

Gelatin-zirconium Dioxide Nanocomposite as a Ni (II) Selective Potentiometric Sensor: Heavy Metal Separation and Photocatalysis

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The present work represents the synthesis of gelatin-zirconium dioxide nanocomposite (GT/ZONC) ion exchanger by sol-gel method. GT/ZONC was characterised by various techniques such as FTIR, XRD, SEM and TEM. To understand the ion-exchange capabilities of the material different physicochemical properties such as effect of eluent concentration, elution behaviour, thermal stability, pH titration and distribution coefficient were studied. XRD pattern confirms the semi crystalline nature of nanocomposite with low intensity peaks. TEM results confirmed the formation of material in the nano-range with particle size of 36nm. pH titration studied showed the monofunctional nature of the material. The distribution coefficient results revealed that the GT/ZONC was highly selective for Ni (II) ions. Some binary separation of metal ion pairs such as Ni²⁺ - Zn²⁺, Cu²⁺ - Al³⁺, Pb²⁺ - Cu²⁺, Co²⁺ - Ni²⁺, Cd²⁺ - Pb²⁺, Mg²⁺ - Cd²⁺, Zn²⁺ - Mg²⁺, Co²⁺ - Al³⁺ were accomplished onto GT/ZONC column. GT/ZONC was investigated for the photocatalytic degradation of methylene blue and degraded 82% of MB within 5 hrs of solar irradiation. Ni (II) ion selective membrane electrode was fabricated with a quick time response and wide pH working range.

Keywords: Gelatin, zirconium dioxide, nanocomposite, ion selective electrode, heavy metals, methylene blue

1. INTRODUCTION

The removal organic and inorganic pollutants from natural water sources have been attracted considerable attention due to their adverse effects on human health and environment. The small amount of these pollutants poses serious effects to the aquatic living organisms. Various industries

such as tannery and bleaching, chemicals, mining, metal finishing and pharmaceutical etc. discharged a large amount of pollutants such as heavy metals, dyes, phenols, antibiotics etc. into aqueous environment. The heavy metals such as Hg (II), Pb (II), Cd (II), Cu (II), Ni (II) and Co (II) etc. are highly toxic, non-biodegradable and carcinogenic in nature [1–4].

Among all these metal ions, nickel is one of the lethal heavy metal. Nickel metal has been widely used in many industries for the production of non-ferrous alloys, stainless steel and nickel based super alloys with high corrosion and temperature resistance properties. The excess of nickel metal bring serious lung and kidney problems, gastrointestinal distress, cardiovascular disorders, pulmonary fibrosis and skin dermatitis.

Dyes are the colored compounds which interferes the penetration of sunlight into aqueous system and decreases the solubility of gases in water. It also retards the process of photosynthesis and affects the growth of aquatic life [5–7]. Methylene blue is a basic dye used for dyeing by various industries such as cotton, wools, hair and paper etc. [8]. Methylene blue is also known as methyl thioninium chloride ($C_{16}H_{18}ClN_3S$) with molar mass of 319.85 g/mol. It can causes several health effects such as hypertension, precordial pain, dizziness, mental confusion, headache, fever, fecal discoloration, nausea, vomiting and abdominal pain etc. Therefore, these pollutants must be removed from the environment.

Different techniques such as chemical precipitation, membrane filtration, coagulation and flocculation, electrochemical treatment, adsorption and ion exchange etc. have been employed for waste water treatment. Among all of these methods, ion exchange method is of great significance due to its high efficiency of sorption of metal ions from aqueous media [9–15].

In recent years, a number of organic and inorganic ion-exchangers have been synthesised for the removal of pollutants. But due to some limitations existing with both of them. The organic ion-exchangers have poor mechanical strength and low thermal stability while inorganic ion-exchangers are non-reproducible with low chemical and mechanical strength. To overcome the limitations of both organic and inorganic ion-exchangers, composite ion-exchangers have been synthesized. These composite materials have better ion exchange capacity, granule metric properties, chemical stability, thermal stability, reproducibility and better selectivity for heavy metal ions as compared to pure inorganic and organic materials [16–20]. These composite materials have been used as a catalyst, ion-exchanger [21,22], ion selective electrode [23–25].

Recently, the natural polymeric materials such as starch, cellulose, protein, chitin, pectin, chitosan, gelatin, alginates etc. have been used for the preparation of composites due to their low cost and renewable nature [5]. Gelatin is a translucent, colorless, brittle, flavorless food produced by partial hydrolysis of collagen extracted from the skin, bones and connective tissues of animals. It has been widely used in pharmaceutical, nutrients, photographic areas and as a binder [26–28].

This work represents the synthesis, characterisation and ion exchange behaviour of the GT/ZONC ion exchanger. Various techniques such as FTIR, XRD, SEM and TEM were used for the analysis of the material. GT/ZONC has been explored for the separation of metal ions and photocatalyst for the photodegradation of methylene blue (MB) under solar exposure. On the basis of K_d values, ion selective membrane electrode of GT/ZONC has been fabricated for the detection of Ni (II) in aqueous system.

2. EXPERIMENTAL

2.1. Reagents and instruments

Gelatin (CDH Pvt. Ltd., India), orthophosphoric acid (CDH Pvt. Ltd., India), zirconium dioxide (CDH Pvt. Ltd., India), sodium chloride (Otto Chemie. Pvt. Ltd. India), sodium hydroxide (Otto Chemie. Pvt. Ltd. India) and metal nitrates such as cobalt nitrate, nickel nitrate, lead nitrate, cadmium nitrate, aluminium nitrate, copper nitrate, zinc nitrate, magnesium nitrate were purchased from Sigma-Aldrich, India. All the reagents used are of analytical grade and dilutions were made using double distilled water. The X-ray diffraction pattern of GT/ZONC was recorded by X'pert Pro Analytical, Netherlands. Fourier transform infrared spectrum of GT/ZONC was recorded by Perkin Spectrum-400 using KBr disc method. The scanning electron microscopes of GT/ZONC at different magnifications were obtained using QUANTA 250 FEI D9393. TEM images of nanocomposite were obtained by Hitachi H7500 model, Germany.

2.2. Synthesis of gelatin-zirconium dioxide (GT/ZONC) ion exchanger

Gelatin-zirconium dioxide nanocomposite (GT/ZONC) ion exchanger was synthesized using sol-gel method at 0–1 pH [29]. In this process, 1.0 N zirconium dioxide and different volume of gelatin gel were mixed at 50–60° temperature with constant stirring. The pH of resulting mixture was adjusted to 0–1 by adding 0.1 N HNO₃. The mixture was stirred for 2 h with continuous stirring and kept for 24 h with occasional shaking. Then, the precipitates were filtered and washed with double distilled water to remove the impurities. The precipitates obtained were dried at 50°C in a hot air oven and converted into H⁺ by adding in 0.1 N HNO₃ solutions for 24 h with occasional shaking. It was then filtered, washed with distilled water and dried at 60°C. Different samples of ion exchanger were synthesized and ion exchange capacities were determined as shown in Table 1. The sample with highest ion exchange capacity was selected for further detail study.

2.3. Physico-chemical properties

2.3.1 Ion exchange capacity (IEC)

The ion exchange capacity of GT/ZONC ion exchanger was determined by standard column process as discussed in literature [18]. In this process, 1.0 g of nanocomposite in H⁺ form was taken in a glass column. 1M solution of alkali and alkaline earth metal nitrate was used as eluent to elute the H⁺ ions at flow rate of 20–25 drops/min. The collected effluent was titrated against a standard solution of 0.1M NaOH using phenolphthalein as an indicator. IEC was calculated by following formula:

$$\text{Ion exchange capacity (IEC)} = \frac{N \times V}{W} \text{ meq/g}$$

where N is the normality, V is the volume of alkali and W is the amount of ion exchanger taken.

2.3.2. Effect of eluent concentration

The optimum concentration of eluent required for the complete elution of H⁺ ions from the ion exchanger was determined. In this, 1.0 g of dry ion exchanger in H⁺ form was taken in glass column and 250mL of sodium nitrate solutions of different concentrations were passed through the column with a flow rate of 20-22 drops/min to elute the H⁺ ions. The collected effluent was titrated against 0.1 M NaOH solution using phenolphthalein as a indicator.

2.3.3. Elution behavior

In this, 1.0 g of GT/ZONC (in H⁺ form) was eluted with 1.0 M NaNO₃ solution. The effluent was collected in fractions of 10 mL at a flow rate of 20-25 drops/min. Each collected fraction was titrated against standard sodium hydroxide solution and total release of H⁺ ions was determined.

2.3.4. Thermal studies

The effect of temperature on the ion exchange capacity of GT/ZONC was studied by heating 1.0 g of GT/ZONC at different temperatures for 1 h in digital muffle furnace. After cooling, the ion exchange capacity was determined by standard column process as mentioned in section 2.3.1.

2.3.5. pH titration

pH titration of GT/ZONC ion exchanger was performed as per method as discussed earlier [30]. In this method, 0.5 g of nanocomposite ion exchanger in H⁺ ions form was taken in 100 mL conical flasks. The equimolar solution of alkali metal hydroxides (NaOH, KOH) and their chlorides (NaCl, KCl) in different volume ratio were mixed in the flasks. The final volume of the solution was maintained at 50 mL in each flask. The pH of the solution was recorded after every 24 h until the equilibrium attained. Then, the pH was then plotted against the mill equivalents of OH⁻ ions added.

2.3.6. Distribution coefficient studies (K_d)

The distribution coefficient of different metal ions onto GT/ZONC was determined by batch method. In this process, GT/ZONC ion exchanger (in H⁺ form) was taken in 20 mL of different metal ions solutions and kept for 24 h with continuous shaking. The concentration of metal ions before and after the equilibrium was determined by titrating against standard 0.01 M ethylenediamine tetraacetic acid. The distribution coefficient values were calculated using following formula [31]:

$$K_d = \frac{I-F}{F} \times \frac{V}{M} \text{ mL/g}$$

where I is the initial amount of the metal ion in the solution phase, F is final amount of metal ion in the solution phase, V is the volume of the solution (mL) and M is the amount of nanocomposite (g).

2.3.7. Binary separation of metal ions

The binary separations of different metal ion pairs were achieved on the column of GT/ZONC. In this, 1.0 g of GT/ZONC (in H⁺ form) was placed into glass column fitted with glass wool and washed with distilled water [32]. The mixture of different metal ions such as Ni²⁺-Zn²⁺, Cu²⁺-Al³⁺, Cu²⁺-Pb²⁺, Co²⁺-Ni²⁺, Cd²⁺-Pb²⁺, Cd²⁺-Mg²⁺, Zn²⁺-Mg²⁺ and Co²⁺-Al³⁺ was passed through the column 3 to 4 times at a flow rate of 20-25 drops/min. The column was then washed with double distilled water to remove the unabsorbed metal ions. The absorbed metal ions were then eluted with different concentrations of acid at a flow rate of 20-25 drops/min. The effluents were collected in 10 mL fractions and the metal ion concentrations were determined using titration analysis [33].

2.3.8. Photocatalytic activity

The photocatalytic activity of GT/ZONC was carried out in a batch reactor at 30±0.5°C [34,35]. In this method, 2 x 10⁵ M solution of methylene blue (MB) dye was prepared in distilled water. 0.1 g of GT/ZONC was added into 100 mL solution of MB with continuous stirring. The slurry of dye solution and catalyst suspension was placed in dark to attain adsorption-desorption equilibrium. Then exposed to sunlight for photocatalysis. 5mL of solution was withdrawn at different intervals of time and centrifuged. The absorbance was recorded at 653 nm and kinetics of MB degradation was studied using pseudo first order kinetic model. The percent degradation of dye was calculated using formula as:

$$\% \text{ Degradation} = \frac{C_0 - C_t}{C_0} \times 100$$

where C₀ is the initial concentration and C_t is instant concentration of dye sample.

2.3.9. Preparation of GT/ZONC ion exchange membrane

The ion exchange membrane of GT/ZONC ion exchanger with different thicknesses were prepared as per method discussed in literature [36,37]. In this, GT/ZONC ion exchanger was grounded to fine powder and mixed with different amount of PVC in 10 mL tetrahydro furan (THF) to form slurry. The resultant slurry was spread between the folds of glossy paper and 2.0 Kg cm⁻² pressure on the plates was applied. The membranes were dipped in double distilled water to remove the glossy paper. In this way, three films of different thickness (0.27 mm, 0.25 mm and 0.24 mm) were prepared and cut into the shapes of disc for detail studies.

2.3.10. Characterization of membrane

Characterization of membrane was done to understand the performance of the membrane. The parameters such as porosity, water content, swelling thickness of membrane were determined as per the procedure given below:

2.3.10.1. Water content (% total wet weight)

Water content of membranes was determined by soaking into the water to eradicate the dissolved salt. Then it was quickly soaked with Whatman filter paper to remove the moisture. Then, the membranes were immediately weighted and dried. The water content was calculated using formula follow as:

$$\% \text{ Total wet weight} = \frac{W_w - W_d}{W_w} \times 100$$

where W_w is the weight of wet membrane and W_d is the weight of dry membrane

2.3.10.2. Porosity

The porosity of the membranes was determined by the volume of water incorporated in the cavities per unit membrane volume. The porosity of membranes were calculated as follow:

$$\text{Porosity} = \frac{W_w - W_d}{\rho LA}$$

where W_w and W_d are weight of wet/soaked membrane, ρ is the density of water, A is the area and L is thickness of the membrane.

2.3.10.3. Thickness and swelling

The thickness of the membranes was measured using screw gauze. The swelling of membranes was measured by calculating from the thickness of membrane before and after equilibrating the membrane with 1M NaCl for 24 h.

3. FABRICATION OF THE ION SELECTIVE MEMBRANE ELECTRODE

The membrane sheet (M-3) of thickness 0.24 mm was cut in the shape of disc and mounted at the lower end of a Pyrex glass tube (o.d. 0.8 cm, i.d. 0.6) with polyvinyl chloride (PVC). It was allowed to dry in air for 24 hrs. Then, the glass tube was filled with standard metal ion solution and a saturated calomel electrode was inserted in the tube for electrical contact. Another saturated calomel electrode was used as external reference electrode. The fabrication of ion selective electrode may be represented as follow:



Different parameters of electrode such as electrode response curve, pH range and response time were measured to analyse the characteristics.

3.1. Electrode response and membrane potential

In this, a series of standard solutions of different concentrations ($1 \times 10^{-1} - 1 \times 10^{-10}$) were prepared and potential were recorded. Before determining the electrode potential, the conditioning of membrane electrode was done by soaking in $1 \times 10^{-1} \text{ molL}^{-1} \text{ Ni(NO}_3)_2$ solutions for 1 hour. Then, the potential of each solution was determined by potentiometer and graph was plotted against concentrations of respective ion solution.

3.2. Effect of pH

In this, a series of solutions of different pH ranged from 1-10 were prepared at constant concentration of $1 \times 10^{-2} \text{ molL}^{-1}$. Then, the values of electrode potential were recorded and plotted against pH.

3.3. Response time

In this, the electrode was firstly dipped in $1 \times 10^{-3} \text{ mol L}^{-1}$ solution of the metal ion and then immediately shifted to another solution of $1 \times 10^{-2} \text{ mol L}^{-1}$ with constant stirring. Then, the potential was recorded just after dipping the electrode in the solution at the interval of 10 sec and the potentials were plotted against time.

4. RESULTS AND DISCUSSION

Different samples of nanocomposite with varying concentration of gelatin were synthesised as shown in Table 1. Sample 7 (S-7) has highest ion exchange capacity of 0.84 meq/g hence considered for further detailed studies. The greater ion exchange capacity (IEC) of the nanocomposite was due to the incorporation of gelatin into the precipitates of zirconium dioxide. The inorganic part of nanocomposite provides large surface area and good mechanical and binding properties [38].

Table 1. Condition of the synthesis and ion exchange capacity of various samples of GT/ZONC ion exchanger

Sample No.	Zirconium dioxide (M)	Gelatin (%)	pH	I.E.C. (meq/g)
S-1	1	0.3	0-1	0.18
S-2	1	0.6	0-1	0.21
S-3	1	0.8	0-1	0.12
S-4	1	0.9	0-1	0.08
S-5	1	1.2	0-1	0.25
S-6	1	1.8	0-1	0.50
S-7	1	2.0	0-1	0.84

The effect of eluent concentration on the ion exchange capacity of GT/ZONC ion exchanger was represented in Fig 1 (a). The optimum concentration of sodium nitrate required for the complete removal of H⁺ ion from ion exchanger was found to be 0.9 M. Fig 1 (b) demonstrates the elution behavior of GT/ZONC ion exchanger. It has been found that 150 mL of sodium nitrate was used to elute the maximum amount of H⁺ ions from ion exchanger.

The pH titration curve for GT/ZONC using NaOH-NaCl and KOH-KCl system was shown in Fig 1 (c). The plot shows one inflection point which indicated the monofunctional nature of the nanocomposite ion exchanger. GT/ZONC has been appeared to be strong cation exchanger, as the initial pH of the solution was very low when no OH⁻ is added to the system [39]. With the addition of NaOH, a steep rise in pH was observed which confirms the strong acidic nature of the material.

Fig 1 (d) demonstrates the X-ray diffraction patterns of GT/ZONC ion exchanger. The X-ray powdered diffraction pattern of nanocomposite showed a number of peaks at different 2θ value. The low intensity small peaks inferred the semi crystalline nature of the material.

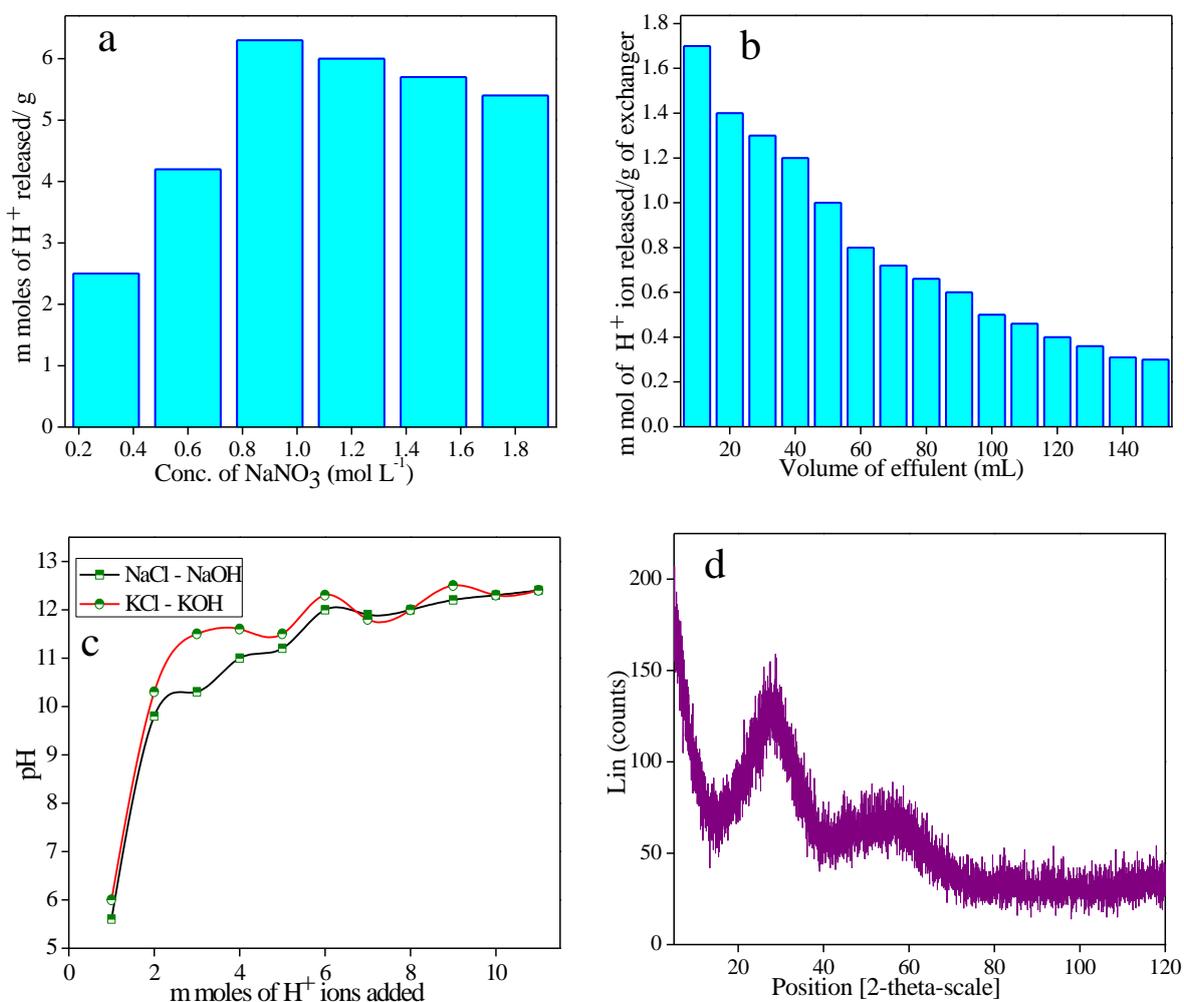


Figure 1. (a) Effect of eluent concentration (b) elution behaviour (c) pH titration curve and (d) XRD spectrum of GT/ZONC

The effect of temperature on the ion exchange capacity of GT/ZONC ion exchanger was described in Table 2. It has been found that the ion exchange capacity of the material decreased with temperature due to the degradation of the organic counterpart. GT/ZONC ion exchanger retained its ion exchange capacity of 1.2 meq/g upto 300°C.

Fig 2 (a) represents the FTIR spectrum of GT/ZONC ion exchanger. A number of peaks were observed which indicated the binding of gelatin to zirconium dioxide. The broad peak at 3321 cm^{-1} was attributed to N-H stretching of gelatin. The absorption peak at 1643 cm^{-1} corresponds to carboxylic acid stretching [40]. A peak at 1542 cm^{-1} was due to asymmetrical stretching of nitro compound. A peak at 660 cm^{-1} shows the bending vibrations of C-H deformation. Fig 2 (b) show the band gap of GT/ZONC ion exchanger and found to be 3.0 eV [41]. It falls in the region of semiconductor therefore acts as a good photocatalyst in the presence of sunlight.

Table 2. Effect of temperature on ion exchange capacity of GT/ZONC ion exchanger

Sr. no.	Temperature ($^{\circ}\text{C}$)	Appearance (color)	Weight loss (g)	Na^+ ion exchange capacity (meq/g)
1	100	White	0.99	2.2
2	200	White	0.99	2.6
3	300	Brown	0.99	1.2
4	400	Light brown	0.98	1.3
5	500	White	0.98	1.0
6	600	White	0.95	1.1

The SEM images of GT/ZONC ion exchanger at different magnifications were shown in Fig 3 (a-b). It has been observed that GT/ZONC ion exchanger exhibits rough surface and granular morphology. The SEM micrographs of GT/ZONC confirmed the formation of nanocomposite. TEM images of GT/ZONC ion exchanger at different magnifications were shown in Fig 3 (c-d). The darker portion confirmed the wrapped gelatin onto the inorganic part. TEM images confirmed the particle size ranged between 36 nm and 55 nm have indicated the formation of nanocomposite.

Distribution studies for eight metal ions in two solvent systems were performed and results were shown in Table 3. It has been observed that GT/ZONC ion exchanger exhibits higher K_d value for Ni (II) as compared to other metal ions. The selectivity of metal ions depends upon the charge, pore size, complex formation, the nature of solvent and pH [42]. The most of the metal ions have high K_d value in hydrochloric acid due to the strong bond formation between metal with the composite material in acidic medium.

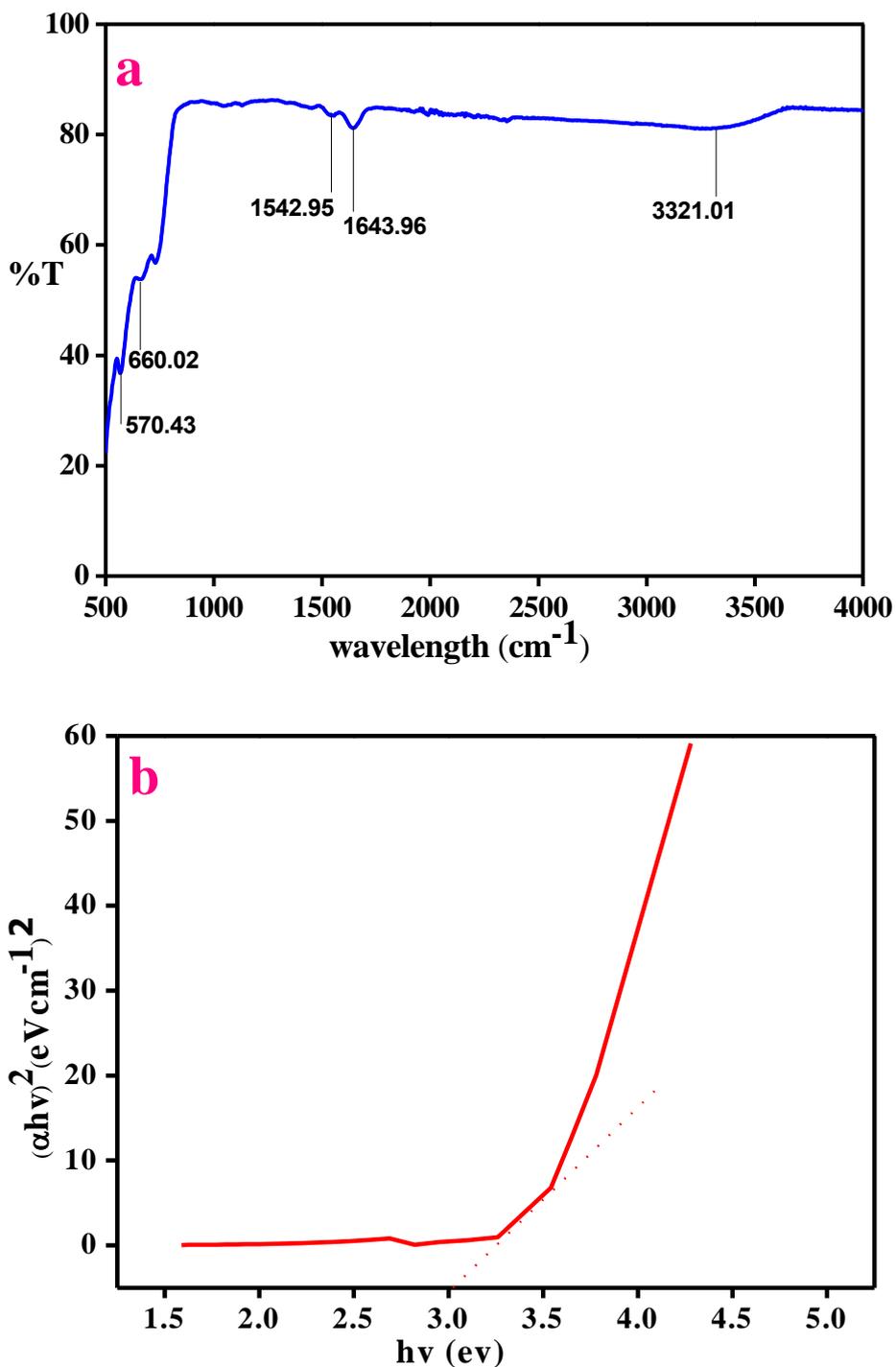


Figure 2. (a) FTIR spectrum of GT/ZONC and (b) Tauc plot of GT/ZONC ion exchanger

The separation capacity of GT/ZONC was attained for different metal ion pairs such as Ni²⁺ - Zn²⁺, Cu²⁺ - Al³⁺, Pb²⁺ - Cu²⁺, Co²⁺ - Ni²⁺, Cd²⁺ - Pb²⁺, Mg²⁺ - Cd²⁺, Zn²⁺ - Mg²⁺, Co²⁺ - Al³⁺. The graphs of elution behavior were shown in Fig 4. The elution of ions depends upon the metal-ligand stability. The weekly retained metal ions were eluted first, followed by strong ones. The separation of metal ions was very sharp, reproducible and quantitative [43-59]. The results of separation were summarized in Table 4.

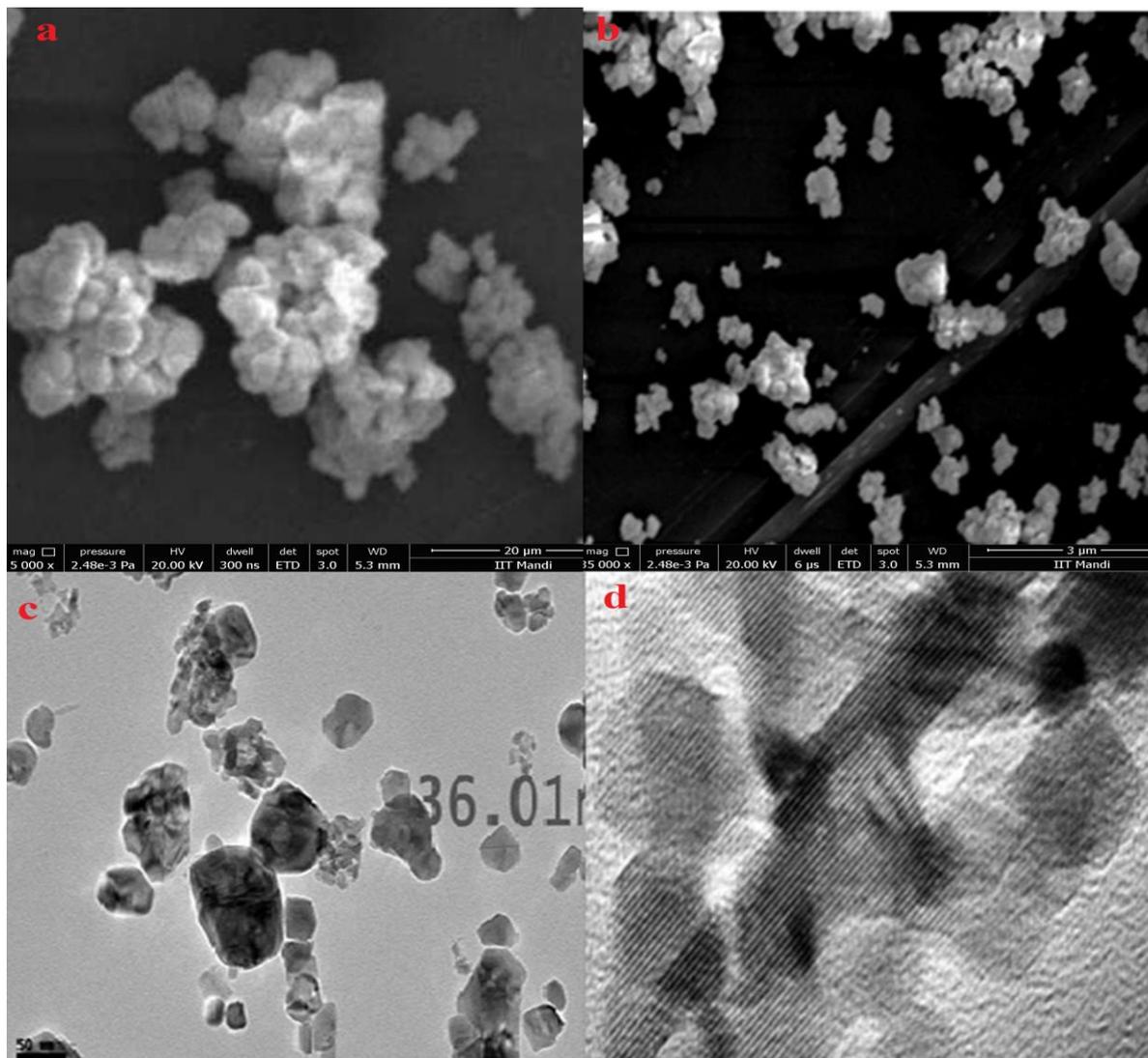


Figure 3. Scanning electron images of (a-b) GT/ZONC ion exchanger and (c-d) Transmission electron micrographs of GT/ZONC

Table 3. Distribution coefficient values of metal ions onto GT/ZONC ion exchanger

Sr. No.	Metal ions	K _d values	
		DMW	HCl (0.1M)
1	Zn ²⁺	15.78	17.19
2	Cd ²⁺	11.11	12.89
3	Mg ²⁺	35.0	36.07
4	Cu ²⁺	17.64	19.08
5	Al ³⁺	20.0	24.66
6	Pb ²⁺	28.57	30.01
7	Ni ²⁺	63.63	65.0
8	Co ²⁺	9.09	11.11

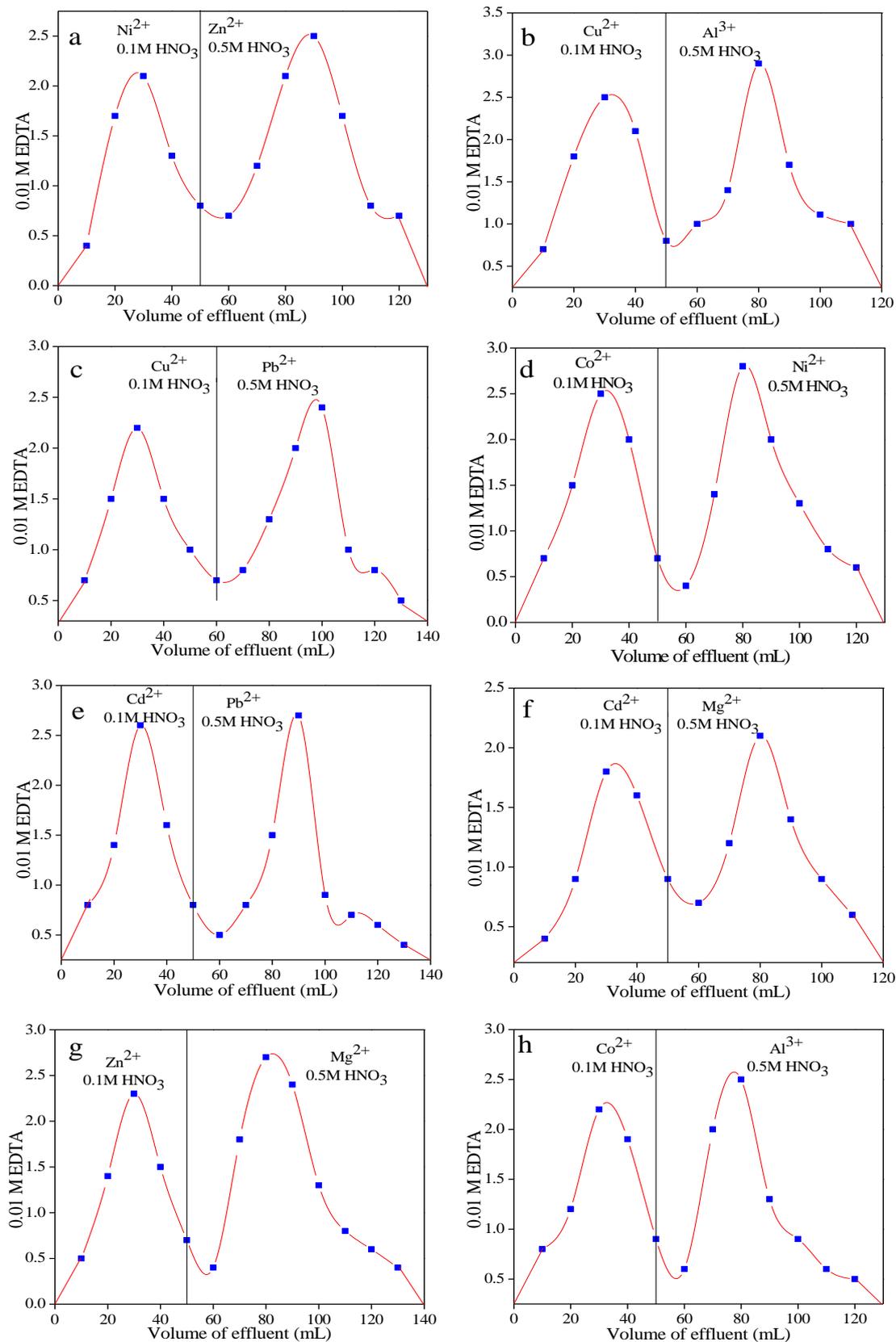


Figure 4. Binary separation of metal ions onto GT/ZONC ion exchanger column

The effect of photodegradation of MB using GT/ZONC was studied. Fig 5 (a) describes the degradation of MB in dark followed by adsorption desorption equilibrium. It has been observed that 62 % MB was adsorbed in dark.

Fig 5 (b) represents the % degradation of MB in dark followed by photocatalysis. It has been found that 82% of MB was degraded within 300 minutes of solar irradiation.

Fig 5 (c) shows the absorption spectra of GT/ZONC at different time intervals. The gradual decrease in adsorption hump confirmed the degradation of the dye continuously. Fig 5 (d) represents the degradation of MB followed by pseudo first-order kinetic model. The photodegradation of MB using GT/ZONC follows pseudo-first-order kinetics with rate constant $K = 0.0049 \text{ min}^{-1}$ and $R^2 = 0.998$.

Table 5 represents the results of thickness, swelling, porosity and water content of GT/ZONC ion exchange membrane. The membrane (M-3) with thickness 0.24 mm was selected for further studies due to its less thickness, porosity and low water content.

Table 4. Binary separation of metal ions onto GT/ZONC ion exchanger

Sr. No.	Binary mixtures	Eluent used	Volume of eluent required for elution of metal ions (mL)	Amount loaded (mg)	Amount found (mg)	Recovery (%)
1	Ni(II)	0.1N HNO ₃	50	5.86	3.69	62.90
	Zn(II)	0.5N HNO ₃	70	6.53	5.81	88.90
2	Cu(II)	0.1N HNO ₃	50	6.3	5.00	79.36
	Al(III)	0.5N HNO ₃	60	2.64	2.40	90.90
3	Cu(II)	0.1N HNO ₃	60	6.3	4.82	76.50
	Pb(II)	0.5N HNO ₃	70	20.7	18.2	87.92
4	Co(II)	0.1N HNO ₃	50	5.89	4.24	71.98
	Ni(II)	0.5N HNO ₃	70	5.86	5.39	91.97
5	Cd(II)	0.1N HNO ₃	60	11.2	8.09	72.23
	Pb(II)	0.5N HNO ₃	70	20.7	16.78	81.06
6	Cd(II)	0.1N HNO ₃	50	11.2	6.20	55.00
	Mg(II)	0.5N HNO ₃	70	2.4	1.70	70.00
7	Zn(II)	0.1N HNO ₃	60	6.5	4.50	69.00
	Cd(II)	0.5N HNO ₃	70	2.4	2.21	91.00
8	Co(II)	0.1N HNO ₃	50	5.8	4.23	72.00
	Al(III)	0.5N HNO ₃	70	2.69	2.29	85.00

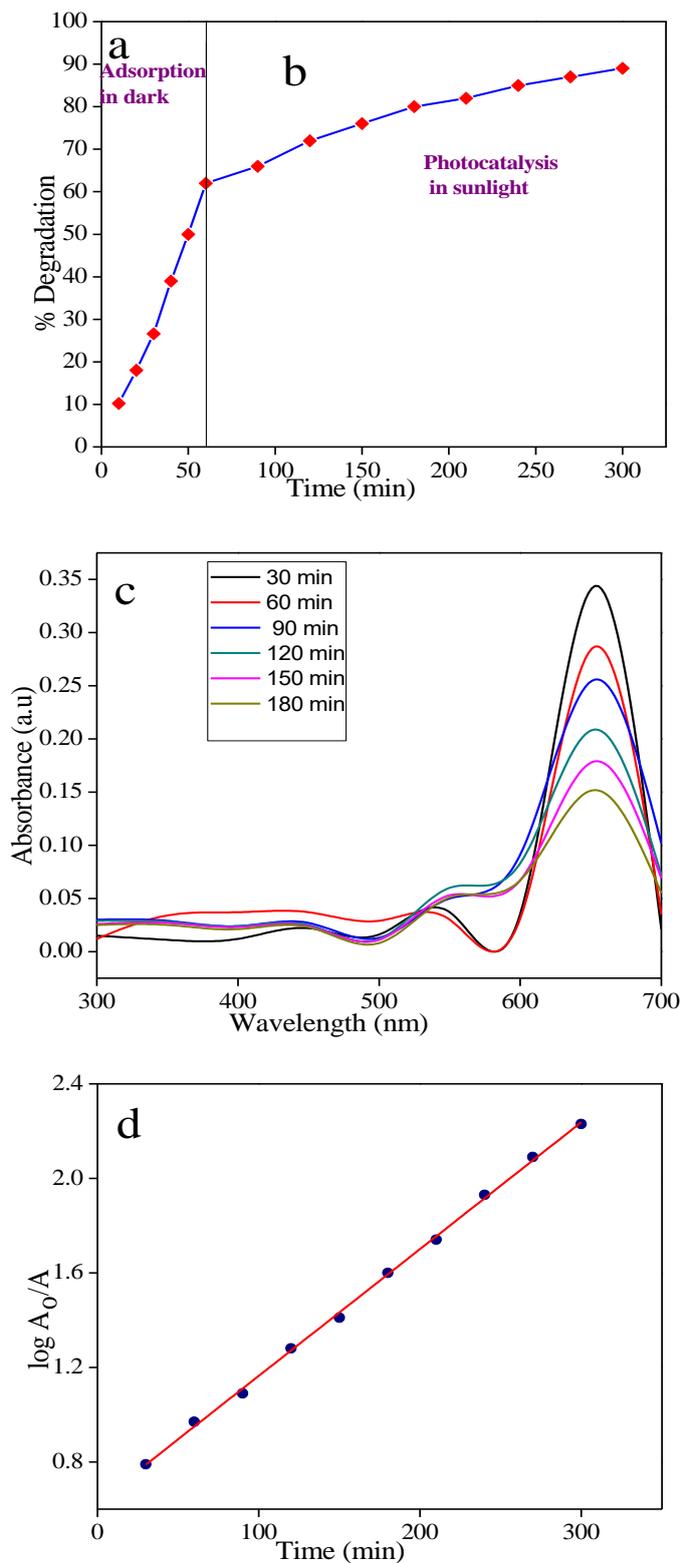


Figure 5. (a) % degradation of MB in dark followed by photocatalysis (b) UV-Vis absorption spectra of MB at different irradiation time (c) Pseudo-first-order kinetics graph for photodegradation of MB onto GT/ZONC

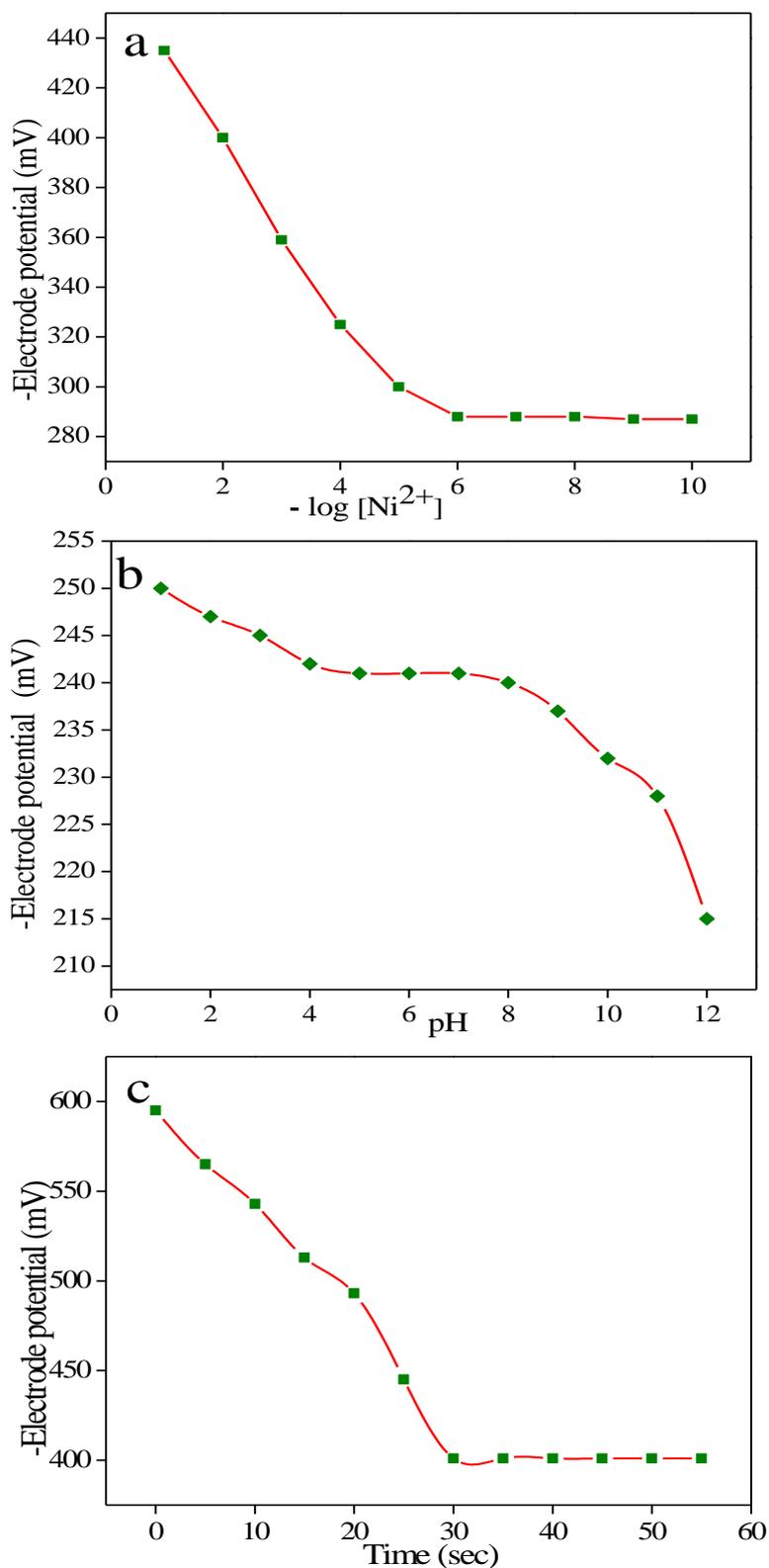


Figure 6. (a) Calibration curve of GT/ZONC ion exchanger membrane electrode in Ni(NO₃)₂ solution (b) Effect of pH on the potential response at 1 × 10⁻² mol/L of Ni²⁺ (c) Time response curve

Fig 6 (a) represents the electrode response of heterogeneous precipitate based membrane electrode against different concentrations of Ni^{2+} ions. A linear response was obtained in the concentration ranged from $1 \times 10^{-1} \text{ molL}^{-1}$ to $1 \times 10^{-6} \text{ molL}^{-1}$, which indicates the working concentration of electrode. The slope of electrode response was found to be 15.26 mV.

Fig 6 (b) shows the effects of pH on the potential response for a fixed concentration of Ni^{2+} ions. It was evident that the electrode potential was unchanged within the pH range 4.0-8.0. After that, the electrode was unable to work due to the formation of Ni (II) hydroxides [44,45]. Thus the optimum pH range for operation of electrode was 4.0-8.0.

The response time in contact with $1 \times 10^{-2} \text{ mol L}^{-1} \text{ Ni}^{2+}$ ion solution was determined and the results were shown in Fig 6 (c). The response time of the membrane was found to be 30 seconds.

5. CONCLUSION

Gelatin-zirconium dioxide nanocomposite ion exchanger was synthesized by simple sol-gel method. The nanocomposite was characterised by different techniques such as FTIR, SEM, TEM and XRD. TEM studies confirmed the formation of nanocomposite. Distribution studies revealed that GT/ZONC was highly selective for Ni (II) ions. 82% of MB was degraded by GT/ZONC within 300 minutes of solar exposure. An ion selective membrane electrode of GT/ZONC was fabricated for the detection of Ni (II) ions. The membrane electrode shows good linear response in concentration ranged from $1 \times 10^{-1} \text{ molL}^{-1}$ to $1 \times 10^{-6} \text{ molL}^{-1}$, with pH range 4.0-8.0 and quick response time of 30 seconds. Hence, it may be concluded that GT/ZONC ion exchanger can be potentially used for the detection of Ni(II) ions in aqueous system.

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