SORPTION STUDIES OF SOME BIOLOGICALLY IMPORTANT UNIVALENT SALTS USING POLYANILINE PICRATE AS SORBENT

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Polyaniline picrate (PANIPI) was synthesized via facile chemical polymerisation route. The as synthesized PANIPI was characterized using UV-Visible, FT-IR and PXRD spectroscopic techniques. Adsorption capacity of the as prepared resin was evaluated from the sorption process. Sorption isotherms were constructed using Langmuir, Freundlich, Redlich-Peterson and Temkin models. The spectral changes after the sorption process were studied using UV-Visible and FT-IR techniques. Facile pH for the adsorption is found to be 5-7. A comparison of ion exchange capacities of PANIPI revealed selectivity of 3:2 for sodium and potassium chlorides. The nanosized PANIPI is a potent antimicrobial agent and can be utilized as a biocompatible material.

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Introduction

Univalent ions like Li^+, Na^+, K^+, NH_4^+ and Cl^- are biologically important as they are involved in osmoregulation occuring in all living cells. The mobility of these ions across the cell membrane is facilitated through ion channels.[1] The specific role of these channels is to provide proper Na^+/K^+ ionic balance in living species. Many macrocyclic ligands and polymer analogues have been utilized to understand various ion recognition and transport in biological tissues.[2]

Sorption processes[3] are used widely to understand the ion transport mechanism across polymeric materials. Mechanism of sorption depends on the chemical nature of the metal ion, adsorbent and environmental conditions such as ionic strength, pH and temperature.

Among various conducting polymers[4,5] which possess unique features for incorporating and adsorbing ions in the polymer matrix, polyaniline (PANI)[6-8] has attracted researchers due to its ease of preparation and high environmental stability. PANI hybrid materials are shown to possess excellent applications in tissue engineering,[9,10] antimicrobial wound dressings[11-13] and as coatings for cotton fabrics,[14] making it a highly biocompatible material. Of all polyanilines, PANIPI possess a unique feature of having a chromogenic dopant picric acid, making it an excellent material to visualize the exchange of ions. The paucity of data in PANIPI prompted us to use it as a probe to evaluate the sorption process and exchange mechanism.

In this article we have synthesized PANIPI via a facile one pot procedure and analyzed its antimicrobial activities. The as synthesized polymer is characterized by UV-Vis, FT-IR and PXRD techniques. The morphology of the sample is analyzed using SEM. Herein univalent chloride salts (LiCl, NaCl, KCl and NH₄Cl) are utilized to explore the sorption characteristics on the polymer PANIPI, which is very simple and "green". Moreover, the exchange of ion is detected by visible spectroscopy proving it as an efficient adsorbent for probing ion selectivities. In addition, the antimicrobial activities of the PANIPI renders it as a biocompatible material.

Experimental

Materials and Methods

All the chemicals and reagents used were of analytical grade. Double distilled water was employed for all the experiments.

Synthesis of PANIPI

The PANIPI was synthesized by chemical oxidative polymerisation.[15] Aqueous solution of aniline (0.1 M) and picric acid (0.05 M) was magnetically stirred and ammonium peroxydisulphate (0.1 M) was added dropwise over an interval of one hour until a dark green precipitate was obtained. At the end of the stipulated time the solution was filtered on a Whatmann No.1 filter paper and washed with distilled water and alcohol. The resulting dry powder was further stirred ultrasonically (ultrasonic cleaning bath 50 kHz, Ultrasonic Ney) with alcohol, acetone and ether filtered and dried. The as prepared precipitate was stored in a vaccum desiccator and used directly for the sorption experiments and antimicrobial studies.

Spectral analysis

PANIPI (1 mg) was dissolved in 25 ml of DMF and the UV-Visible spectra of the solution obtained were recorded

in the region 300-1000 nm using Perkin–Elmer Lambda 25 spectrophotometer. FT-IR spectra were recorded as KBr pellets on a Perkin Elmer RXI FT-IR spectrophotometer. X-ray diffraction measurements were made with a Rigaku Ultima III X-ray diffractometer using CuK_α target (λ = 1.5418 Å).

Sorption Experiments

Sorption capacity of the adsorbent was evaluated by the batch process. PANIPI (1 mg) and salts of varying concentrations (25 ml, 10^{-6}-10^{-1} M) were ultrasonically stirred for 30 mins. After 30 mins, solutions were withdrawn, filtered and the concentration of the picrate ion released (C_e) was ascertained from the calibration curves at absorption maxima (λ_{max}=360 nm). Release of picrate ion (C_0) in the absence of salts was considered as the standard. pH measurements (Digital pH meter EQ 160, Equiptronics) were used to study the dosage effect of sorbent (10 mg) and adsorbate (2 M). The midpoints of the pH curves were taken for determining the $K_{PI^-}^{Cl^-}$ values.

Effect of pH was calculated by varying pH from 1 to 14. Alkali metal ion concentrations were estimated using flame photometer (Elico 360 A) and ammonium ions by Nessler's method. The separation factors α, were determined from these values.

Sorption isotherms such as Langmuir, Freundlich, Redlich-Peterson and Temkin isotherms were applied for this study. For accuracy, all the experiments were performed thrice and the mean of the three values were taken with an error of 2 %. Graphs were constructed with Origin 8.6 software and the slopes and intercepts were calculated using linear regression analysis.

Antimicrobial studies

Antibacterial and antifungal activities of PANIPI were tested against various gram positive and gram negative bacteria and fungus (*Candida albicans*) obtained from microbial type culture collection and gene bank (MTCC), Institute for Microbial Technology, Chandigarh, India employing agar well diffusion method.[16]

For antibacterial studies, nutrient agar medium and for antifungal studies potato dextrose agar were used. The agar media were sterilized in aliquots of 15 ml at a pressure of 6.804 kg for 15 minutes. The nutrient agar media were transferred into sterilized petri dishes in a laminar air flow unit. Petriplates were prepared by transferring the nutrient agar and kept in laminar air flow unit. After solidification of the media, the strains were swabbed on the petri plates and a sterile cork borer was used to puncture the solidified agar mass. Four wells of uniform dimension were prepared and a drop of PANIPI in DMSO (25, 50 75, 100 µg ml^{-1}) was added using micropipette and incubated for 48 hours at 37 °C in the incubation chamber. Zone of inhibitions were measured using Intech antibiotic zone reader (model IN-1215, India). Triplicates were used to ensure the activity of the synthesized material.

Results and Discussion

Structural characterization of sorbent

In the UV-Visible spectra (Fig. 1a) of PANIPI (1 mg) in DMF (25 ml), the signature peaks of the PANI matrix are observed at 360 nm and 621 nm.[17,18] The characteristic picrate ion peak (360 nm) seems to be merged with the intense Π–Π* band of PANI matrix.
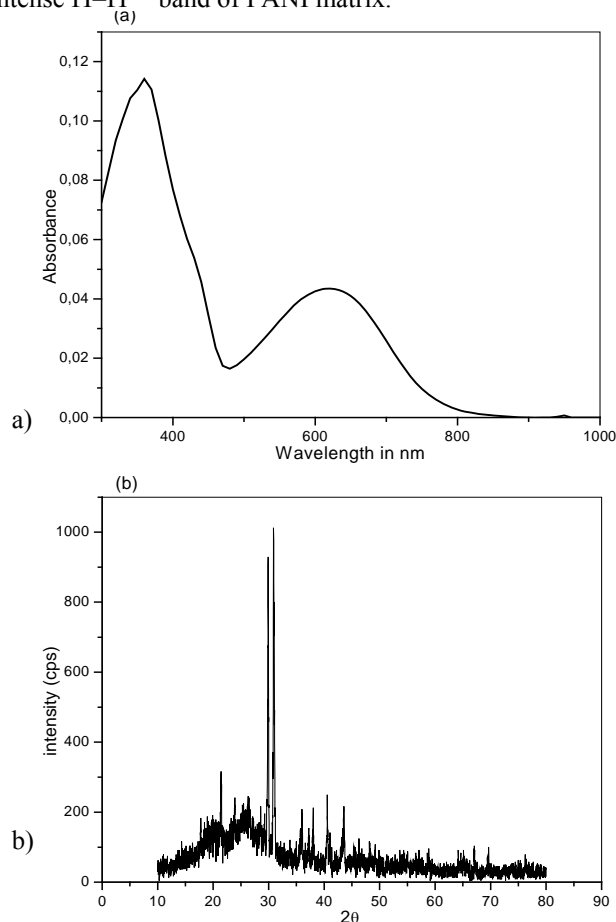

Figure 1. UV-Visible spectrum (a) and PXRD pattern (b) of PANIPI

In the FT-IR spectrum (Table 4) of PANIPI, bands at 3425, 3246 cm^{-1} correspond to N-H stretching vibrations, while the C-H stretching vibrations are observed at 3080, 2984, 2847 and 2827 cm^{-1}. Peaks around the region 3400-2800 cm^{-1} which are partly masked by the extended absorption tail of the protonated PANI[19] correspond to emeraldine salt (ES) structure. The stretching vibrations at 1588 and 1491 cm^{-1} are assigned to quinoid (N=Q=N) and benzenoid (N=B=N) moieties.[20] At 1300 cm^{-1} the stretching vibrations of C-N and NO_2 have overlapped. The absorption at 1137 cm^{-1} is due to charge delocalistion on the polymer backbone.[21] The bending vibrations in the PANI matrix appear as three distinct bands at 797, 699 and 504 cm^{-1}.

PXRD pattern (Fig. 1b) of PANIPI exhibits crystalline morphology with well defined sharpening of peaks at 2θ values of 30° (d~ 2.90 Å). The domain size was calculated using Scherrer's formula[22] and is found to be 2-9 nm. This small size provides large surface area for the sorption of ions. The SEM micrograph of PANIPI[15] shows granular morphology.

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Sorption Isotherms

PANIPI was equilibrated with salt solutions of varying concentrations, ultrasonically at ambient conditions. Ion exchange occurs readily with the picrate ion present on the resin. Ultrasonic stirring ensured the elimination of concentration gradients that arise during the sorption process.

Langmuir Isotherm

The linearised Langmuir isotherm[23] (1) is used to find the maximum amount of salts adsorbed (q_m) by PANIPI. From the slope and intercept (Fig 2a), K_L (Table 1) the coefficient related to affinity is determined.

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \qquad (1)$$

Further analysis of Langmuir equation is made on the basis of separation factor (R_L)[24] calculated using equation (2).

$$R_L = \frac{1}{1 + K_L C_0} \qquad (2)$$

As R_L is less than one, the sorption process is favoured, which implies the presence of homogenous active binding sites on the PANIPI surface, resulting in monolayer chemisorption.

Thermodynamic Studies

Gibbs free energy change (Table 1) calculated using equation (3) is found to be negative indicating the feasibility and spontaneity of the sorption process.

$$\Delta G° = -RT \ln K \qquad (3)$$

Freundlich Isotherm

The sorption data are further fitted to Freundlich adsorption isotherm[25] (Fig 2b), describing the sorption equilibrium for both monolayer and multilayer adsorption. Freundlich isotherm constants K_F (sorption capacity) and n (intensity of sorption) are calculated (Table 1) from the expression (4),

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

The n values obtained for the sorption process fulfills Freundlich isotherm condition[26] ($0 < n < 1$). Though Langmuir and Freundlich isotherm conditions are obeyed, both monolayer and multilayer adsorption of ions occur on PANIPI. In order to improve the R^2 values Redlich Peterson and Temkin models are employed.
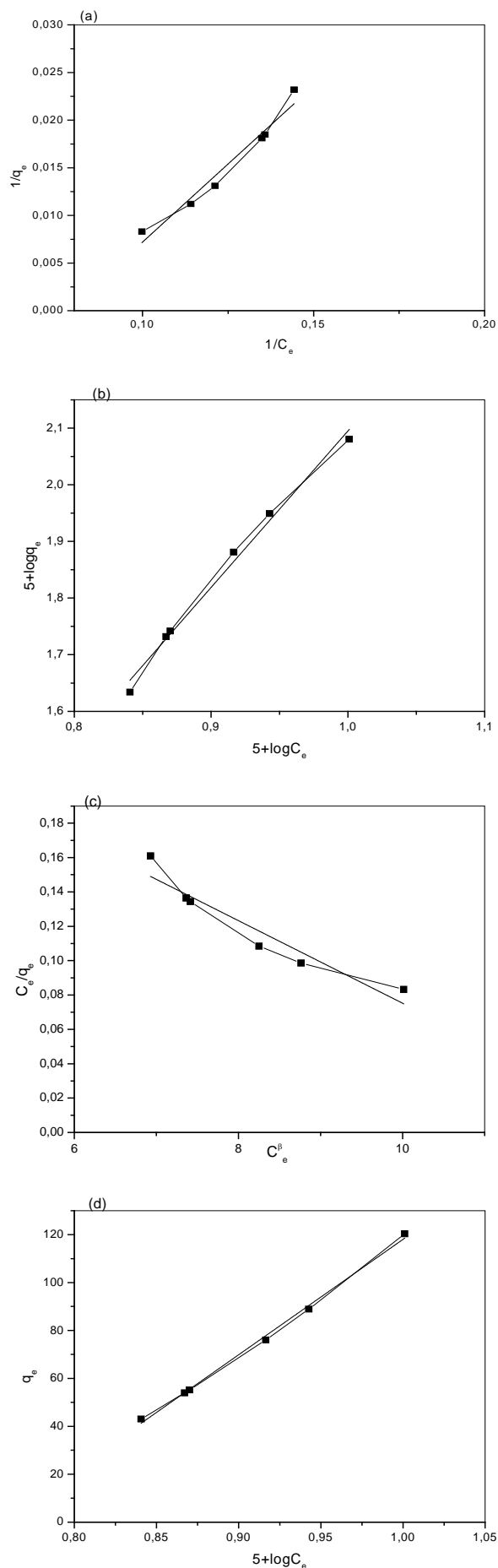

Figure 2. Sorption isotherm of NH$_4$Cl (a) Langmuir (b) Freundlich (c) Redlich-Peterson (d) Temkin

Table 1. Isothermal Parameters of Langmuir and Freundlich sorption Isotherms for PANIPI as adsorbent

Salts	Langmuir constants				Freundlich constants				$-\Delta G°$, kJ mol^{-1}
	q_m, mg g^{-1}	K_L, L mg^{-1}	R^2	[a]$S.D$	K_F, L mg^{-1}	n	R^2	$S.D$	
NH$_4$Cl	39.11	0.078	0.954	0.004	0.215	0.362	0.988	0.013	6.426
LiCl	5.36	0.013	0.763	0.014	0.001	0.188	0.935	0.014	5.224
NaCl	26.74	0.080	0.904	0.026	0.124	0.335	0.983	0.011	6.239
KCl	7.15	0.013	0.965	0.019	0.013	0.242	0.988	0.010	5.279

[a]standard deviation

Table 2. Isothermal Parameters of Temkin and Redlich-Peterson sorption Isotherms for PANIPI as adsorbent

Salts	Redlich Peterson constants				Temkin constants				Cationic radius r, Å
	K_{RP}, Lmg^{-1}	α_{RP}	R^2	$S.D$	K_T, L mg^{-1}	b_T, kJ mol^{-1}	R^2	$S.D$	
NH$_4$Cl	3.169	0.076	0.896	0.017	5.687	0.012	0.996	0.015	1.48
LiCl	0.756	0.123	0.648	0.069	5.328	0.015	0.994	0.032	[a]3.40
NaCl	2.386	0.080	0.826	0.057	5.502	0.012	0.995	0.083	0.95
KCl	1.653	0.103	0.923	0.023	5.429	0.014	0.998	0.089	1.33

[a]hydrated radius

Redlich- Peterson Isotherm

Redlich-Peterson isotherm[27] (Fig. 2c) is used as a compromise between Langmuir and Freundlich models. The linear form of this equation (5) contains three unknown parameters

$$\frac{C_e}{q_e} = \frac{1}{K_{RP}} + \frac{\alpha_{RP}}{K_{RP}} C_e^{\beta} \qquad (5)$$

K_{RP}, α_{RP} and β. A minimization procedure is adopted to maximize the coefficient of determination R^2. However, the low value of R^2 (Table 2) indicate that this model is not suitable for the sorption process.

Temkin Isotherm

The Temkin[28] isotherm equation (6) relates,

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \qquad (6)$$

K_T the equilibrium binding constant (mg L^{-1}) and b_T the Temkin constant related to energy of adsorption (kJ mol^{-1}). These values are determined from the slope and intercept (Table 2) of the plot q_e vs log C_e (Fig. 2d). The Temkin isotherm model exhibit a high R^2 (0.99) value compared to other models applied.

Based on all these results and from the plot of K_T vs cationic radii (Fig. 3), the relative order of sorption of univalent chlorides on PANIPI resin is given below

$$NH_4^+ > Na^+ > K^+ > Li^+$$
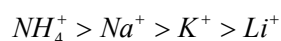
It can be seen that ammonium ion exhibits the maximum sorption potential (K_T). This may be due to the presence of hydrogen bonding on the amine sites of PANI matrix. Among the alkali metal chlorides, NaCl has the highest sorption potential (K_T). This may be due to the ionic nature and size of NaCl. When KCl is used as the adsorbate, the sorption potential is lower than NaCl probably due to the bigger size of K$^+$ compared to Na$^+$. Li$^+$ being the smallest among the alkali metal chlorides prefer to exist as a hydrated species and therefore possess low sorption potential.
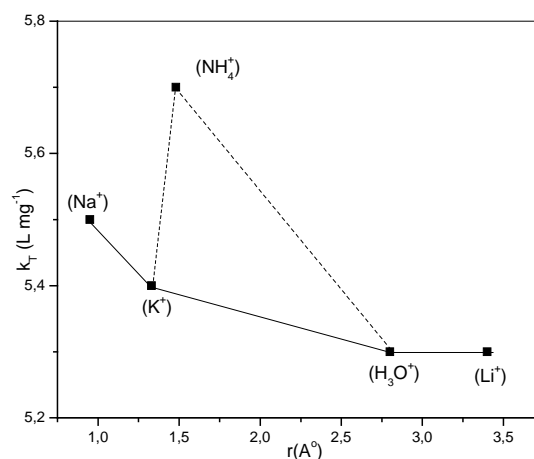
Figure 3. Temkin constant K_T (L mg^{-1}) vs ionic radii r (Å)

Sorption at high concentration

As sorption process will be complete at higher ionic strengths, the experiments were conducted at higher concentration (2 M) with 10 mg of PANIPI resin. The observed decrease in pH with time (Fig. 4) indicates the sorption of ions on PANIPI resin with subsequent release of picric acid in aqueous solution. At high concentration also, NH$_4^+$ is found to possess high exchange capacity as inferred from $K_{PI^-}^{Cl^-}$ and α values (Table 3).

**Table 3.** UV-Visible spectral results and ion exchange characteristics of PANIPI resin

Salts	λ_{max}, nm		y	^a1-y	$^bK_{PI^-}^{Cl^-}$	^cIEC, meq g^{-1}	$^b\alpha$
	Benzenoid (B)	Quinoid (Q)					
PANIPI	360	621	0.70	0.30	-	-	-
NH$_4$Cl	361	620	0.57	0.42	4.89 x 10^{-7}	1.99	27.69
LiCl	361	617	0.62	0.37	6.30 x 10^{-7}	1.96	12.96
NaCl	378	577	0.91	0.09	5.62 x 10^{-8}	2.71	0.74
KCl	365	619	0.63	0.36	4.89 x 10^{-7}	1.99	0.70

$^a1-y=OD_Q/OD_B$ [chlorides]; ^{b}2 M; ^{c}10^{-1}-10^{-6} M

Table 4. FT-IR Spectral data of PANIPI before and after sorption

Vibrational assignment	N-H str	Ar C-H str /NH$_2^+$	C=N$^+$	N=Q=N	N=B=N	CN str	Ar C-N-C bending	C-H bending	C-C ring deformation	Cl stretching	C-N-C torsion
PANIPI	3425 3246	3080, 2984, 2847 2827	2800-2400	1588	1491	1300	1137	797	699	-	504
NH$_4$Cl	3407 3219	3081, 2925	2471, 2343	1574	1490	1282	1133	798	702	610	504
LiCl	3440	2830	2358	1596	1491	1300	1139	790	697	609	504
NaCl	3409 3225	3010-2951, 2900	2400-2000	1585	1495	1303	1141	804	703	590	505
KCl	3430	2808	2483 2361	1588	1491	1300	1135	795	699	612	503

The varying trends of these parameters for the alkali metal ions may be due to competition between sorption and desorption process.
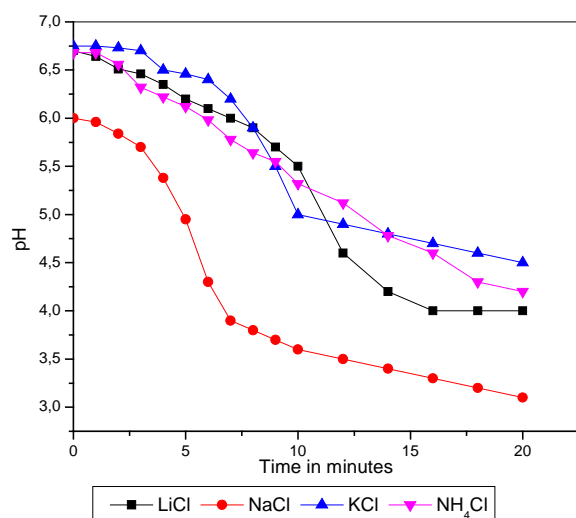

Figure 4. Variation of pH with time [2 M salts]

Sorption Mechanism

A tentative mechanism is proposed for the sorption process. The easily polarisable picrate ion renders hydrophilicity and the chloride ions are attracted towards the PANI surface (Scheme I). Anion selectivity is influenced by the counterions, since Cl$^-$ ion is small and highly electronegative compared to the picrate ion. Hence the movement of anions occur as ion pairs. The anions bind to the imine sites on the quinoid rings and the NH groups on the benzenoid rings. This phenomenon causes changes in the stretching frequencies of the NH group at 3200 cm^{-1} and also affects the C-N-C bending vibrations. The sorption of ions initially occurs as a monolayer. Multilayer formation on PANI surface, may take place subsequently due to ion pairing.

Effect of pH

The sorption process of PANIPI is found to be highly pH dependent. In acidic medium, protonic acid doping of PANIPI readily occurs releasing the picric acid. However, in this pH range sorption is not a favoured process. This may be due to the doping of the vacant imine sites on the PANIPI resin.
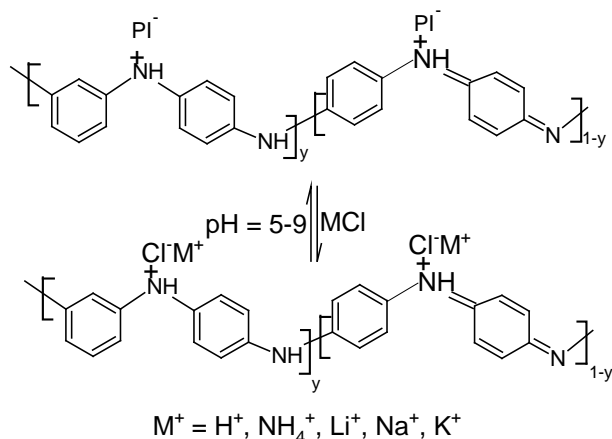
Scheme I. Sorption process on PANIPI

The favourable pH range for sorption process is 5-9 as can be inferred from the adherence to the isotherm models (Fig. 5). Above pH 9, the solutions tend to be alkaline and dedoping of PANIPI to emeraldine base (EB) may result. As the pH increases further, OH^- ions bind to the imine sites on the PANI matrix producing a hydroxylated emeraldine base[29] (Scheme II).
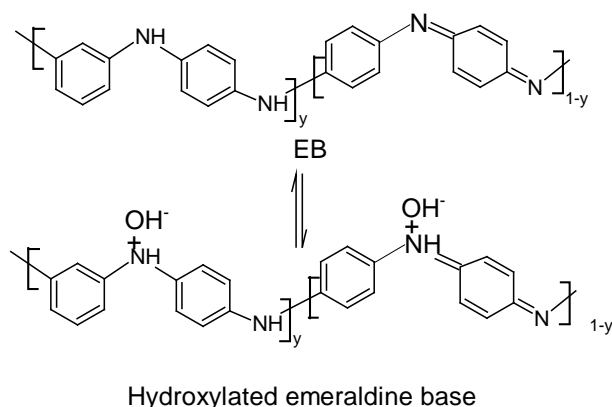
Scheme II. Emeraldine base structures in alkaline medium

Structural characterization after sorption

UV-visible spectra

PANIPI is found to contain ~70% benzenoid and ~30% quinoid forms as inferred from benzenoid and quinoid absorption intensities in the UV-Visible spectra (Table 3). Sorption process may lead to the changes in these percentages depending on the electrolytes used (Table 3). Sorption of electrolytes such as NaCl produce 90 % of benzenoid forms compared to PANIPI, while NH_4Cl produce only 60 % benzenoid forms. LiCl and KCl does not alter the composition of these forms originally present in PANIPI.

FT-IR spectra

The changes in the IR spectral bands of PANIPI after sorption, confirm the presence of ion pairs of the electrolytes on PANI matrix. The peaks at 3425 and 3246

cm^{-1}, due to amine and imine stretching of N-H in PANIPI are sensitive to ions. These vibrations are either blue or red shifted after the sorption process depending upon the electrolytes used. (Table 4). NaCl shows a blue shift (15 and 24 cm^{-1}), whereas LiCl and KCl show red shifts. The band features around 2800-2400 cm^{-1} confirms the presence of ES structure in PANI. Quinoid and benzenoid ring vibrations at 1588, 1491 cm^{-1} are not much affected. The stretching vibrations around 1300 cm^{-1}, characteristic of ES structure are blue shifted for NaCl, KCl and NH_4Cl whereas red shifted for pseudo protonic acid dopant LiCl.[30] In NH_4Cl, a twin band found at 1284 cm^{-1} indicates electronic transitions within the ring, besides confirming the binding of ammonium ion to NH of benzenoid rings. The chloride ions existing as ion-pairs on the PANI matrix are inferred from vibrations in the region 590-612 cm^{-1}.
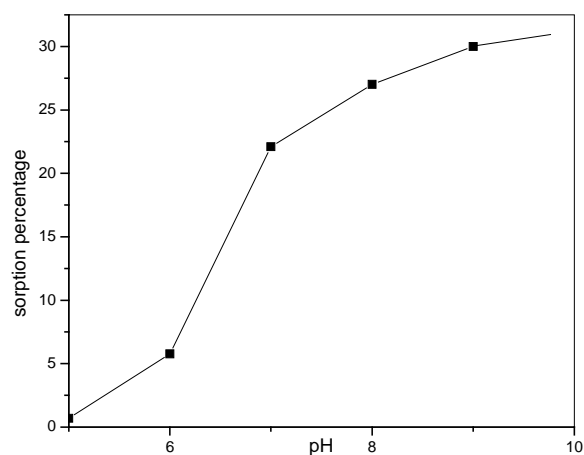
Figure 5. Sorption percentage as a function of $[H^+]$

Ion exchange capacity

The ion exchange capacity $(IEC)^{31}$ of PANIPI towards these ions vary between 1.95-2.71 meq g^{-1} (Table 3). These values indicate the suitability of PANIPI as a good polymeric material suitable for ion transport. The IEC ratio of Na^+-K^+ (3:2) agrees well with the distribution of ions in sodium-potassium pumps (3:2) present in living cells. It is quite intriguing to find that PANIPI acts similar to Na^+/K^+ ATPase pumps in cells.[32] The other ion selectivities of PANIPI is similar to potassium (Table 3). Hence it could be inferred that PANIPI is highly selective and is able to discriminate between the various ions, similar to the cell membranes present in the living organisms. The added advantage of PANIPI is that it also possesses antimicrobial activities making it a highly suitable material for tissue implants.

Antimicrobial Activity of PANIPI

PANIPI exhibits considerable antibacterial activity for the bacterial strains tested. The zone of inhibitions obtained for PANIPI in DMSO (25-100 μg mL^{-1}) against gram positive (*Staphylococcus aureus*) and gram negative (*Shigella dysenteriae, Salmonella enterica, Klebsiella pneumonia*) bacteria are shown in Fig 6a. The minimum inhibitory concentration (MIC) of 50 μg mL^{-1} of PANIPI is required

for *Streptococcus pyogenes, Bacillus subtilis, Enterococcus faecalis* (gram positive) and *Escherichia coli, Pseudomonas aeruginosa* (gram negative) bacteria (Fig 6b).
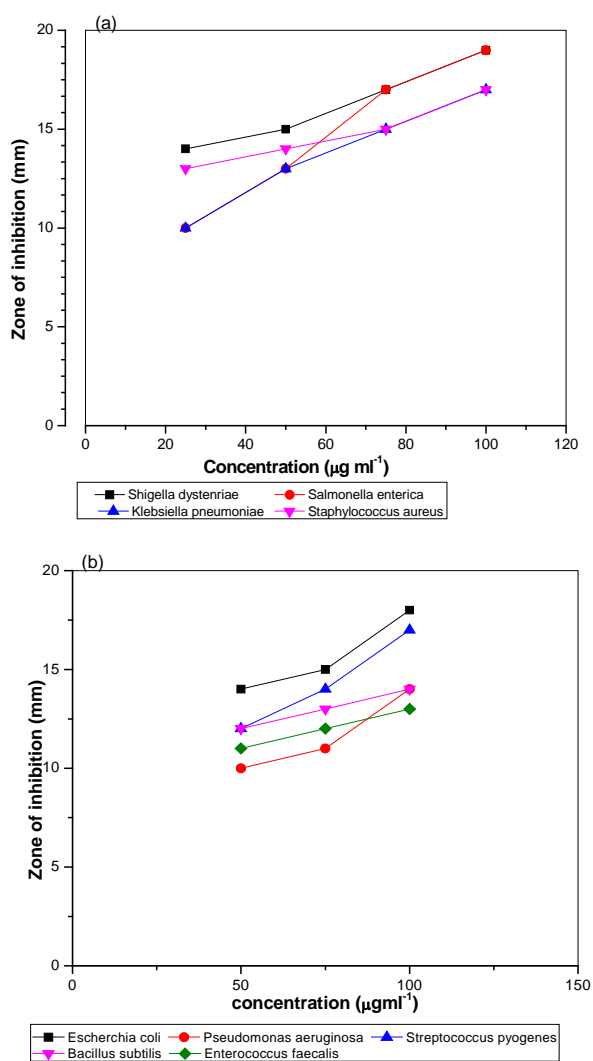
The X-ray diffraction studies (Fig. 2) reveal that the size of PANIPI fall in nanometer regime. Nanomaterials[33] are known to disturb the balance between oxidant and anti-oxidant processes occurring in the living cells. Hence it could be envisaged that the nanosized PANIPI[34] binds electrostatically to cell membranes creating an imbalance in oxidative reductive mechanism leading to cell lysis and death.

Conclusions

In summary, we have synthesized PANIPI via facile chemical polymerisation route. The as synthesized PANIPI is characterized using UV-Visible, FT-IR and PXRD spectroscopic techniques. The morphology of the samples are analysed using PXRD and SEM. The Π- Π* transitions of quinone-imino groups were confirmed from the UV-Visible spectral data. The ES structure of PANIPI is also confirmed by FT-IR analysis. Sorption capacity of the as prepared PANIPI is evaluated from the sorption process. Among the sorption isotherms such as Langmuir, Freundlich, Redlich-Peterson and Temkin isotherms, Temkin isotherm is found to be satisfactory as evidenced from the R^2 values. The relative order of sorption is found to be $NH_4^+ > Na^+ > K^+ > Li^+$. The UV-Visible absorption and FT-IR spectra of PANIPI after the sorption process confirm the presence of ion pairs in the PANI matrix . From the IEC results it is found that Na^+/K^+ ratio is similar to that of Na^+/K^+ ATPase pump in living cells. PANIPI shows excellent antimicrobial activities against various bacterial and fungal strains. From these results it is concluded that, the nanosized PANIPI can be utilized as a biocompatible material for fabrication of biological membranes.

Acknowledgement

Figure 6. Antibacterial effect of PANIPI against bacteria

As the concentration of PANIPI is increased, the zone of inhibition also increased. PANIPI is also found to be an effective antifungal agent when tested against *Candida albicans*. The zone of inhibition produced is comparable with that obtained against *Shigella dysenteriae* (Fig. 7) (MIC 25 µg ml^{-1}).
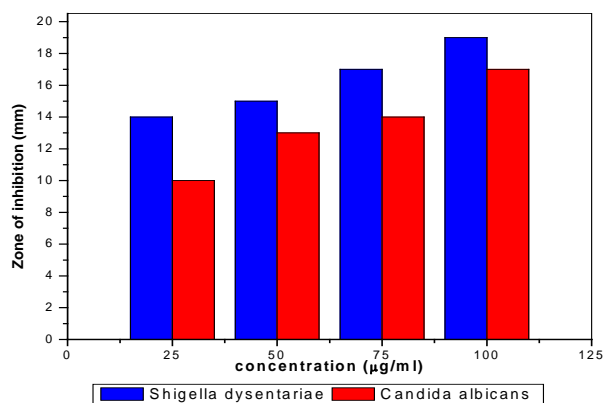

Figure 7. Comparison of antibacterial and antifungal effect of PANIPI

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