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Synthesis of zinc oxide nanoparticles impregnated clay tablets and their potential applications as point of use water purification intervention

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ABSTRACT

The aim of the study was to develop novel materials for the decontamination and disinfection of water at point of use (POU) level. Composites of ZnO nanoparticles with clay were prepared by novel synthetic route. The nanoparticles of ZnO in the clay were in situ synthesized at elevated temperature without using any other chemical as reducing agent. The ZnO-clay composites were molded into tablets for POU water purification treatment. The said composites were characterized by UV, FTIR, XRD, thermogravimetric analyzer and SEM. The tablet removed 98.8% Pb(II), 98.6% Ni(II), 96.4% Co(II) and 89.9% Cd(II) ions from the synthetic waste solution after 4 h of the experiment. The kinetic studies revealed that the process of removal was found to be following pseudo-second order kinetics. The tablets containing different composition of ZnO were also tested against *Escherichia coli* (ATCC-25922) and results revealed that the greater inhibition zone (15 mm) was formed for tablet which contains 40% ZnO. The release of Zn ions in water (not more than 5 ppm) was in the permissible limit as explained in WHO guidelines. The results reveal that the ZnO-clay tablets are appropriate candidates at POU for the disinfection and decontamination of water.

Keywords: POU; Disinfection; Nanoparticles; Tablets

1. Introduction

Clean and safe water is among the basic requirements for human health. As per the data provided by World Health Organization (WHO) more than a billion of people do not have access to clean and adequate water sources [1]. The use of water contaminated with various microbial pathogenic species such as bacteria, protozoans, and viruses cause different waterborne diseases such as typhoid, hepatitis, and cholera. In all parts, of the world, variety of contaminants such as heavy metal ions, traditional compounds, nitrosamines, and endocrine disrupters enter water supply as a result of different human activities. The consumption of unsafe water snatches the lives of millions of people each year and 3,900 children lose their lives each day against the waterborne diseases [2,3]. Due to serious public health concerns and environmental issues, it is quite necessary to disinfect and decontaminate water in order to obtain clean and safe drinking water [4]. Conventional water purification techniques such as distillation, bio-sand, filtrations, reverse osmosis, and coagulation–flocculation suffer some shortcomings to decontaminate all toxic metal ions and other hazardous species [5]. Traditional methods such as fabric filtration and boiling are being practiced, but they are labor intensive and energy consuming. Chlorination and solar disinfection methods have their limitations in turbid water systems. Chlorine is most often used as point of use

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(POU) intervention for water disinfection but the problem with chlorine is as it disturbs the taste of water which most of the people dislike [6,7]. In the absence of a centralized system for the water sources purification, drinking water requires to be decontaminated and disinfected at household level. As per WHO suggestion, the better way to treat poor quality drinking water is to devise POU at household level. POU interventions have been found quite effective and efficient in improving the quality of water at household level [8–10]. Presently, there are a variety of POU water treatment technologies in practice. These include ceramic filters and tablets, chlorine based methods, and combined flocculent–disinfectant [11–15]. Though, these POU interventions have reliable and better performance in a laboratory set up, the efficiency of these POU methods rely on different elements such as ease of use of method, user-compliance, existing poor hygienic and sanitation conditions which limit their use to a greater extent [16]. The silver-contained ceramic tablets for POU water treatment technology using saw dust, clay, water, and silver nitrate. Upon placing in household water, the tablet releases silver ions at controlled rate which kill microbial pathogens present in water and also the concentration of silver remained below the permissible limit of WHO [17]. In our present research project, we have in situ synthesized the zinc oxide nanoparticles (ZnO-NPs) in the clay matrix and then the tablets of the said composites have been prepared for POU water treatment technology. The clay collected was termed as silty clay (SC) as it contains some quantity of silt beside clay. The potentials of the said silty clay and its composite with ZnONPs (tablets) were examined for Cd(II), Co(II), Ni(II), and Pb(II) removal from synthetic aqueous media. Also these tablets were tested against *Escherichia coli* (ATCC-25922) as robust, simple, low cost and socially acceptable POU water purification intervention at household level to disinfect and decontaminate water in order to obtain clean and safe water.

2. Experimental

2.1. Collection of clay

SC was obtained from Balochistan province of Pakistan near Chaman city in the Khojak mountains ranges. First, the silty clay was kept in oven for 24 h at 100°C to remove all water content present in SC. The said clay was sieved through 80 mesh. The clay obtained after sieving was used as such in research without any modification and further treatment.

2.2. Synthesis of tablets of ZnO-NPs with SC

10 g of SC was taken in a conical flask and 10 mL of zinc nitrate (10%) solution was added to it. This mixture was stirred on hot plate for 30 min. and then the mixture was poured in a china dish and the solvent was evaporated from it. 1.5 g of the mixture was put in the dye and was pressed by the hydraulic manual press for 15 min. at a pressure of 10 tons. The tablets formed were then kept in the furnace at 600°C for 4 h. After heating, the tablets obtained were stable. In similar fashion, tablets of different ZnO compositions (20%, 30%, and 40%) were prepared and in all the compositions, the quantity of SC was kept 10 g.

2.3. Characterization

FTIR-spectrometric (Agilent technologies, USA) analysis was performed to know the composition and nature of silty clay and ZnONPs-clay composite. The synthesis of ZnONPs was also confirmed by UV spectrometry (Sanyo, Japan). X-ray diffraction was performed with D-5000 diffractometer (Siemens, Germany) system using Mo-K a graphite monochromated radiation in order know the various constituents present in the clay mineral. The morphologies of surface and microstructure of ZnONPs and ZnONPs-clay samples were assessed by SEM-EDS (S-4800, Hitachi, Japan) as well to obtain elemental chemical compositions of clay. The thermogravimetric analyzer (TGA, Q500, TA Co., USA) was operated under air atmosphere at a rate of 10°C/min ranging from 25°C to 1,000°C for thermal stability of tablets.

2.4. Synthetic waste solutions preparation and analytical determination

TraceCERT® certified reference material, each element standard (Sigma-Aldrich, USA), certified in accordance with ISO/IEC 17025 was employed in this study for preparation of synthetic waste solution (50 ppm of each present in 100 mL solution) of Cd(II), Co(II), Ni(II), and Pb (II). GenPure water system (Thermo Scientific, USA) was used to obtain ultrapure water (18 MΩ cm resistivity). PG-990 model atomic absorption spectrometer from PG instruments, UK, equipped with fully integrated atomizer, auto-sampler and D2 background corrector was employed for analytical determination of elements. Computer interfaced AA Win Lab® software was utilized for data interpretation. For FAAS analysis, air/acetylene flame was utilized for the analysis of elements. Hollow cathode lamp as analytical line source was operated at 228.8 nm (Cd), 240.7 nm Co(II), 232.0 nm (Ni) and 217.0 nm Pb(II). Peak height was employed for signal evaluation and quantification. Acetylene flow rate was adjusted at 1,500–1,700 mL/min while air pressure maintained at 40 psi was optimized in our earlier studies [18].

2.5. Adsorption scheme of Cd(II), Co(II), Ni(II) and Pb(II) on ZnONPs-clay tablets

The ZnONPs-clay tablets were placed in this system and the samples for analysis were collected from it after definite intervals of time. The samples were obtained after 0.5, 1, 1.5, 2, 4, 24, 72, and 144 h. The samples were investigated by AAS to know the concentration of the respective ions after the process of adsorption. Knowing the initial concentration, C_0 (mg/L), and equilibrium concentration, C_e (mg/L), of metal ions, the percentage removal of all the ions were calculated using the formula.

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

2.6. Antibacterial assay

The ZnONPs-clay tablets were investigated for antibacterial activities against gram negative bacteria *Escherichia coli* (ATCC-25922) The stock cultures were collected from the Institute of Biochemistry and Biotechnology, University of the Punjab, Lahore. Strains were recultured in the specific culture media, that is, tryptic soy broth. Inoculum was spread with the help of sterile L-shaped glass spreader and then placed in shaking incubator for 24 h. at 37°C. In the present work, 1–3 × 10^8 cfu/mL of gram negative (*Escherichia coli*) were obtained after setting with broth to an optical density at 0.2 to 0.3 at 620 nm wavelength using spectrophotometer. Sterilized forceps was used to place ZnONPs-clay tablets onto the medium. Incubation time for antibacterial studies was 24 h at 37°C and zone of inhibition was visualized surrounding the tablet. The zones of inhibition (mm) were measured using digital vernier caliper (Starrett 799A-6/150, USA), evaluated the antibacterial activities and all studies were performed in triplicates.

3. Results and discussion

3.1. Characterization

The SC and ZnONPs-clay tablet were characterized by FTIR spectroscopy as depicted in Fig. 1a. The clay minerals, in general, contain variety of constituents such as alumino-silicate, tetrahedral silicates and aluminate ions, octahedral metal cations, hydroxyl groups, and various diffused layer cations. While analyzing FTIR spectra, in the range 3,400–3,750 cm^{-1}, O–H– stretching modes are observed. Around wavenumber 600–950 cm^{-1}, bending modes of metal–O–H are noticed. Si–O and Al–O stretching give rise to peaks between 700 and 1,400 cm^{-1} and the bending vibrations of the same bonds are found from 150 to 600 cm^{-1}. In case of SC, FTIR spectra recorded contains peaks of bending vibrations for Fe–Al–OH at 877 cm^{-1} and for Al–O–H at 987 cm^{-1}. The stretching vibrations due to O–H groups has given peaks around 3,600 and 3,400 cm^{-1}, The peak due to Si–O stretching appeared at 1,426 cm^{-1} in the spectra while peak appearing at 779 cm^{-1} is because of Al–O bending vibration [19]. The FTIR spectra of ZnONPs-clay composite has also the same peaks with slight shifting due to clay modification with nanoparticles.

The UV-Visible spectra of ZnONPs-clay were recorded from 200 to 800 nm range. The absorbance spectra with lambda max at 365 nm were noted showing the successful formation of ZnONPs as depicted in Fig. 1b. The value was in close agreement with the literature [20]. The XRD spectra of SC and ZnONPs-clay tablet have been depicted in Fig. 2. The spectra of SC contain peaks at (2 theta) values of 22°, 26°, 28°, and 30°. These peaks are characteristic peaks of alumina, silica, and aluminosilicates groups. The spectra suggest that aluminosilicates are the main constituent of the clay sample. The spectra of clay closely resemble other spectra of clay minerals. The XRD spectra of ZnONPs-clay tablet contain peaks for ZnONPs in addition to clay peaks. The peaks at (2 theta) values around 34°, 32°, and 36° are due to ZnONPs present in the sample. These peaks have emerged in the spectra due to 100, 002, 101, planes of ZnO. The peaks make it sure that ZnONPs are present in the composites [21–23].

The thermal stability of ZnONPs-clay tablet was investigated at a heating rate between 20°C and 950°C under nitrogen atmosphere as is shown in Fig. 2. It is generally presumed that the thermal stability of composite increases with increase in filler loading. In present case at lower temperature, no considerable loss of mass is noticed in the ZnONPs-clay tablet. The slower degradation of tablet started at around 250°C. This may be attributed due to destruction of small molecules present in the clay mineral. The decrease in mass of tablets continues linearly till 600°C. Afterwards the largest mass loss is noticed at around 770°C. This sound loss of mass is due to the destruction of the basic structure of clay mineral. This is concluded from the TGA studies that the tablet made of ZnO and clay is thermally stable over a wide range of temperature.

The SEM images of SC and its composite with 40% of ZnO nanoparticles were captured at different resolutions as shown in Fig. 3. The SEM of clay shows roughness and heterogeneity on the surface of clay as it is made of particles of different size ranging from very small to large particles. It contains relatively larger silt particles in addition to fine particles of clay. In case of ZnONPs-clay composites, the morphology is different from that of pristine clay because of the presence of nanoparticles of ZnO in clay matrix which are evenly distributed in the matrix. From SEM-EDS, the content

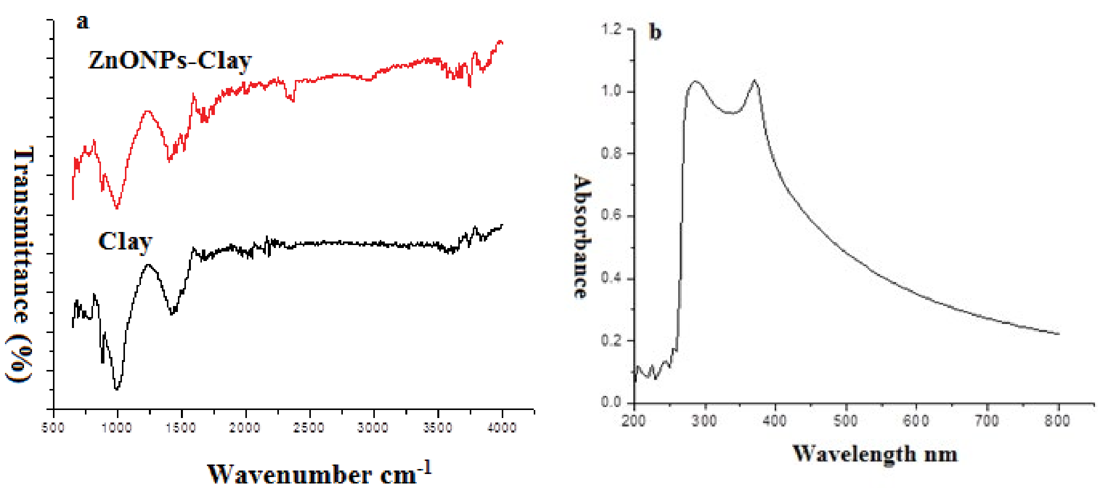

Fig. 1. FTIR (a) and UV (b) spectra of silty clay and ZnONPs-clay.

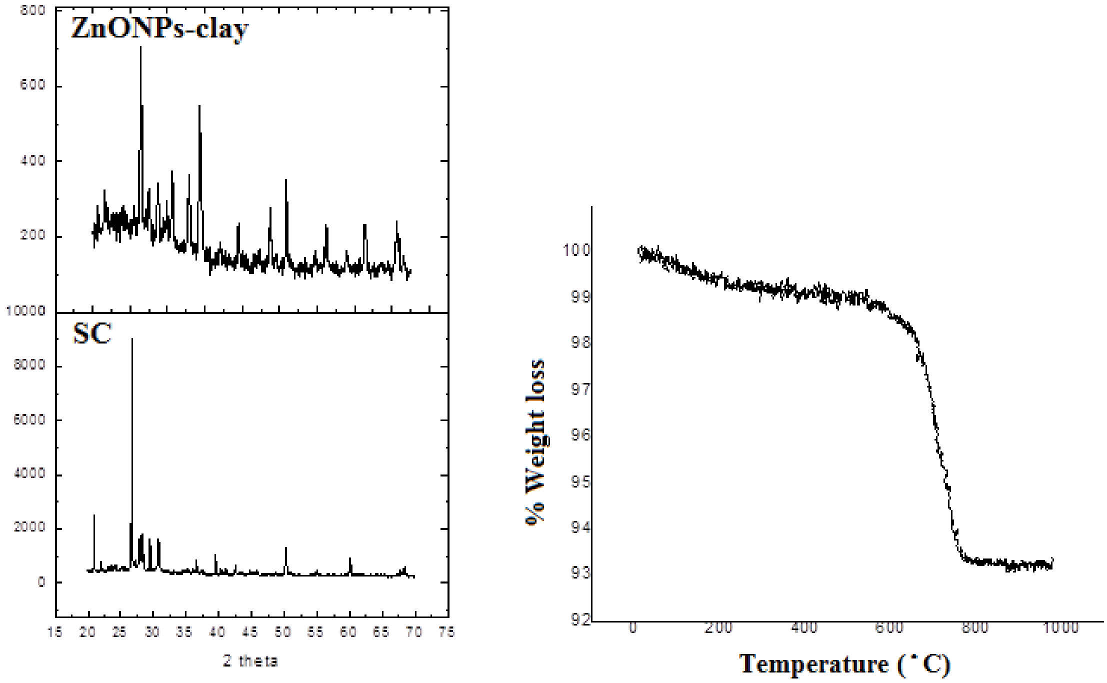

Fig. 2. XRD spectra of SC and ZnONPs-clay and TGA analysis of ZnO-clay tablet.

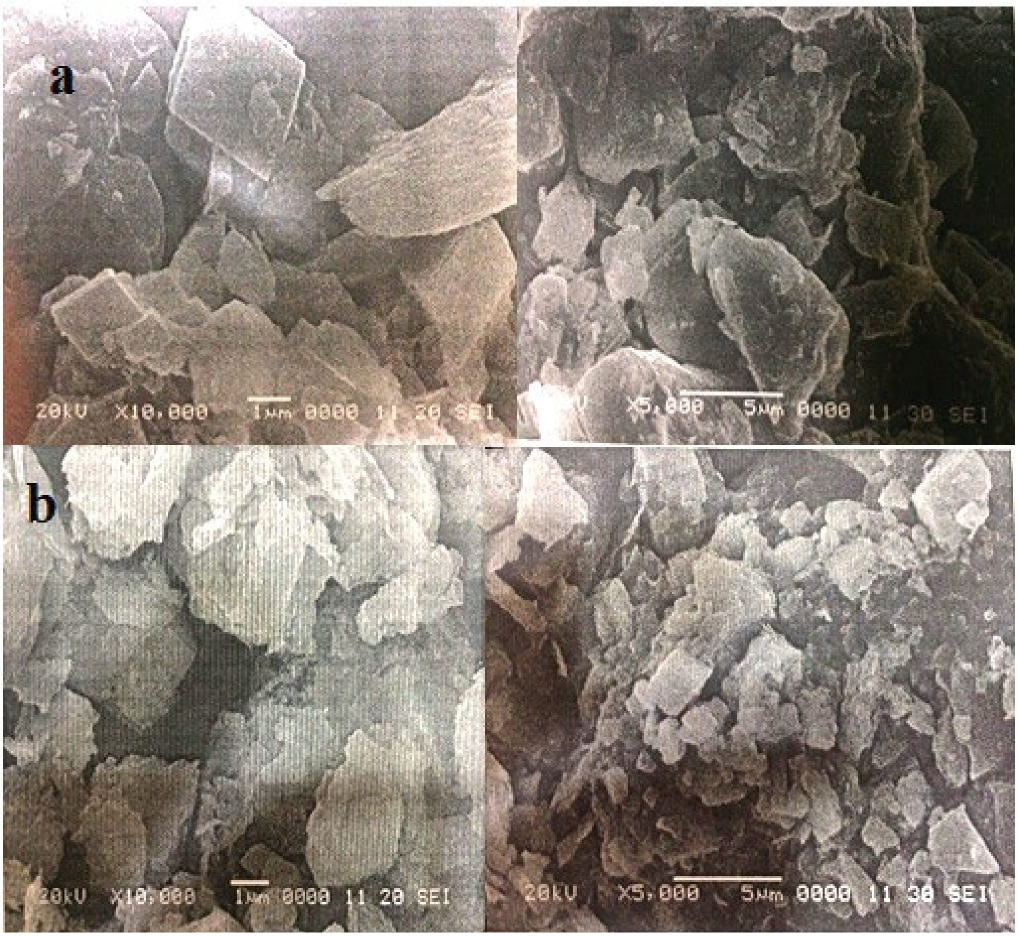

Fig. 3. SEM images of SC (a) and ZnONPs-clay.

of analyzed elements in the clay revealed that silicon (22.2%) is the element that is presented in higher quantities. While the remaining quantities are as follows Mg: 3.4%; K: 1.9%; Ca: 7.9%; Fe: 4.8%, and Al: 5.1%.

3.2. Removal of metal ions by ZnONPs-clay tablet

The efficiency and robustness of ZnONPs-clay tablets placed in synthetic waste solution was evaluated in terms of its capability to remove metal ions from the system. Since both clay and ZnONPs are reportedly efficient adsorbents for the adsorption of metal ions and dyes from contaminated media. The tablet was found quite active and efficient in removing the metal ions from the synthetic system. First, the pre analysis of metal ions present in synthetic waste solution was carried out by AAS. Afterwards, the samples collected from synthetic waste solution (SWS) were checked for metals concentration after regular intervals by noting the absorbance values. The samples were analyzed after 0.5, 1, 1.5, 2, 3, 4, 24, 48, and 72 h for the of Pb(II), Cd(II), Ni(II), and Co(II) ions concentration in synthetic media. The percentage removal of metal ions against time has been plotted (Fig. 4). It was observed that the metal ions started adsorbing on the ZnONPs-clay tablets. It can be seen that Pb(II) adsorbed on the tablets rapidly and in first hour more than 90% removal of Pb(II) was noted and after 4 h, almost all the Pb(II) was removed from the system (98.8%). Similarly, Co(II) also showed strong adsorption efficiency and in 4 h 96.5% removal of Co(II) was recorded. For Ni(II) adsorption on tablet, 98.6% removal was noticed in 4 h. The removal of Cd(II) by the ZnONPs-clay tablets was a relatively slower process. Up to 2.5 h, some 80% removal was observed for the Cd(II) ions. Even after 4 h, the removal noted for Cd (II) was around 89.9%. The removal reached 94% after 3 d for Cd(II). Overall, it has been observed that the porous ZnONPs-clay tablet has strong potential for eradication of metal ions from contaminated aqueous media, by accumulating them around itself and thereby decontaminating the waste and water systems.

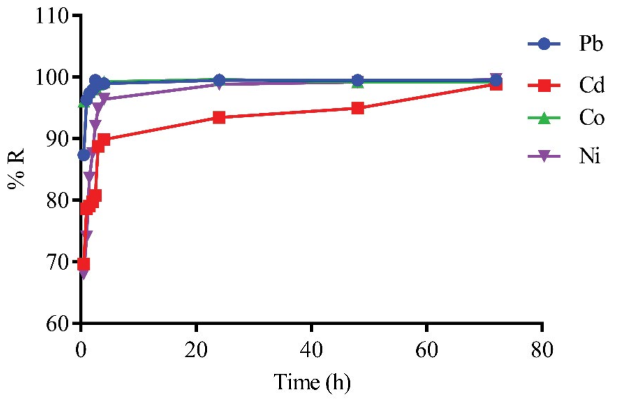

Fig. 4. % Removal of Pb(II), Co(II), Cd(II) and Ni(II) ions with time (h).

The effectiveness of adsorption process could be explained on the basis of hydration radii and Pauling's electronegativity [24,25]. So the selectivity and fast adsorption of Pb, Co, and Ni over Cd may be attributed to their smaller hydrated radius (Pb^{2+} = 0.401 nm, Ni^{2+} = 0.404 nm, Co^{2+} = 0.423 nm, Cd^{2+} = 0.426 nm) whereas the Pauling's electronegativity is in order Pb(II) 2.33 > Ni(II) 1.91 > Co(II) 1.88 > Cd(II) 1.69.

3.3. Kinetic studies

In order to investigate the kinetic studies of the removal of metals ion by the ZnONPs-clay tablet, various kinetic models such as pseudo-first order, pseudo-second order (PSO), and intra particle diffusion models were applied to interpret the data. The figure below depicts that PSO was followed by the adsorption process of all the four metals on the ZnONPs-clay tablet. In all the four cases of Pb(II), Cd(II), Ni(II), Co(II), the R^2 values were closer to unity (Fig. 5) suggesting that two species are involved in the rate determining step of the process.

3.4. Antibacterial activity

The antibacterial potentials of the ZnONPs-clay tablet were checked against *Escherichia coli* (ATCC-25922) bacteria by means of disc diffusion method on agar media (Fig. 6). The antibacterial efficiency of each tablet is seen in the form of inhibition zone made around them. The greater the inhibition zone, the better the antibacterial efficiency of the tablet. The results show that 40% ZnO-clay tablet has greater inhibition zone having value 15 mm while the remaining concentrations 10%–30% ZnONPs-clay showed the inhibition zone in ranged between 5 and 11.3 mm. The inhibition

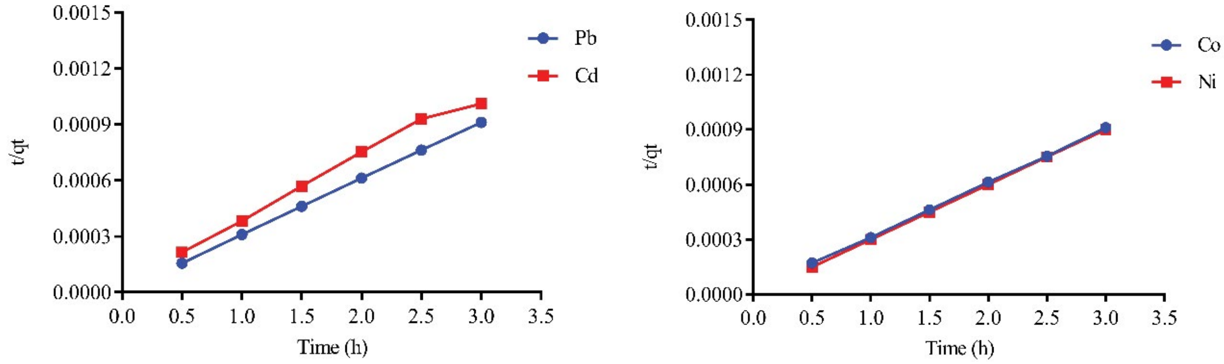

Fig. 5. Kinetic studies of the removal of Pb(II), Co(II), Cd(II), and Ni(II) ions with time (h).

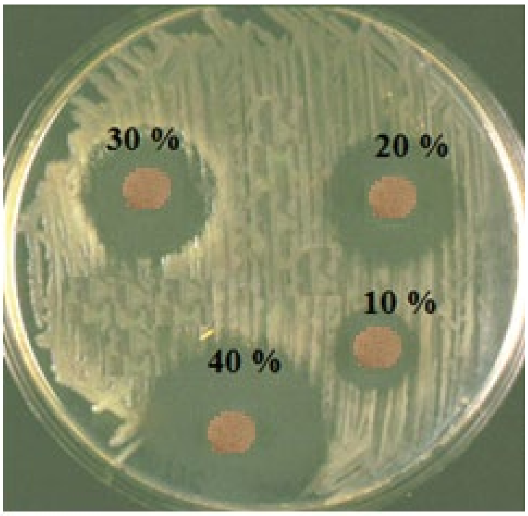

Fig. 6. Zone of inhibition of ZnONPs-clay tablets of different concentrations.

zone shows that due to the antibacterial activity of tablets, bacteria are unable to grow in the specific zone around the tablet and thus its further growth is inhibited. The bactericidal effect of ZnO nanoparticles in ZnONPs-clay tablets can be attributed to their size in nanometer (nm) range and peculiar features. Although, bulk material ZnO show antimicrobial efficiency as well, far better results of bactericidal aspects of ZnONPs against variety of organisms have been seen. The smaller size ZnO nanoparticles in nano-scale has the advantage of better penetration to the bacterial cells, causing disruption of cell membrane and, hence, behave as an active antibacterial agent.

4. Conclusion

ZnONPs in clay have been successfully fabricated and tablets were formed. The composites were characterized by various spectroscopic techniques including UV, FTIR, XRD, TGA and SEM-EDS. The TGA analysis showed that the tablets were thermally stable even at high temperature. Upon placing the tablet in the synthetic waste system, all the four metals ions such as Pb(II), Cd(II), Ni(II), and Co(II) ions were removed around 90% from the media after 3 h of the experiment. The antimicrobial activities of the tablets of different ZnO composition tablets against *E. coli* showed promising results. It was noted that the greater inhibition zone was formed around tablet containing 40% ZnONPs. The inhibition zone decreased as the ZnO concentration decreased in the tablets. This POU water purification and disinfection could provide safe drinking water at household level, even in emergencies, especially in the aftermath of disasters when energy shortages and disinfection infrastructure deficiencies are critical.

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