International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Zirconium (IV) phosphate/poly(gelatin-cl-alginate) Nanocomposite as Ion Exchanger and Al³⁺ potentiometric Sensor

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Received: 25 September 2017 / Accepted: 26 November 2017 / Published: 16 December 2017

Zirconium (IV) phosphate/poly(gelatin-*cl*-alginate) (ZP/PGA) nanocomposite ion exchanger was studied as potentiometric sensor for the detection of aluminium ions in aquatic system. ZP/PGA has been analysed by X-ray diffractometer (XRD), Fourier transform infra-red spectrogram (FTIR), thermo-gravimetric analysis (TGA), field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM). TGA and XRD analysis revealed that ZP/PGA nanocomposite was highly thermo-stable and semi-crystalline in nature. The pH results show the bifunctional nature of ZP/PGA nanocomposite. Distribution studies concluded the greater sensitivity of material for aluminium ions (K_d=65). Thus, the assembly of potentiometric sensor for the estimation of Al³⁺using ZP/PGA was attempted. Linear Nernstian response was detected over wide concentration. The binary separations such as Ni²⁺-Al³⁺, Zn²⁺-Al³⁺, Co²⁺-Mg²⁺, Cu²⁺-Mg²⁺, Cd²⁺-Pb²⁺, Co²⁺-Pb²⁺, Zn²⁺-Cu²⁺, Ni²⁺-Cd²⁺ have been attempted onto ZP/PGA column. The efficiency of ZP/PGA was investigated for remediation of methylene blue (MB) and methylene green (MG) under solar irradiations. ZP/PGA also showed good antimicrobial activity for *E. coli*.

Keywords: Nanocomposite, heavy metals, ion selective electrode, photocatalysis, antimicrobial.

1. INTRODUCTION

The presence of pollutants in water system posed serious effect to all living organisms. The contaminated water contains miscellaneous noxious waste for example heavy metals, dyes, bacteria, phenols and pesticides etc.[1-4]. Metallic compounds are migrated from diverse technological sectors into the surroundings and accumulated throughout the bionetwork. The higher level of heavy metals in

water system causes harmful effect to the living organisms. The consumption of metals causes various illnesses such as pneumonitis, diarrhoea, fever, encephalopathy, vomiting, nausea, gastrointestinal haemorrhage, haemolysis and kidney diseases etc. to human being [5].

The several industrial routes such as dyestuffs, textile, leather, foodstuffs, cosmetics etc. continually discharged the coloring materials into the water sources. Dyes effluents are recognized as highly toxic, non-biodegradable and carcinogenic. Different routes such as adsorption, photocatalysis, precipitation, ion exchange, membrane filtration etc. were investigated for the remediation of pollutants. The ion exchange method was found superior to other due to cost effective, energy efficient and easy handling.

Recently, the drawbacks of both inorganic and organic ion exchangers encouraged for synthesis of composite materials [6-9]. Hence, the importance of composite materials increased in different areas like membrane separations, adsorption, catalysis, sensing, drug delivery etc.

However, biopolymer supported nanocomposites were extensively used due to their stability, biodegradability, low-cost and easy availability. Meanwhile, the properties like hydrophilic nature and brittleness of bio-polymers restrict their worth in various fields. To overcome the limitations of natural polymers, chemical modifications approach has been insighted by various researchers [10, 11].Graft co-polymerisation technique is the most exploited techniques used add new functionality to the polymers.

Gelatin and alginate is non-toxic biodegradable polymer, which offers widespread applicability such as adhesive, absorbent pad, wound dressing, plasma expander and biopharmaceutical materials [12-16]. Alginate is a polysaccharide copolymer consists of homopolymeric blocks of (1-4)-linked β -D-mannuronate (M) and C-5 epimer α -L-guluronate (G) residues and found in brown algae. Alginate possesses unique properties like toughness, visco-elasticity and adsorptive nature which boosted their functioning in different sectors [17-20].

In this, we described the preparation of ZP/PGA ion exchanger using simple method. ZP/PGA nanocomposite has been characterized using different instrumental systems such as FTIR, XRD, FESEM, TGA and HRTEM. Moreover, binary separations have been attempted onto the ZP/PGA column. ZP/PGA was utilized for the remediation of MB and MG dyes under solar irradiations. Furthermore, antimicrobial behavior of nanocomposite was investigated for *E. coli*. The ZP/PGA nanocomposite was used to prepare Al^{3+} selective electrode.

2. EXPERIMENTAL

2.1. Materials

Zirconium oxy chloride, orthophosphoric acid, nitric acid and tetra hydrofuran were bought from Central Drug House, India. All metal nitrates, gelatin and alginate were acquired from Qualigens Pvt. Ltd., India.

2.2. Characterization technique

996

KBr disc method in range of 4000-400 cm⁻¹ were explored to determine the FTIR spectrum of ZP/PGA nanocomposite using Perkin–Elmer, USA, model Spectrum-BXSHIMADZU (1730, Japan) spectrometer. SEM images were recorded by Nova Nano FESEM 450 (FEI Technai) and TEM micrographs of ZP/PGA nanocomposite were analyzed on FEI 200 Kv Tecnai transmission electron microscope. XRD pattern was recorded on Phillips (Holland, PW 1148/89). Thermal analysis (TGA) of material was performed using thermogravimetric analyzer (Perkin Elmer TGA7). The nanocomposite was heated in the intervals of 20°C min⁻¹ in the atmosphere of oxygen.

2.3. Synthesis of zirconium (IV) phosphate/poly(gelatin-cl-alginate) nanocomposite

Co-precipitation followed by in-situ polymerization method has been used for preparation of ZP/PGA. In first step, zirconium (IV) phosphate was synthesized by mixing 0.1 N ZrOCl₂ and 0.1 N H_3PO_4 in 1:2 volume ratio at pH 0-1. It was unceasingly stirred for 2 hrs, filtered and washed with distilled water. Then, the precipitates were dried in an oven at 60°C. In next step, a fixed amount of alginate and gelatin was mixed to form the gel in warm water with continuous stirring. Then, gel was transferred into the zirconium (IV) phosphate precipitates at 60-70°C with shaking for 2 hrs. Definite amount of initiator and cross linker were mixed to above solution with continuous shaking. The resulting mixture was kept for 2 hrs with continuous stirring. The precipitates were filtered and dried at 50°C. The material was changed into H⁺ using 0.1 N nitric acid. Then, the precipitates were filtered and dried at and dried. The other samples were also prepared by same procedure and sample S-3 having high ion exchange capacity has been selected for subsequent work.

2.4. Physicochemical properties

2.4.1. Ion exchange capacity (IEC)

In this, fixed amount of ZP/PGA was placed in a column fitted with glass wool at bottom. Then, 0.1 M HNO₃ was circulated through the column to convert the material into H^+ form. Now, H^+ ions were eluted from the column using alkali nitrates. Then, the obtained effluent was titrated using method reported in the literature [21].

2.4.2. Thermal behavior

In this, 1.0 g of material was heated at temperature ranged from 100-600°C for 1 hour. After cooling, the ion exchange capacity of each sample was calculated by column method as discussed in section 4.1.

In this, 250 mL of NaNO₃with different concentration (0.1M, 0.4M, 0.7M, 1.0M, 1.3M, 1.6M, 2.0M) were circulated through a glass column containing 1.0 g of ion exchanger at flow rate of 20-25 drops/min. The effluents were collected and titrated with standard NaOH. To study the efficiency of column, NaNO₃ solution with high value of IEC was passed through the column containing 1.0 g of material (in H^+ form). The effluent was collected in 10 mL fractions at a flow rate 20-25 drops/min. The each fraction was titrated with sodium hydroxide.

2.4.4. pH titrations

The pH titration was studied by method referred in the literature. In this process, 0.5 g of ZP/PGA nanocomposite was placed in 250 mL conical flasks. The final volume in flasks was adjusted to 50 mL, by adding0.1M solutions of NaCl-KCl and NaOH-KOH in different volume ratios. pH of each one was noted after 24 hrs to attain equilibrium.

2.4.5. Distribution coefficient (K_d)

The sorption study was explored to investigate the ability of nanocomposite for heavy metal removal. The distribution coefficient studies of eight metal ions onto ZP/PGA were determined by batch method. In this, 200 mg of ZP/PGA nanocomposite (in H^+ form) was put into metal nitrate solutions (20 mL) and kept for 24 hrs. Then, the metal solutions were filtered and titrating with 0.01 M EDTA [21]. K_d values of different metals were calculated from the formula as mentioned somewhere in literature [20].

2.4.6. Binary separations

The quantitative separations of eight metal ion pairs were attempted onto ZP/PGA nanocomposite columns. In this, 1.0 g of dry nanocomposite (in H^+ form) was placed in a glass column fitted with a glass wool. The column was washed carefully with double distilled water. Then, the mixture of two different metal ions each with 0.1 molL⁻¹concentration was passed through ZP/PGA nanocomposite column at a flow rate of 25 drops/min. This procedure was repetitive for 2-3 times to confirm the sorption of metal on the nanocomposite. The separation ability of metal ions were accomplished by collecting effluent in 10 mL fractions and titrated with 0.01 molL⁻¹EDTA [21, 22].

2.4.7. Photocatalytic studies

The photocatalytic activity of ZP/PGA nanocomposite was studied for the photodegradation of methylene blue (MB) and malachite green. In this, 100 mg of nanocomposite was added into MB $(1.5 \times 10^{-5} \text{ M})$ and MG (2×10^{-5}) solutions. The resulting solutions were kept in dark to achieve the

adsorption-desorption equilibrium. Then, the solutions were exposed to solar light for photodegradation of dyes. Now, 5 mL of each dye solutions were withdrawn at different time period and centrifuged to separate the particles of nanocomposite. The kinetics of photocatalytic degradation of MB and MG was calculated at 662 nm and 625 nm. The degradation percentage of dyes was determined using formula as described in literature [23-25].

2.5. Preparation of membrane using ZP/PGA

Different membranes of ZP/PGA were prepared as per method discussed in the literature [26].In this, the composite was grounded to fine powder. It was mixed with different amount of PVC in 10-15 mL tetra hydro furan (THF) to form the slurry. The resultant slurry was spread over the glossy paper and 2.0 Kg cm⁻² pressure was applied over it for 24 hrs. Then, the paper was removed by dipped in double distilled water and the membrane gets separated from it. In this way, three films of different characteristics were prepared and cut into the shapes of disc by a sharp edge blade for detail studies.

2.5.1. Optimization of membrane

Before the membrane was fabricated to the electrode, some parameters have been studied as discussed below [27-29]:

2.5.1.1. Water content

Total wet weight of membranes was calculated by soaking the membranes into double distilled water to elute the diffusible salt. Before weighing, the membranes were dried quickly to remove the surface moisture. It was then weighed directly using weighing balance and the membranes were dried for 24 hrs. The total wet weight was calculated by formula as discussed in literature [43].

2.5.1.2. Porosity

In this, the porosity of membranes was studied by the volume of water incorporated in the voids per unit volume of membrane. It was determined by equation as reported in literature [43].

2.5.1.3. Thickness and swelling

Average thickness of the membranes was determined by screw gauze. To determine the swelling behavior of membranes, the difference between average thicknesses of the membrane (when dipped in 1 molL^{-1} NaCl) for 24 hrs and weight of dry membrane was taken.

2.6. Fabrication of ion-selective membrane electrode

In this arrangement, the membrane of 0.20 mm thickness was cut into a disc form and fixed at the lower end of glass tube with polyvinyl chloride (PVC). It was dried and the tube was filled with 0.1 M aluminium nitrate solution. A saturated calomel electrode (SCE) was injected in the tube containing 0.1 M Al(NO₃)₃and another SCE was used as an external reference electrode. The whole sequence can be shown as:

Internal reference	Internal electrolyte	Membrane	Sample	External reference
electrode	0.1 M Al^{3+}		solution	electrode

The different parameters of electrode were measured in details to analyze its characteristics as discussed below:

2.6.1. Electrode response or membrane potential

The solutions of Al(NO₃)₃ with different concentrations ranged from 1×10^{-1} to 1×10^{-10} were prepared to examine the membrane potential. Firstly, the electrode membrane was conditioned by soaking in 0.1 molL⁻¹solution of Al(NO₃)₃ for 5–7 days and then the potentials were determined using potentiometer. The observed potential values of electrode were plotted against selected concentration of the ion.

2.6.2. Effect of pH

In this, the solution of Al(NO₃)₃ at different pH ranged from 1–12 was prepared at constant ion concentration $(1 \times 10^{-2} \text{ molL}^{-1})$ by adding 0.1N HCl and 0.1N NaOH solution. Then, the electrode potential of each solution at different pH was recorded and plotted against pH values.

2.6.3. The response time

In this, the electrode was first dipped in $Al(NO_3)_3$ solution of $1 \times 10^{-3} \text{ molL}^{-1}$ for 10 sec and then shifted to solution having 10-fold higher concentration($1 \times 10^{-2} \text{ molL}^{-1}$) with constant stirring. Then, the electrode potential was measured in both the solutions and graph was plotted between potentials versus time. The time duration when the potentials reached to constant value signifies the response time of the electrode.

2.6.4. Potentiometric titration

In this, 10 mL of $1 \times 10^{-3} \text{ molL}^{-1}$ of Al (III) solution was prepared in 50.0 mL beaker. The resulting solution was titrated with $1 \times 10^{-2} \text{ molL}^{-1}$ EDTA. The obtained electrode potential values were plotted against standard EDTA solution.

3. RESULTS AND DISCUSSION

The synthesized nanocomposites have been enumerated in the Table 1. Scheme 1 represents the synthesis of ZP/PGA nanocomposite ion exchanger. Sample S-3 showed highest ion exchange capacity (IEC) of 1.03 meq/g and greatest stability over other samples. Therefore, S-3 was taken further for detailed analysis. The ion exchange capacity of nanocomposites was increased due to incorporation of organic material with inorganic part. The organic part provides enlarged surface area and enhanced mechanical strength [30].

S. no.	А	В	С	Temperature	Color	Ion exchange
	(g)	(g)	(g)	°C)		capacity (meq/g)
S-1	0.5	0.4	1.0	60°C	White	0.70
S-2	0.5	0.4	1.5	60°C	Light yellow	0.89
S-3	1.0	0.8	2.0	60°C	Yellow	1.03
S-4	2.0	1.2	2.5	60°C	Dark yellow	0.64

Table 1. Optimization of reaction parameters and ion exchange capacity of ZP/PGA

A: Gelatin; B: Alginate; C: Zirconium (IV) phosphate



Scheme 1. Synthesis of ZP/PGA nanocomposite

The temperature effect on ion exchange capacity of ZP/PGA nanocomposite was described in Table 2. 83.49 % of retention in IEC upto 400°C was found due to the loss of surface water molecules and conversion of material into oxide form. Fig 1(a) demonstrates the decreased order of IEC values with increase in temperature.

Fig 1(b) represents the effect of eluent concentration on the ion exchange capacity of ZP/PGA nanocomposite. The optimized concentration NaNO₃ for complete elution of (H^+ ions) was 0.7 M.

Fig 1 (c) depicts the elution behavior of ZP/PGA nanocomposite. It has been recorded that 150 mL of 0.7 M NaNO₃was required for the elution of H^+ ions from column.

Fig 1(d) elucidates the pH titration curve for NaOH–NaCl and KOH–KCl systems. Two inflection points in the curve indicated the bifunctional nature of ZP/PGA nanocomposite. The weak acidic groups were un-dissociated when the pH low and solutions were neutralized by adding NaOH [31].Therefore, the weak acidic group was dissociated and the ion exchange process moves toward completion. The sharp rise in pH at the end occurred due to the exchange of strong acidic groups with Na⁺ ions.



Figure 1. (a) Effect of temperature on ion exchange capacity (b) Effect of eluent concentration (c) Elution behavior (d) pH titration curve of ZP/PGA nanocomposite ion exchanger

Temp. (°C)	Temp. (°C) Color		Ion exchange capacity (meq/g)	% Retention in IEC
50	White	_	1.03	100
100	White	0.81	0.92	89.3
200	Dark brown	0.77	0.90	87.37
300	Black	0.64	0.89	86.40
400	Black	0.61	0.86	83.49
500	White	0.59	0.72	69.90
600	White	0.39	0.68	66.01

Table 2. Ion exchange capacity of ZP/PGA nanocomposite ion exchanger at different temperatures

3.1. Characterization of ZP/PGA nanocomposite

Fig 2 (a) inferred the FTIR spectrum of ZP/PGA nanocomposite. Peak at 3446 cm⁻¹ assigned to stretching vibrations of –OH group of coordinate water molecule [32]. Peaks at 1631 cm⁻¹ and 1412 cm⁻¹ were due to bending of -NH₂ with free water molecule and symmetric stretching of -COOH group [33]. The sharp peaks at 1721 cm⁻¹ and 1026 cm⁻¹ attributed to C=O stretching of amide and C-C symmetric stretching vibration. The peaks at 1219 cm⁻¹ and 512 cm⁻¹ corresponds to stretching of hydrogen bonded phosphate and Zr-O vibrations [34]. Fig 2 (b) represents the XRD of ZP/PGA nanocomposite. The low intensity peaks confirmed the semi crystallinility of nanocomposite.

Thermal decomposition study of ZP/PGA nanocomposite was illustrated in Fig 2 (c). The results inferred that 11.82 % weight loss was recorded upto 100°C. It was due to the loss of surface water molecule [35]. Further, 19.89 % of weight loss was found between 200°C to 470°C attributed to the removal of internal water molecules caused by the condensation of –OH groups [36]. The weight loss of 24.11 % was observed between 470 °C to 500 °C with due to conversion of phosphate group to pyrophosphate [37]. Further, weight loss of 17.33 % was found between 500 °C to 700 °C due to organic part breakdown and upto 1000°C no weight loss was observed.

The band gap of ZP/PGA was calculated using tauc relation and found to be 3.19 eV which indicates that the synthesized material is semiconductor in nature. The tauc plot of ZP/PGA nanocomposite was depicted in Fig 2 (d).



Figure 2. (a) FTIR spectrum of ZP/PGA nanocomposite (b) XRD spectrum of ZP/PGA nanocomposite (c) TGA curve of ZP/PGA nanocomposite (d) Tauc plot of ZP/PGA nanocomposite ion exchanger.

Fig 3(a - b) shows the SEM images of ZP and ZP/PGA nanocomposite. The morphological changes described that the smooth and uniform surface of ZP completely reformed to irregular and rough surface due to incorporation of organic part which confirms the formation of composite material.

TEM results of ZP/PGA nanocomposite at different resolutions were described in Fig 3(c - d).TEM micrographs showed the mixed morphology with small interstitial gaps which favor the sorption of metal ions and dyes. The particles size was ranged between 20–24 nm inferred the formation of nano material. The SAED pattern (Fig3c inset) inferred the semi crystalline nature of ZP/PGA nanocomposite.



Figure 3. SEM images of (a) ZP (b) ZP/PGA nanocomposite (c-d) TEM images of ZP/PGA nanocomposite at different magnifications (SAED pattern inset)

3.2. Distribution coefficient

The distribution coefficient studies of ZP/PGA were evaluated for eight metal ions in different solvent as summarized in Table 3.The values of distribution coefficient were found higher for Al^{3+} . The order of K_d values onto ZP/PGA was $Al^{3+}(65.00) > Mg^{2+}(41.66) > Pb^{2+}(36.66) > Cd^{2+}(29.00) > Cu^{2+}(21.05) > Zn^{2+}(20.83) > Co^{2+}(16.66) > Ni^{2+}(16.00)$. The higher distribution coefficient values in DMW in contrast to other medium were due to slow release of H⁺ ions onto ZP/PGA column. It results less adsorption of metal ions in strongly acidic medium and vice versa [39, 40].

Table 3. K _d values	of different metal	ions using Z	ZP/PGA nanocompos	site column at	different solvent
system					

G N		K _d (mL/g)		
Sr. No.	Metal ions	Distilled Water	0.1N HNO3	0.5N HNO ₃
1	Al ³⁺	65.00	56.34	50.34
2	Cu^{2+}	21.05	14.24	9.18
3	Mg^{2+}	41.66	35.65	31.23
4	Cd^{2+}	29.00	26.67	22.32
5	Co^{2+}	16.66	12.41	8.44
6	Ni ²⁺	16.00	15.35	14.32
7	Zn^{2+}	20.83	16.33	13.67
8	Pb^{2+}	36.66	33.33	24.98

3.3. Binary separation of metal ions

The separation ability of ZP/PGA nanocomposite was established by accomplishing binary separations of metal mixtures. Fig 4and Table 4demonstrates the binary separations such as Ni²⁺-Al³⁺, Zn²⁺-Al³⁺, Co²⁺-Mg²⁺, Cu²⁺-Mg²⁺, Cd²⁺-Pb²⁺, Co²⁺-Pb²⁺, Zn²⁺-Cu²⁺, Ni²⁺-Cd²⁺. The elution of metal ions on ZP/PGA depends upon the stability of metal eluting ligand [41]. The separations were found relatively sharp and recovery was quantifiable and reproducible in nature.



Figure 4. Binary separation of metal ions onto the ZP/PGA nanocomposite ion exchanger column

Table	4.	Binary	separation	of	metal	ions	accomplished	onto	ZP/PGA	nanocomposite	ion	exchanger
	co	lumn										

Binary mixtures	Amount loaded (mg)	Amount found (mg)	% Recovery	Eluent used	Volume of eluent required for elution of metal ions (mL)
Ni ²⁺	5.86	3.93	67.10	0.1 N HNO ₃	50
Al ³⁺	2.69	2.53	92.27	0.5 N HNO ₃	60
Zn^{2+}	6.53	3.92	60.00	0.1N HNO ₃	50
Al ³⁺	2.69	2.53	94.27	0.5 N HNO ₃	60
Co ²⁺	5.89	2.59	44.70	0.1N HNO ₃	40
Mg ²⁺	2.43	1.72	71.00	0.5 N HNO ₃	50
Cu ²⁺	6.35	3.55	56.00	0.1N HNO ₃	50
Mg ²⁺	2.43	1.94	79.83	0.5 N HNO ₃	60
Cd^{2+}	11.24	9.44	84.00	0.1N HNO ₃	40
Pb ²⁺	20.72	19.06	92.00	0.5 N HNO ₃	50
Co ²⁺	5.89	5.24	89.04	0.1N HNO ₃	40
Pb ²⁺	20.72	19.27	93.00	0.5 N HNO ₃	50
Zn^{2+}	6.53	4.31	65.78	0.1N HNO ₃	40
Cu ²⁺	6.35	5.40	85.06	0.5 N HNO ₃	50
Ni ²⁺	5.86	4.69	80.03	0.1N HNO ₃	50
Cd ²⁺	11.24	9.89	88.32	0.5 N HNO ₃	60

3.4. Photocatalytic degradation

The photocatalytic degradation of MB and MG was investigated onto ZP/PGA nanocomposite. Figs 5 (a) and 6 (a) describes the % degradation of MB and MG in dark followed by photocatalysis. 24.90 % and 32.18% of MB and MG were removed in dark. And, 94.33% of MB was removed within 5 hours of solar illumination. While 86.63% MG was degraded in 3 hours of irradiation.

Figs 5 (b) and 6 (b) illustrated the decrease in absorption spectra of MB and MG in different intervals of irradiation time. The adsorption hump decreased continuously with different irradiation time which indicated that ZP/PGA nanocomposite degraded both dyes gradually.

The degradation of MB and MG followed by pseudo first-order kinetic model as shown in Figs 5 (c) and 6 (c). It was recorded that MB has higher value of regression coefficient (R^2 = 0.983) as compared to MG (R^2 =0.964). The results summarizes that ZP/PGA nanocomposite effectively degraded both the dyes.



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 ZP/PGA nanocomposite.



Figure 6. (a) % degradation of MG in dark followed by photocatalysis (b) UV–Vis absorption spectra of MG at different irradiation time (c) Pseudo-first order kinetics graph for photodegradation of MG onto ZP/PGA nanocomposite

3.5. Ion selective electrode studies

The ion exchanger was investigated for the preparation of heterogeneous ion selective membrane electrode. The different parameters such as mechanical stability, uniform surface and thickness of the ZP/PGA electrode have been studied as presented in Table 5.Sample 3 (M-3) with minimum thickness 0.20 mm was designated for detailed studies because this membrane has also less water content, swelling and porosity. The different parameters of selected electrode membrane were described in Fig 7.

Membrane	Mixing ratio	Thickness (mm)	Water content (%)	Porosity	Swelling of % weight of wet membrane
M-1	1:1	0.33	11.33	2.3×10^{-4}	0.003
M-2	1:2	0.27	8.76	4.3×10^{-3}	0.002
M-3	2:1	0.20	6.90	6.0×10^{-4}	0.004

Table 5. Characteristics of ZP/PGA nanocomposite ion exchange membrane



Figure 7. (a) Calibration curve of ZP/PGA nanocomposite ion exchanger membrane electrode in Al(NO₃)₃solution (b) Time response curve (c) Effect of pH on potential response at 1×10^{-2} mol/L Al³⁺ (d) Potentiometric titration of Al (III) ions against EDTA solution with ZP/PGA membrane electrode

Fig 7 (a) showed a linear response in the concentration ranged from $1 \times 10^{-1} \text{ molL}^{-1} \text{to } 1 \times 10^{-6} \text{ molL}^{-1}$ with continuous decrease of electrode potential value. The slope of electrode response was observed at 20.55 mV. Thus, the working concentration range of material were found from $1 \times 10^{-1} \text{ molL}^{-1}$ to $1 \times 10^{-6} \text{ molL}^{-1}$ for Al³⁺ ions and below these concentrations nonlinear response was observed [42, 43].

Fig 7 (b) shows the response time of ZP/PGA nanocomposite membrane electrode in 1×10^{-2} molL⁻¹ Al³⁺ solution. The rapid response time of electrode for the detection of Al³⁺was ~40 seconds.

Fig 7 (c) exhibits the effect of variation of pH (1 to 12) on electrode potential for a fixed concentration $(1 \times 10^{-2} \text{ molL}^{-1})$ of Al³⁺ ions. The electrode potential remains unaffected for pH ranged between 5.0 and 8.0. Below pH – 5 and above pH-8, the membrane electrode was not able to work due to proton selectivity of the material and formation of Al (III) hydroxides.

Fig 7 (d) shows the potentiometric titration curve for Al^{3+} ions against EDTA solution with ZP/PGA membrane electrode. The electrode potential of membrane decreased with addition of EDTA due to complex formation with aluminum ion [43-55].

4. CONCLUSION

ZP/PGA nanocomposite was synthesized by co-precipitation trailed by in-situ polymerization method. The XRD analysis inferred the semi-crystallinity of the ZP/PGA. TEM results confirmed the formation of nano size particles. ZP/PGA nanocomposite showed more selectivity for Al^{3+} . The degradation of MB (94.33%) and MG (86.63%) were observed with more regression coefficient. ZP/PGA was investigated for antimicrobial activity for *E.coli*. ZP/PGA was exploited for the fabrication of sensor for the detection of Al (III) in aqueous system.

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