothermal synthesis and characterization of zinc oxide nanosheets (ZnO-NSs) and their application for the removal of Cr\textsuperscript{6+} ion from aqueous solution. The morphological investigations by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) confirmed the high-density growth of nanosheets with the typical sizes in the range of 145.8–320.25 nm. The typical surface area of the synthesized ZnO-NSs, observed by Brunauer-Emmett-Teller (BET), was found to be 947 m\textsuperscript{2}/g. The synthesized ZnO-NSs were used as efficient absorbent for the removal of Cr\textsuperscript{6+} ion from aqueous solution. Various parameters such as pH, contact time, amount of adsorbate and adsorbent on the removal efficiency of Cr\textsuperscript{6+} ion was optimized and presented in this paper. At optimized conditions, the highest value for removal was 87.1% at pH = 2 while the calculated maximum adsorption capacity was ~87.37 mg/g. The adsorption isotherm data were found to be best fitted to Temkin adsorption isotherm and the adsorption process followed the pseudo-first-order kinetics. Furthermore, the toxicity of ZnO-NSs were also examined against fibroblast cells, which show favorable results and proved that it can be used for wastewater treatment.

Keywords: ZnO nanosheets; Cr(VI) ion; adsorption isotherms; fibroblast cells

1. Introduction

Global industrialization is ever developing but at the same time, environmental pollution is ever-worsening [1–3]. Nanostructured materials are distinct materials which possess dimensions in the range of 1–100 nanometers [4–6]. The nanostructured materials exhibited different and significant properties as compared to their bulk counterparts with the similar compositions [7]. In recent years, nanoparticles have been studied as potential adsorbents because of their high-surface to volume ratio, interesting and specific thermal, electrical, mechanical, chemical, optical and magnetic properties [8–11]. Therefore, because of higher surface area, chemical activity and adsorption capacities, the nanoparticles exhibited high adsorption capacity [10]. The main factors affecting are high surface area, adsorption activity, location of atoms on the surface, low internal diffusion resistance, surface binding energy and chemical activity of the material [12–14]. Nanomaterials used for the removal of heavy metal should be less toxic and possess high adsorption capacity to absorb pollutants [15,16]. With the huge demand of energy production, the use of heavy
metals was increased significantly which exponentially rise the risk of exposure of heavy metals to the human being [3,4]. Due to the toxicity and occurrence of nickel (Ni), chromium (Cr), lead (Pb), arsenic (Ar), and mercury (Hg), these heavy metals are extensively studied by the researchers [13]. It is known that the Cr and its compounds at higher concentrations are introduced into the aquatic and terrestrial ecosystem through a variety of sources [17]. Chromium mainly exists in two forms, i.e., chromate (CrO$_4^{2−}$) and dichromate (CrO$_7^{2−}$) ions. Cr(IV) compounds and chromates of potassium, calcium and sodium is considered as cancer causing agents for human beings. Chromium-ion has multiple oxidation states but the oxidation states +3 and +6 are more abundant and comparatively more stable [18]. Interestingly, the Cr(III) is low toxic while hexavalent Cr(VI) is highly toxic, since it can exert carcinogenic, teratogenic and multigenic effects to human and other organisms [19]. Thus, to avoid health hazards, it is required to develop a cheap, facile and ecofriendly alternative solution for chromium removal [20]. To date, various methods for the removal of chromium were introduced and reported in the literature such as advanced oxidation processes, coprecipitation, adsorption, filtration, electrochemical treatment and many other techniques [21–25]. Among these methods, the surface adsorption is a compatible process for the extraction of heavy metals from aqueous solution as it is one of the most economical and highly efficient process [26,27]. As suggested by the United States Environmental Protection Agency, the contaminants level for chromium should be up to 0.1 mg/L [28]. Therefore, it is highly required to remove chromium ions from the water for a healthy life.

Nowadays, nanomaterials with nanoscale (usually 1–100 nm) dimensions also prove to be influential approach for eradication of heavy metals ions from aqueous solution [28–32]. Heavy metals have high atomic weight, high density and high specific gravity. Some heavy metals are released by various industries like electroplating, mining, automobile, pharmacy, textile and dyes, chromate manufacturing, leather tanning, aluminum production, metal cleaning and processing sectors. Chromium has multiple applications in different industrial processes like electroplating, printing, dyeing, tanning and other metallurgy related industries [32]. The waste products of such companies severely contaminate the environment and affect the growth of plants, animals and humans [33,34]. Various metal oxides based on ferric, vanadium, titanium and zinc were used for the extraction of Cr(VI)-ions and reported in the literature [35–37]. Among various metal oxides, the zinc oxide (ZnO) nanomaterials are considered as one of the most important and functional materials due to its properties and wide applications [35]. Various ZnO nanomaterials were effectively used for the extraction of Cr-ions [38,39]. Kataria and Garg et al. reported the synthesis of ZnO nanoflowers via hydrothermal technique and utilized them for the extraction of Pb and Cd-ions from wastewater [38]. Modwi et al. [39] synthesized Cu/ZnO nanocomposites and used it for lead-ions removal. It is considered that the 2D nanosheets could be a suitable material as adsorbent due to their high surface to volume ratio and flexible nature compared to nanorods [40–42]. The 2D nanostructure possess nanometer-scale thickness with specific surface atomic configuration which may enhance the adsorption capabilities.

In this paper, we report the micro plasma assisted synthesis and characterization of ZnO-NSs and their absorption behavior for the extraction of Cr$^{6+}$ ion from wastewater. Several characterizations were used to analyze the physicochemical and morphological properties of ZnO-NSs.

2. Experimental Details

2.1. Synthesis of ZnO Nanosheets

ZnO-NSs synthesis was carried out as follows: prepare a solution of 5 mM Zn(NO$_3$)$_2$·6H$_2$O and 1-mM sodium dodecyl sulfate (SDS) using 100 mL distilled water at 60 °C. Then micro plasma assisted electrolysis was performed under a self-regulated atmospheric pressure micro plasma (AMP) reactor for one hour. The reactor contained a copper electrode (2 × 3 mm, anode), a stainless-steel capillary tube (0.02 × 6 cm, cathode) and argon gas flow. A high voltage of 1000 V was applied to the initiate the reaction. Af-
ter the completion of the process, the precipitate collected and typically washed numerous times by deionized water and dried overnight at 70 °C for 5 h under vacuum [43].

2.2. Characterizations

Powder diffraction (XRD, Rigaku Ultima IV, Japan) and Fourier transform infrared spectroscopy (Perkin Elmer Frontier FTIR, Waltham, MA, USA) were used to characterize the physicochemical properties of ZnO-NSs. Microstructural and morphological properties of nanostructured ZnO were examined by scanning electron microscopy (JEOL, JSM 6100, Akishima City, Tokyo, Japan) and transmission electron microscopy (Hitachi H 7500, Chiyoda-ku, Tokyo, Japan). The surface area of ZnO-NSs was determined by means of adsorption-desorption isotherm, recorded with a BET, BELSORP MINI-II (BEL Japan). Atomic Absorption Spectrometry (AA-620, Shimadzu, Kyoto City, Kyoto Prefecture, Japan) was used to examine the concentrations of Cr$^{6+}$ within the adsorbent samples.

2.3. Removal of Cr$^{6+}$ Ions Using ZnO Nanosheets

Potassium dichromate ($K_2Cr_2O_7$) is used as the source for chromium stock solution (100 mg/L). Diluted sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions were used to obtain desired pH (2–12) solution. The required concentrations (10–100 ppm) based Cr$^{6+}$ solution was prepared from stock. The different amount (2–20 mg) of ZnO-NSs was introduced into the Cr$^{6+}$ solution (20 mL) under agitation. After that, ZnO-NSs treated solution was centrifuged and atomic absorption of spectroscopy, (AAS) was performed to measure the Cr content. The percentage removal of Cr$^{6+}$ ions was assessed through Equation (1) [31]:

$$\text{% Removal} = \left(\frac{\text{Initial Conc. of Cr} - \text{Conc. of Cr after removal}}{\text{Initial Conc. of Cr}}\right) \times 100$$ (1)

The influence of some significant variables including solution pH, temperature effect, adsorbate and adsorbent concentration, on extraction of Cr$^{6+}$ has investigated by surface adsorption process [44]. Various kinetic models and isotherms were used to investigate suitable process of sorption with high efficiency [31]. The equilibrium adsorption capacities of the ZnO-NSs was calculated through Equation (2) [45]:

$$\text{Adsorption capacity} = \frac{(C_0 - C_e)V}{W} \text{ mg/g}$$ (2)

where $C_0$ (mg L$^{-1}$) and $C_e$ (mg L$^{-1}$) denoted the initial and equilibrium Cr$^{6+}$ concentrations in aqueous solution, $V$(L) is the volume of the solution, and $W$ (g) is the mass of adsorbent mass.

2.4. Cytotoxicity of As-Synthesized ZnO Nanosheets

Normal fibroblast cell lines (L929) were used for Trypan blue assay to check the toxicity of ZnO nanosheets. The cell culture was facilitated in MEM with 10% FBS and 100 U/mL penicillin-streptomycin. The sample of ZnO nanosheets was incubated after the successful seeding of fibroblast cells (100,000 cells per 100 µL). Trypan blue, a dye widely used for staining the cells, was utilized and the sample was incubated for 10 min. The cytotoxicity of ZnO nanosheets was investigated through fluorescence microscopy (Zeiss, Oberkochen, Germany).

3. Results and Discussion

3.1. Characterizations of As-Synthesized ZnO Nanosheets

Figure 1 shows the typical x-ray diffraction (XRD) pattern of as-synthesized ZnO nanosheets. The observed XRD pattern exhibited various diffraction peaks appeared at $2\theta = 31.3^\circ$, $34.2^\circ$, $35.9^\circ$, $47.3^\circ$, $56.4^\circ$, $62.8^\circ$, $66.2^\circ$, $67.8^\circ$ and $69.0^\circ$ indicating the ZnO crystal planes of (100), (002), (101), (102), (110), (103), (200), (112) and (201), respectively.
The observed diffraction peaks are attributed to the pure ZnO and well consistent with the JCPDS card no. 076-0704 and reported literature [46,47]. The observed diffraction pattern possesses fine peaks, which indicate the good crystallinity of the synthesized ZnO nanosheets. The crystalline size of the synthesized material was calculated using Debye-Scherrer formula [48–50] and found to be nearly 70 nm. By comparing the observed diffraction pattern with the standard JCPDS Card no. 076-0704 of ZnO pure phase, it was observed that the relative intensity of (100) peak is greater than (101) peak which confirms the crystal growth perpendicular to (100) plane.

![Figure 1. Typical XRD pattern of as-synthesized ZnO nanosheets.](image)

The morphologies of the synthesized ZnO-NSs were examined by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) and results are shown in Figure 2. Figure 2a,b exhibit the typical SEM images of as-synthesized product which confirmed the successful growth of nanosheet-shaped structures. The nanosheets are grown in very high density, thus overlapping each other. The typical size of the nanosheets is in the range of 1–1.2 µm. Some smaller nanosheets are also seen in the observed SEM micrographs. Figure 2c,d show the typical TEM images of the nanosheets. For the TEM analysis, the synthesized ZnO nanosheets powder was ultrasonicated in acetone and a drop of acetone which contained nanosheet was placed on the copper grid and examined. Due to ultrasonication, the nanosheets are broken into small sizes. As observed in the TEM images, various sizes of nanosheets are seen. Interestingly, the nanosheets exhibited smooth and clean surfaces.

Figure 3a displays the FTIR spectrum, which confirmed the chemical composition of the prepared material. Various peaks in the FTIR spectrum were observed. The broadband at ~3296 cm\(^{-1}\) is attributed to O-H stretching vibrational mode [51]. The presence of well-defined peaks at 1630 and 1416 cm\(^{-1}\) are associated with carbon and oxygen vibration stretching mode of C-O and C=O, respectively [52]. The presence of these carboxylate in the spectra is due to the adsorption of CO\(_2\) [53]. The transmission peak at 927 cm\(^{-1}\) is due to the formation of the tetrahedral coordination of Zn [54]. A well-defined peak at 798 cm\(^{-1}\) and 454 cm\(^{-1}\) are assigned to the vibrational mode of the Zn-O molecule, which confirms the formation of the ZnO nanostructure [55].

By applying adsorption-desorption isotherm using Brunauer-Emmet-Teller (BET), the surface area of the synthesized ZnO nanosheets was examined. The plot of adsorption-desorption nitrogen isotherm between relative pressure vs. volume adsorbed presents the amount of nitrogen gas adsorbed on to the surface of adsorbent as well as amount of that gas desorbs at normal temperature. This amount of gas adsorbs into the mesoporous area due to high temperature operation and this mesoporosity is revealed by hysteresis behavior. Figure 3b depicts the typical adsorption-desorption isotherm of as-synthesized ZnO nanosheets. According to the observed adsorption-desorption isotherm graph, the calculated surface area of the synthesized ZnO nanosheets was found to be 948 m\(^2\)/g. This BET surface
area is still too high to achieve ideal performance as an adsorbent [56]. The interconnected porous structure would significantly upsurge the effective surface area that improves the adsorption performance [57]. The size of the adsorbent pores also affects the adsorption process. Adsorption of Cr\(^{6+}\) ions on the surface of the ZnO-NSs upsurges as the pore size decreases since the contact point between the surface of adsorbate and adsorbent increases [58].

Figure 2. Typical (a,b) SEM images and (c,d) TEM images of as-synthesized ZnO nanosheets.

Figure 3. Typical (a) FTIR spectrum and (b) Adsorption-desorption isotherm of as-synthesized ZnO nanosheets.
3.2. Adsorption of Cr\textsuperscript{6+} Ions over ZnO Nanosheets

Kinetics behavior shows the efficiency of the adsorbent and speed of adsorption, adsorption constant and desorption constant values for adsorbent. Kinetics also decides the order of reaction and value of adsorption capacity with time. The observations have proved that the solution pH is the supreme parameter in controlling adsorption, seems with important impacts on the chemistry, solubility, surface charges, dissociation of the analyte and functional groups of adsorbent [59–61]. The effect of solution pH (2–12) on the removal efficiency (%) of Cr\textsuperscript{6+} ions is illustrated in Figure 4. The dissociation of water molecules generates H\textsuperscript{+} and OH\textsuperscript{-} ions which may adsorb at the interface of aqueous solution-ZnO nanosheets that can affect the variation in adsorption with time [62]. The pH of solution influences metal speciation chemistry and surface metal binding sites of the sorbent [63]. The pH of the solution may affect the surface properties of adsorbent and ion formation properties of chromium [64]. From Figure 4a, maximum adsorption was observed at low value of pH while diminution in adsorption rate was observed at high value of pH due to less competition offered by OH\textsuperscript{-} ions with Cr\textsuperscript{6+} ions. The adsorption reaches a maximum of pH 2 which was considered as optimized pH value for Cr ions removal. However, the percentage of removal of ions from aqueous solution was observed to be decreased with an increase in the pH value. Cr\textsuperscript{6+} may be accessible in the form of Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2–}, HCr\textsubscript{2}O\textsubscript{7}\textsuperscript{–}, CrO\textsubscript{4}\textsuperscript{2–} and HCrO\textsubscript{4}\textsuperscript{–} ions that depends on some parameters such as solution pH, Cr\textsuperscript{6+} concentration and temperature [65].

Adsorbent administration is another essential parameter obligatory to attain the desired level of treatment. Several studies have shown that the adsorbent dose is an important factor that affects the rate of adsorption at the solid-liquid interface [66]. As the sample dosage increases the % elimination of the Cr ions is also greater than before, at optimum pH and time. However, removal capacity (expressed, for example, in mg/g) decreases if the dosage is increased and it may change the pH of the solution also. Furthermore, Figure 4b revealed the maximum quantity adsorbed, \(Q_e = 87.37\) mg/g, was reached by 100 mg ZnO-NSs.

Figure 4c revealed the effect of Cr\textsuperscript{6+} ions concentration on the removal rate was also evaluated for the optimal ZnO-NSs dose. As the concentration of Cr ions rises, the Cr\textsuperscript{6+} ions removal rate also enhanced with saturation at high Cr concentrations. Initially, adsorption/removal efficiency was higher observed since surface contact of adsorbate particles increased [67]. After some time, all the adsorption sites were fully occupied by the adsorbate that leads to the saturation in the adsorption of Cr-ion removal process [68].

Figure 4d displays that the contact time significantly affects chromium removal rates. The removal rate of Cr\textsuperscript{6+} ions also upsurges as contact time rises up to 300 min because of the availability of empty space or voids and the energy transfer of Cr ions take place in the direction of the ZnO-NSs sample surface [32]. Due to high contact time of adsorption, the collision between particle of adsorbate and adsorbent will be higher which increases the adsorption capacity or enhanced % removal [69]. The highest value of removal of Cr-ions was found at 300 min and the highest value of percentage removal of the chromium ions was observed to be 87.37%.

The adsorption procedure was also analyzed to determine the effect of temperature on the adsorption rate [35]. The temperature vs. chromium removal rate using ZnO-NSs is shown in Figure 5. It is observed that with increase in temperature, the removal rate of chromium also increases. Increase in removal efficiency with increase in temperature indicates that the process is endothermic in nature. This effect is consequence of chemical reaction involved in adsorption process. As temperature is increased, mobility and diffusion of ions also increased. Thus, adsorption of Cr\textsuperscript{6+} ions increased. However, after reaching saturation point, this intercalation of ions stops and decrease in slope can be observed in the graph. The growth in Cr adsorption was observed up to 50°C, and after that rate of chromium adsorption decreases.
3.3. Equilibrium Studies

To justify the adsorption phenomenon and also to look out for adsorption parameters that verify the adsorption system during the operation, Langmuir and Temkin isotherm models [70] were applied and results are presented in Figure 6a,b. These adsorption isotherm models describe an appropriate fit with experimental data with good correlation coefficients [71]. To justify the adsorption phenomenon and also to look out for adsorption parameters that verify the adsorption system during the operation, Langmuir, Temkin and Freundlich isotherm models [72] were applied and results are presented in Figure 6a,b. These adsorption isotherm models describe an appropriate fit with experimental data with good correlation coefficients [73]. Equations (3) (Langmuir), (5) (Temkin) and (6) (Freundlich) were used for adsorption analysis [74]. The study for the feasibility of adsorption studied through separation factor (R_L) as shown in Equation (4) [75]. The Temkin isotherm model (Equation (5)) was used to know the relationship between adsorbent and adsorbate interaction [71]. The Freundlich isotherm model was applied to know the multilayer adsorption on the surface of adsorbent.

The Temkin isotherm model takes into account the effects of indirect adsorbate/sorbent interactions on the adsorption process [72]. Temkin isotherm model (Figure 6b) was found to be best fitted for the existing isotherm course.

**Langmuir isotherm**

\[
\frac{C_e}{q_e} = \left( \frac{1}{K_{Lq_m}} + \frac{C_e}{q_m} \right).
\]

\[ R_L = \left( \frac{1}{1 + K_L C_O} \right) \]

**Temkin isotherm**

\[ q_e = B \ln A_T + B \ln C_e. \]

**Freundlich isotherm**

\[ \log q_e = \left( \log K_f + \frac{1}{n} \log C_e \right) \]

where \( C_e \) = the equilibrium concentration; \( q_e \) = the adsorbent capacity at equilibrium; \( C_0 \) = initial concentration of Cr while \( K_L \) = Langmuir isotherm is constant; and \( q_m \) is
adsorption capacity, are the isotherm constants. $A_T =$ equilibrium binding energy; $B =$ heat of the adsorption; and $C_e$ is the final concentration. $K_f$ is adsorption capacity and $1/n$ is adsorption intensity.

Figure 5. Effect of temperature on the removal of Cr$^{6+}$ ions.

Figure 6. Adsorption isotherm (a) Langmuir isotherm and (b) Temkin isotherm.
These models were considered for the presence of indirect adsorbate/adsorbent interactions on the adsorption process. Table 1 showed the parameters and units of Langmuir, Temkin and Freundlich isotherms. The correlation coefficient ($R^2$) of adsorption isotherm (Langmuir, Freundlich and Temkin) are $R^2 = 0.5638$, $R^2 = 0.9631$, $R^2 = 0.9907$, showed as shown in Table 1. Temkin isotherm model to approve that the adsorption of Cr$^{6+}$ ion onto ZnO nanosheets trails a chemical adsorption procedure.

Table 1. Isotherm parameters.

| Langmuir Isotherm | Freundlich Isotherm | Temkin Isotherm |
|-------------------|---------------------|-----------------|
| $q_m = 53.11 \text{ mg/g}$ | $K_F = 9.4697$ | $B = 0.2866 \text{ J/mol}$ |
| $K_L = 0.1523 \text{ L/mg}$ | $1/n_F = 0.8305$ | $A = 21.5603 \text{ L/mg}$ |
| $R^2 = 0.5638$ | $R^2 = 0.9631$ | $R^2 = 0.9907$ |

3.4. Adsorption Kinetics

Two different kinetic rates models that included pseudo-first-order and pseudo-second-order, were used to analyze the experimental data [73], given in Equations (6) and (7). The pseudo-first-order model explains the surface adsorption that involves chemical adsorption process [74], where the removal of Cr$^{6+}$ ions from an aqueous medium is due to physicochemical interactions between adsorbent and adsorbate.

The pseudo-first-order model was fitted to explain the adsorption kinetics most effectively and the plots are drawn in Figure 7a,b.

\[
\ln(q_e - q_t) = \ln(q_e) - k_1 t 
\]  
\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} 
\]

where $q_e$ is the adsorption capacity at equilibrium (mg/g) and $q_t$ is the amount of Cr$^{6+}$ ions removed at time $t$, and $k_1$ is the pseudo-first-order rate constant while $k_2$ is the pseudo-second-order rate constant and $t$ is the contact time.

These isotherms pronounce the equilibrium conditions of the adsorption procedure, relating the concentrations of the adsorbate in the aqueous medium and solid phases at a definite temperature [55]. The adsorbate–adsorbent systems were evaluated via nonlinear regression investigation, used for the analysis of the experimental data [61]. Pseudo first and second order kinetic model displayed the values of $R^2 = 0.9643$ and 0.9416 respectively (Table 2).

Table 2. Kinetics parameters.

| Pseudo-First-Order | Pseudo-Second-Order |
|--------------------|---------------------|
| $K_1 = 0.0049 \text{ 1/min}$ | $K_2 = 0.1152 \text{ 1/min}$ |
| $q_e = 9.4697 \text{ mg/g}$ | $q_e = 2.5045 \text{ mg/g}$ |
| $R^2 = 0.9643$ | $R^2 = 0.9416$ |
3.5. Removal Mechanism of Cr\textsuperscript{6+} Ions Using ZnO Nanosheets

Figure 8 shows the plausible mechanism for the Cr\textsuperscript{6+} ions adsorption through ZnO nanosheets. The Cr\textsuperscript{6+} ions adsorption mechanism may be described by an ion exchange process [76]. Initially, some of the Cr\textsuperscript{6+} ions are adsorbed on the surface of ZnO-NSs in the form of Cr thin film [35] which was due to the presence of a free adsorption sites or void, a prime requirement for the adsorption of Cr\textsuperscript{6+} ions. In these circumstances, surface unsaturation and struggle between sites for a limited amount of chromium ions were available, causing desorption and resorption of Cr\textsuperscript{6+} ions. However, the wide-ranging adsorption of Cr\textsuperscript{6+} ions upsurges with an increasing number of active sites [77]. Under visible light, the adsorption of positive Cr\textsuperscript{6+} ions on the negatively charged surface of ZnO has occurred with the formation of Cr\textsubscript{2}O\textsubscript{3} plate-like precipitates [35]. In the aqueous medium, accumulation of H\textsuperscript{+} on the surface of ZnO cause surface polarization or protonation [78]. The Cr\textsuperscript{6+} ions may bind to the surface of ZnO-NSs under the electrostatic interaction between the negative charged Cr\textsuperscript{6+} species and the protonated ZnO. It is appropriate to note that the surface reduction reaction will occur after the adsorption of Cr\textsuperscript{6+}.
Obviously, at low pH values (1.0–3.0) the surface of the adsorbent is highly protonated, i.e., the Cr ions in the form of anions are adsorbed onto the positive surface portion of the adsorbent. This is because of the accumulation and congregation of Cr$^{6+}$ ions around the surface of ZnO-NSs. The percentage of adsorption will increase as the surface area of the obtained adsorbent is large. The amount of adsorbent, medium pH and contact time will also decide the adsorption efficiency of ZnO-NSs. The ZnO NSs exhibited excellent adsorption performance compared to the other adsorbent materials reported in the literature. A comparison of the adsorption properties of ZnO NSs with other adsorbent materials is shown in Table 3 [79].

Table 3. The adsorption properties of ZnO NSs compared with other adsorbent nanomaterials.

| Nano Adsorbent       | Metal Ions | pH    | Adsorbent Dose (g/L) | % Removal Efficiency | Ref. |
|----------------------|------------|-------|----------------------|----------------------|------|
| ZnS nanocrystals     | Hg(II)     | 1–6   | 10                   | 99                   | [79] |
| Graphene NS          | Ni(II)     | 7     | 5                    | 77                   | [80] |
| VO$_2$ nanoparticles  | Cr(VI)     | 7     | 10                   | 85                   | [81] |
| Fe$_3$O$_4$-GS       | Zn(II)     | 5     | 2.5                  | 95                   | [82] |
| ZnO nanospheres      | Pb(II)     | 6     | 0.3                  | 75                   | [83] |
| Cu-doped ZnO         | Pb(II)     | 7     | 0.4                  | 88                   | [39] |
| ZnO nano sheets      | Cr(VI)     | 2     | 0.1                  | 87.7                 | Present study |

3.6. Cytotoxicity of ZnO As-Synthesized Nanosheets

ZnO nanoparticles have attracted considerable attention because of its various bio-applications [84]. It has been observed that ZnO nanoparticles cause cytotoxicity to various kinds of cells like HepG2, MCF-7, HT29, Caco-2, rat C6, THP-1 [85]. In addition, the ZnO nanoparticles also exhibited excellent antibacterial and antifungal activity [86].

Figure 9 reveals the image observed from fluorescence microscopy. The trypan blue stained ZnO sample displayed the existence of dead cells through dark blue colored spots while the remaining part of the image showed a light blue color. This indicated that the
cell survival count is more than dead cells which confirmed the low toxicity of the ZnO nanosheets. The observed result indicates that the ZnO nanosheets do not show any major toxic effects against fibroblast cells and can be used for water treatment. The toxicity of a material can be affected by the composition and surface chemistry like charge and texture [87]. The toxic intravenous dose of nanostructured ZnO for body tissue distribution and blood kinetics were reported as 0.05–0.2 mg/kg of body weight [88,89].

![Fluorescence microscopic image of the cytotoxic study.](image)

**Figure 9.** Fluorescence microscopic image of the cytotoxic study.

4. Conclusions

In summary, ZnO-NSs was synthesized, characterized and utilized as an efficient adsorbent material for the removal of Cr(VI) ions from their aqueous solutions. The high surface area of ZnO nanosheets was responsible for the adsorption of Cr\(^{6+}\) ions. The high surface area of the ZnO-NSs sample was confirmed using SEM and BET analysis while the other physicochemical properties were accessed using XRD and FTIR analyses. The cytotoxicity study revealed that the ZnO nanosheets do not show any major toxic effects, thus it is a promising agent for the removal of Cr\(^{6+}\) ions. The maximum adsorption capacity using ZnO-NSs was found to be 87.37 mg/g (\(q_{\text{max}}\)). The adsorption isotherm data was found to be best fitted to Temkin adsorption isotherm and the adsorption process followed pseudo-first-order kinetics. The observed values of Temkin constants were \(a = 0.0065\) and \(b = -0.062\). By cell survival counting from cytotoxicity results, it was observed that ZnO nanosheets are less toxic, thus, it is observed that the ZnO nanosheets do not show any major toxic effects against fibroblast cells and hence, it is a favorable material for water treatment.

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