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Synthesis, characterization and antibacterial activity of cellulose acetate–tin (IV) phosphate nanocomposite

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ABSTRACT

Cellulose acetate–tin (IV) phosphate nanocomposite (CA/TPNC) was prepared using simple method at 0–1 pH. The nanocomposite ion exchanger was characterized using some techniques such as Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and thermogravimetric analysis (TGA/DTA/DSC). The nanocomposite material was explored for different properties such as ion exchange capacity, pH titration, elution behavior, thermal stability, and distribution coefficient. The ion exchange capacity of CA/TPNC was found higher compared to their inorganic counterpart. The distribution coefficient studies of nanocomposite ion exchanger were investigated for different metal ions. On the basis of distribution coefficient studies CA/TPNC material was found more selective for Cd^{2+} and Mg^{2+}. CA/TPNC ion exchange was explored for antibacterial activities against *E. coli* bacteria.

1. Introduction

Extensive industrialization has led to the degradation of aquatic environment due to the discharge of non-degradable and hazardous material into the aquatic system. The toxic heavy metals are common constituents present in polluted water. If the concentrations of these metals are present above certain limit, it causes serious health hazard to living beings (Nabi, Naushad, & Inamuddin, 2007). So it is important to treat the wastewater before discharged to natural water bodies. The toxic metal ions were difficult to remove due to their unmanageable nature and resistant to natural degradation (Gao et al., 2007; Gupta, Agarwal, & Saleh, 2011; Gupta, Ali, & Saini, 2007; Gupta, Ali, Saleh, Nayak, & Agarwal, 2012; Gupta, Chandra, & Lang, 2006; Gupta, Chandra, & Mangla, 2002; Gupta, Gupta, & Rastogi, 2011; Gupta, Jain, & Kumar, 2006; Gupta, Jain, Radhapyari, Jadon, & Agarwal, 2011; Gupta, Jain, & Varshney, 2007; Gupta, Mittal, Malviya, & Mittal, 2009; Gupta, Pathania, Singh, Rathore, & Chauhan, 2013; Gupta, Rastogi, & Nayak, 2010; Jain, Gupta, Bhatnagar, & Suhas, 2003; Goyal, Gupta, & Chatterjee, 2009; Vilhera, Goncalves, & Mota, 2004; Zeng, Pan, & Gao, 2008; Zhao, Zhao, Le, Zeng, & Gao, 2007). Due to multifold increase in water pollution, there have been growing interests in the fabrication of new composite ion exchanger with diverse applications.

Many organic and inorganic ion exchangers have been reported in literature with wide utility but suffer from certain limitations. The organic exchangers were unstable at high temperature and ionization radiation (Gupta, Pathania, Agarwal, & Singh, 2012; Nabi & Naushad, 2008). The fine powder form of inorganic ion exchangers made them unsuitable for column operation (Khan, Alam, & Inamuddin, 2005; Mojumdar, Varshaney, & Agarwal, 2006; Nabi, Naushad, & Bushra, 2009a; Nabi, Naushad, & Bushra, 2009b). Composite ion exchangers have been prepared by incorporating an organic polymer into the matrix of inorganic precipitates using sol–gel mixing method (Clearfield, 1982; Khan et al., 2005; Khan, Niwas, & Alam, 2002; Siddiqui, Khan, & Inamudin, 2007). The organic part enhanced the mechanical properties and surface area by providing more exchanging sites on inorganic counterpart of the composite ion exchange materials (Khan et al., 2005; Mojumdar et al., 2006; Nabi et al., 2009a, 2009b).

Composite ion exchangers have received attention because it possessed interesting mechanical, chemical, electrochemical, optical and magnetic properties (Hassan, Marei, Badr, & Arida, 2001; Khan & Paquiza, 2011). Therefore, composite ion exchangers have been used as adsorbent, catalyst, ion selective electrode, antimicrobial activity, chromatography and environmental science engineering (Arrad & Sasson, 1989; Gupta, Ali, et al., 2007; Gupta, Jain, et al., 2007; Gupta, Pathania, et al., 2013; Nabi et al., 2009a, 2009b; Nabi, Shahadat, Bushra, Shalla, & Ahmed, 2010; Sanghavi, Mobin, Mathur, Lahiri, & Srivastava, 2013; Sanghavi, Sitaula, et al.,

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2013; Sanghavi & Srivastava, 2013; Mittal, Gupta, Malviya, & Mittal, 2008; Mittal, Mittal, Malviya, & Gupta, 2009; Mittal, Mittal, Malviya, & Gupta, 2010; Mittal, Mittal, Malviya, Kaur, & Gupta, 2010). The composite materials at nano level have many properties superior to the bulk materials due to their selectivity, specificity and wide range of applicability (Gupta, Pathania, et al., 2013). Thus, the efforts have been made to magnify the chemical, mechanical and thermal stability and selectivity of composite ion exchangers (Bushra, Shahadat, Raeisssi, & Nabi, 2012; Islam & Patel, 2008; Nabi & Naushad, 2008).

Cellulose based nanocomposites have been reported worldwide due to their cost-effectiveness, high-volume application, easy process ability, renewable nature and possibility of recycling. Nanocomposites based on cellulosic material have been reported in the literature (Gadhari, Sanghavi, & Srivastava, 2011; Gupta, Pathania, et al., 2013; Park & Kadla, 2012; Sanghavi & Srivastava, 2010; Yang et al., 2012). The biopolymer based materials have been used effectively and economically for wastewater treatment.

The antimicrobial activities of nanocomposite against microorganism were investigated by different research groups using various methods (Nabi, Shahadat, Bushra, Oves, & Ahmed, 2011; Rekha, Nirmala, Nair, & Anukaliani, 2010). The metal nanoparticles have been incorporated into biodegradable polymers such as chitosan, gelatin and both polymers via chemical reduction method to produce composites materials with some extraordinary properties. The effect of polymers and the size of nanoparticles on the antibacterial activity of silver bionanocomposite have been investigated (Ahmad et al., 2012). The nano materials, based on metal ions, exhibit broad spectrum biocidial activity toward different fungi, bacteria and viruses (Greenberg & Graves, 2005).

The literature survey revealed that so far no work has been documented on the synthesis and antibacterial activity of cellulose acetate–tin (IV) phosphate nanocomposite (CA/TPNC) ion exchanger. Thus, the present study deals with the preparation of cellulose acetate–tin (IV) phosphate nanocomposite ion exchanger. The CA/TPNC has been explored for the antibacterial activity against *E. coli* bacteria. CA/TPNC was characterized by scanning electron transmission (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), thermogravimetric analysis, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

2. Experimental

2.1. Reagents

The reagents used were tin (IV) chloride and sodium dihydrogenphosphate (LobaChemia Pvt. Ltd., Mumbai, India), formic acid (E. Merck Ltd., India), and cellulose acetate (CDH, Pvt. Ltd., New Delhi, India). All the reagents were used as received without further purification. Double distilled water was used for the preparation of solutions.

2.2. Instrumentation

A digital pH meter (Elico LI-10, India), FTIR spectrophotometer (Perkin Spectrum-400), X-ray diffractometer (X'pert Pro Analytical, Switzerland), scanning electron microscope (JEOL, JSM-6610LL, Japan), transmission electron microscopy (Hitachi, H7500, Germany), muffle furnace (MSW-275, India), magnetic stirrer and digital oven were used.

2.3. Synthesis of cellulose acetate–tin (IV) phosphate (CA/TPNC)

Cellulose acetate–tin (IV) phosphate nanocomposite ion exchanger was synthesized using sol–gel method at 0–1 pH as per method discussed in the literature (Gupta, Agarwal, Pathania, Kothiyal, & Sharma, 2013). In this, 0.1 M sodium dihydrogen phosphate and 0.1 M tin (IV) chloride were mixed in 1:1 ratio with constant stirring at room temperature. The pH of resulting mixture was adjusted to 0–1 by adding 0.1 N HNO_3. After complete addition, the mixture was stirred for 2 h to obtain the precipitates of tin (IV) phosphate (TP). The gel of cellulose acetate (CA) in formic acid was prepared and added to the precipitates of tin (IV) phosphate with continuous stirring. The resultant mixture was stirred for 4 h on the magnetic stirrer. This mixture was kept for digestion for 24 h with occasional shaking. The precipitates were filtered and washed with double distilled water several times to remove the impurities if present. The precipitates of cellulose acetate–tin (IV) phosphate obtained were dried at 50 °C in a hot air oven. The dried precipitates were converted into H^+ by putting in 0.1 M HNO_3 solution for 24 h with occasional shaking. The precipitates of CA/TPNC were filtered and washed with distilled water to remove the excess of the acid. In a similar way different samples of nanocomposite ion exchanger have been synthesized and ion exchange capacities were determined. The ion exchange capacity of Sample-4 was found maximum and selected for further studies.

2.4. Ion exchange capacity (IEC)

The ion exchange capacity of CA/TPNC was determined by the standard column process as explained earlier in the literature (Pathania, Singh, & Siddiqi, 2013; Siddiqi & Pathania, 2003a; Siddiqi & Pathania, 2003b). In this process, 1 g of CA/TPNC material in H^+ ions form was kept in a glass column fitted with glass wool support at the bottom.1 M sodium chloride solution was used to elute the H^+ ions completely from the CA/TPNC exchanger, maintaining a flow of 1.0 mL min^{-1}. The effluent was collected and titrated against standard alkali solution to determine the total H^+ ions released. The ion exchange capacity of the CA/TPNC was calculated using the formula as:

$$\text{IEC} \quad (\text{mg/g}) = \frac{N \times V}{W} \tag{1}$$

where IEC is the ion exchange capacity. N and V (mL) are normality and volume of the alkali solution, respectively. W (g) is the amount of CA/TPNC.

2.5. pH titration

Topp and Pepper method was used to perform the pH-titration studies (Topp & Pepper, 1949). In this method, 0.4 g of CA/TPNC in H^+ was taken each in 250 mL conical flasks. The equimolar solution alkali metal hydroxides and their chlorides in different volume ratio were added into the flasks by adjusting the final volume as 50 mL. The pH of solutions was recorded at regular interval of 24 h until the equilibrium was established.

2.6. Effect of eluent concentration

A fixed volume (250 mL) of sodium nitrate solution of different concentrations were used for complete elution of H^+ ions from the CA/TPNC. The eluent was passed through column containing 1 g of CA/TPNC with a flow rate of 1 mL min^{-1}. The collected effluent was titrated against 0.1 M NaOH solution.

2.7. Elution behavior

1.0 M $NaNO_3$ eluent concentration was observed for the complete removal of H^+ ions from the CA/TPNC ion exchanger. A column containing 1 g of CA/TPNC in H^+ form was eluted with 1.0 M $NaNO_3$ solution. The effluent was collected in fractions of 10 mL at a flow

Table 1
Condition of syntheses and ion exchange capacity of different samples of CA/TPNC.

Sample no.	A (mol L^{-1})	B (mol L^{-1})	pH	Mixing ratio (v/v)	C (%)	Appearance	IEC (mequiv./g)
S-1	0.1	0.1	0-1	1:1	0	White	0.55
S-2	0.1	0.1	0-1	1:1	1	White	0.68
S-3	0.1	0.1	0-1	1:1	2	White	0.68
S-4	0.1	0.1	0-1	1:1	4	White	1.48
S-5	0.1	0.1	0-1	1:1	6	White	1.10
S-6	0.1	0.1	0-1	1:1	8	White	0.75
S-7	0.1	0.1	0-1	1:1	10	White	0.40

A: tin (IV) chloride; B: sodium dihydrogen phosphate; C: cellulose acetate (in 25 ml formic acid).

rate of 1 mL min^{-1}. Each collected fraction was titrated against standard NaOH solution.

2.8. Thermal stability

The effect of drying temperature on the ion exchange capacity was investigated by heating CA/TPNC at different temperatures in a muffle furnace for 1 h. After cooling the sample in desiccators the ion exchange capacity was determined by standard column method (Innamuddine, Khan, Siddiqui, & Khan, 2007).

2.9. Distribution coefficient studies (K_d)

The distribution coefficients of different metal ions onto CA/TPNC in double distilled water were determined by batch method. In this, 300 mg of CA/TPNC in H^+ charged was equilibrated with 20 mL different metal nitrates in Erlenmeyer flask. The mixture was shaken for 24 h at room temperature to attain the equilibrium. The concentration of metal ions in the solution before and after equilibrium were determined by titrating against standard solution of EDTA (Reilley, Schmid, & Sadek, 1959). The distribution coefficient (K_d) was calculated by using equation

$$K_d \ (\text{mL g}^{-1}) = \frac{I - F}{F} \times \frac{V}{M} \quad (2)$$

where I (g/L) and F (g/L) are the initial and final concentration of the metal ions in solution, respectively. V is the volume of the solution (mL) and M is the amount of CA/TPNC (g).

2.10. Antibacterial activities

The colony forming unit (CFU) method was used to investigate the antibacterial activity of CA/TPNC ion exchanger against *E. coli* bacteria culture. In this method, 1 mL of 0.5 optical density *E. coli* bacteria culture was taken and inoculated into the control and nanocomposite samples. The samples were diluted up to 10^{-3} by serial dilution method and plated on nutrient agar plates. The plates were incubated at 37 °C for 2 h and 24 h. The colonies were counted with the help of colony counter and the results obtained were compared with CFU of *E. coli* culture.

2.11. Fourier transform infrared spectroscopy (FTIR)

FTIR spectrum of CA/TPNC (S-4) was recorded by using KBr disk method. In this technique, 10 mg of material was thoroughly mixed with 100 mg of KBr. An appropriate pressure was exerted to form a transparent disk. The FTIR spectrum of CA/TPNC was recorded between 400 and 4000 cm^{-1}.

2.12. X-ray studies

The X-ray diffraction pattern of the nanocomposite ion exchanger was recorded by X-ray diffractometer using Cu Kα radiation. The spectrum was recorded between 10° and 80° at 2θ.

2.13. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) studies

Scanning electron microphotographs of CA/TPNC (Sample-4) were recorded at different magnifications using scanning electron microscope. The elemental composition of the nanocomposite ion exchanger was determined by energy dispersive X-ray coupled with scanning electron microscopy.

2.14. Transmission electron microscopy (TEM)

The particles size and morphology of CA/TPNC ion exchanger was analyzed using high resolution transmission electron microscopy Hitachi, H7500, Germany.

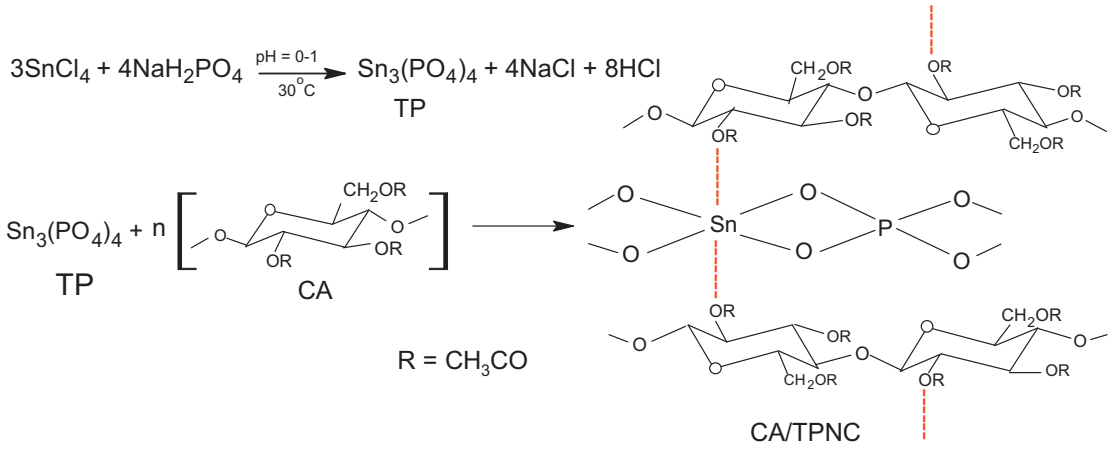

Fig. 1. Proposed reaction for the synthesis of cellulose acetate–tin (IV) phosphate nanocomposite.

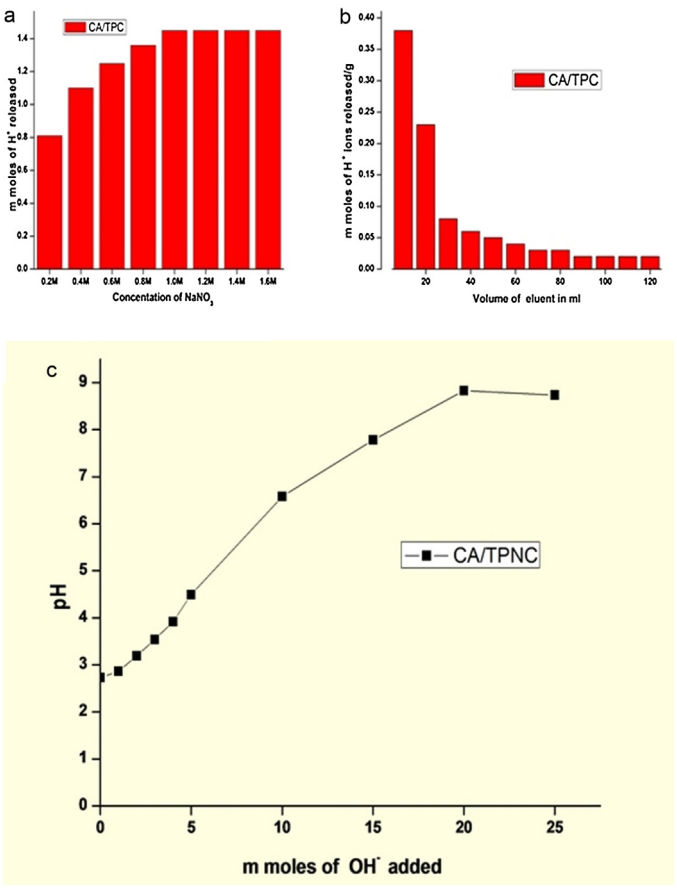

Fig. 2. (a) Effect of eluent concentration on ion exchange capacity of CA/TPNC. (b) Elution behavior of CA/TPNC. (c) pH titration curve of CA/TPNC.

2.15. Thermal analysis

The thermal analysis of CA/TPNC was determined by heating the sample up to 700 °C at a constant rate of 10 °C/min in nitrogen atmosphere.

3. Results and discussion

The various samples of cellulose acetate–tin (IV) phosphate nanocomposite (CA/TPNC) ion exchanger were synthesized by mixing inorganic tin (IV) phosphate and organic cellulose acetate. Table 1 shows the effect of mixing ratio of reagent, reaction temperature and pH on the synthesis of CA/TPNC ion exchanger. The sample, S-4 shows enhanced Na^+ ion exchange capacity (1.48 mequiv./g) and better yield, compared to inorganic counterpart (0.55 mequiv./g) and other samples. Due to better yield, high ion exchange capacity, thermal stabilities and good reproducibility, sample-4 (S-4) was selected for further detailed studies. The increase in Na^+ ion exchange capacity for CA/TPNC may be due to the binding of organic part (CA) with inorganic tin (IV) phosphate (TP) constituents (Fig. 1).

The effect of temperature on the ion exchange capacity of the CA/TPNC (sample-4) was shown in Table 2. It has been revealed that CA/TPNC ion exchanger was thermally stable and retained the ion exchange capacity up to 31.75 mequiv./g at 400 °C. The retention ion exchange capacity was higher compared with other composite ion exchange found in literature (Gupta, Agarwal, et al., 2013). The gradual decrease in ion exchange capacity with temperature was due to degradation of organic counterpart pectin.

The effect of eluent concentration on the release of H^+ ions from the CA/TPNC ion exchanger was shown in Fig. 2. An optimum concentration of sodium nitrate (eluent) was found to be 1.0 M for the complete removal of H^+ ions from the CA/TPNC column. It has been recorded that the rate of elution of H^+ ions from the CA/TPNC was governed by the concentration of eluent used.

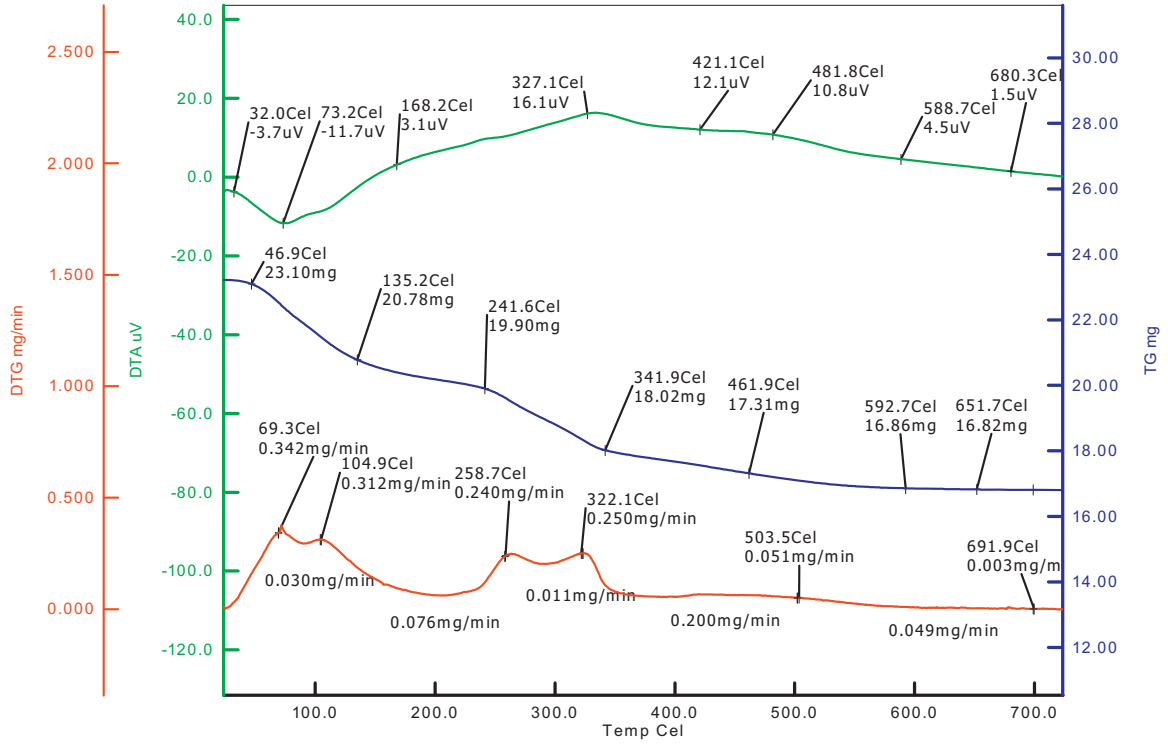

Fig. 3. Thermal analysis of CA/TPNC.

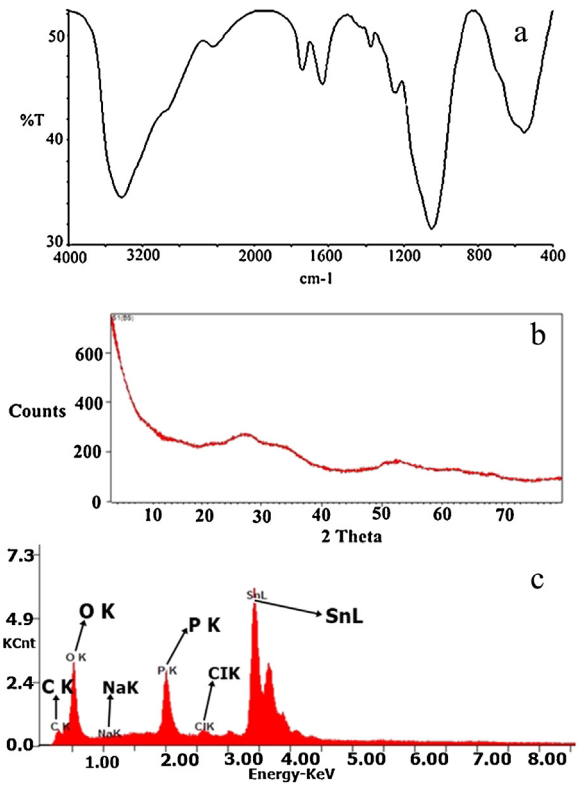

Fig. 4. (a) FTIR spectrum, (b) X-ray diffraction pattern and (c) EDX of CA/TPNC.

Fig. 2 illustrates the elution behavior of CA/TPNC ion exchanger at optimized concentration of eluent. It was established that 120 mL solution of 1.0 M sodium nitrate was sufficient for the complete removal of H^+ ions from CA/TPNC.

The pH titration curve of CA/TPNC ion exchanger under equilibrium condition was studied in NaOH–NaCl as shown in Fig. 2. The results confirmed the monofunctional strong cation exchanger nature of nanocomposite. The strong cationic nature of CA/TPNC ion exchanger was evident from the low initial pH of the solution when no OH^- ions were added to the system (Gupta, Pathania, Singh, Kumar, & Rathore, 2014). Further rise in pH indicated the complete neutralization of H^+ ions of the CA/TPNC exchanger.

The distribution studies (K_d) of 10 different metal ions such as Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+} and Mg^{2+} was explored on the CA/TPNC. The distribution studies exhibited the highly selective nature of CA/TPNC for Cd^{2+} as compared to other metal ions. Hence the nanocomposite ion exchanger can be utilized for detection and segregation of cadmium ions from waste effluents. However, the K_d values showed the sequence of selectivity for different metal ions as Cd^{2+} (568.2) > Mg^{2+} (480.2) > Pb^{2+} (366.2) > Zn^{2+} (344.6) > Cr^{3+} (241.4) > Co^{2+} (232.4) > Fe^{2+} (231.9) > Ni^{2+} (220.0) > Mn^{2+} (152.6) > Cu^{2+} (122.4).

The thermal analysis of CA/TPNC ion exchanger was shown in Fig. 3. It was apparent from the thermogram that initial loss of about 10% up to 140 °C. It may be due to loss of external water molecules present on the surface of the sample (Duval, 1963). The nanocomposite ion exchanger was found thermally stable as only 2% weight loss occurred between 100 and 350 °C. It was due to the conversion of some phosphate into pyrophosphate (Innamuddin et al., 2007). Further, a slight loss of weight about 6% was observed from 350 to 700 °C due to the decomposition of organic part of the nanocomposite material.

The FTIR spectrum of CA/TPNC ion exchanger was shown in Fig. 4(a). The absorption peak at 3432 cm^{-1} may be due to presence of external water molecule. The absorption band at 1744 cm^{-1} may be due to carbonyl group of cellulose acetate. The presence of sharp

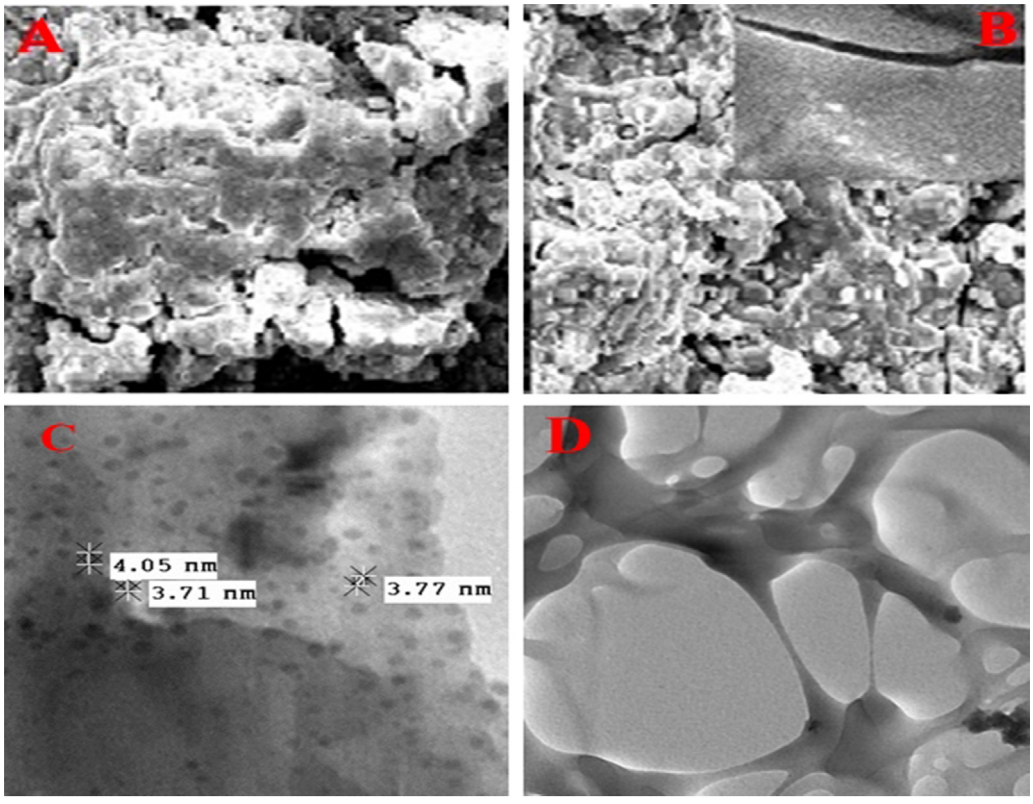

Fig. 5. (A) SEM images. (B) Inset TP. (C and D) TEM images of CA/TPNC.

Table 2
Effect of temperature on ion-exchange capacity of CA/TPNC.

Sr. no.	Heating temperature (°C)	Appearance	Weight loss (%)	Na^+ ion exchange (mequiv./g)	Retention of IEC (%)
1	50	White	Nil	1.48	100
2	100	White	13.6	1.39	93.91
3	150	Brown	17.6	1.21	81.75
4	200	Brown	20.8	1.10	74.32
5	250	Dark brown	26.3	1.01	68.24
6	300	Dark brown	28.3	0.84	56.75
7	350	Dark brown	32.2	0.59	39.86
8	400	Dark brown	37.9	0.47	31.75

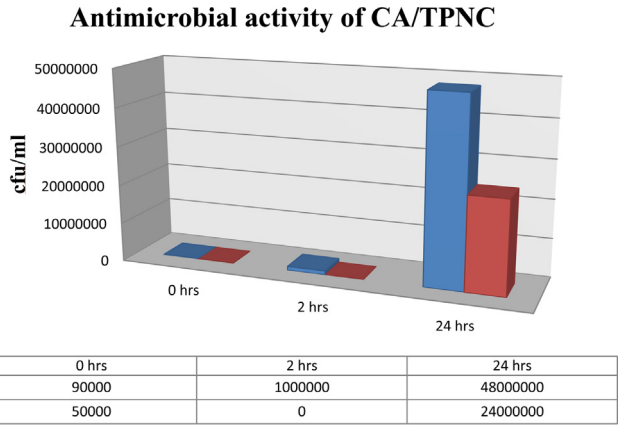

Fig. 6. Antimicrobial activity of CA/TPNC against *E. coli*.

peak at 1633 cm^{-1} may be due to free water molecule and strongly bonded –OH group in the matrix (Pathania et al., 2013). The broad peak observed at 1039 cm^{-1} may be due to PO_4^{3-}, and $H_2PO_4^-$ (Nabi & Naushad, 2008). The absorption band at 490 cm^{-1} may be due to superposition of metal-oxygen stretching vibrations confirming binding between cellulose acetate and tin (IV) phosphate (Siddiqui et al., 2007).

X-ray diffraction (XRD) pattern of CA/TPNC ion exchanger was presented in Fig. 4(b). It showed small peaks thereby suggesting the semi crystalline nature of nanocomposite material.

The EDX spectrum confirmed that tin and phosphate were main components present in the CA/TPNC ion exchanger (Fig. 4(c)).

The surface morphology of CA/TPNC ion exchanger at different magnifications was determined by scanning electron microscopy (SEM) and presented in Fig. 5(A) and (B). The SEM results confirmed the rough morphology of CA/TPNC compared to inorganic counterpart TP.

Transmission electron microscopy (TEM) images of CA/TPNC at different magnification were shown in Fig. 5(C) and (D). The TEM results revealed particle size in the range between 3.71 and 4.01 nm.

The antibacterial activity of CA/TPNC ion exchanger was investigated against *E. coli* bacteria culture and documented in Fig. 6. It was evident that CA/TPNC ion exchanger inhibits the growth of *E. coli* bacteria. This was due to the binding of nanocomposite particles to the outer membrane of *E. coli* which resulted in the inhibition of active transport, dehydrogenase and periplasmic enzyme activity. The maximum antibacterial activity of nanocomposite ion exchanger was observed at 200 μg/mL concentration. It has been observed that with the increase in the concentration of CA/TPNC, the antibacterial effect was more pronounced. This indicates the biostatic nature of nanocomposite ion exchanger.

4. Conclusion

The CA/TPNC ion exchanger with elevated ion exchange capacity and thermal stability was synthesized by co-precipitation method. CA/TPNC was explored for various characterization techniques. The nanocomposite ion exchanger retained good ion capacity at higher temperature. The nanocomposite ion exchanger was investigated to be highly selective for Cd^{2+} compared to other metal ions. TEM study confirmed that nanocomposite ion exchanger was in nano range. CA/TPNC was studied for the antibacterial activity against *E. coli*.

References

Ahmad, M. S., Lim, J. J., Shameli, K., Ibarhim, N. A., Tay, M. Y., & Chieng, B. W. (2012). Antibacterial activity of silver bionanocomposites synthesized by chemical reduction route. *Chemistry Central Journal*, *6*, 101.

Arrad, O., & Sasson, Y. (1989). Commercial ion-exchange resins as catalysts in solid liquid reactions. *Journal of Organic Chemistry*, *54*, 4993–4998.

Bushra, R., Shahadat, Md., Raeisssi, A. S., & Nabi, S. A. (2012). Development of nano-composite adsorbent for removal of heavy metals from industrial effluent and synthetic mixtures; its conducting behavior. *Desalination*, *289*, 1–11.

Clearfield, A. (1982). *Inorganic ion exchange materials*. Boca Raton, Florida: CRC Press.

Duval, C. (1963). *Inorganic Thermogravimetric Analysis*. Amsterdam: Elsevier.

Gadhari, N. S., Sanghavi, B. J., & Srivastava, A. K. (2011). Potentiometric stripping analysis of antimony based on carbon paste electrode modified with hexathia crown ether and rice husk. *Analytica Chimica Acta*, *703*(1), 31–40.

Gao, H. W., Chen, F. F., Chen, L., Zeng, T., Pan, L. T., Li, J. H., et al. (2007). A novel detection approach based on chromophore-decolorizing with free radical and application to photometric determination of copper with acid chrome dark blue. *Analytica Chimica Acta*, *587*, 52–59.

Goyal, R. N., Gupta, V. K., & Chatterjee, S. (2009). A sensitive voltammetric sensor for determination of synthetic corticosteroid triamcinolone, abused for doping. *Biosensors and Bioelectronics*, *24*, 3562–3568.

Greenberg, & Graves, K. (2005). Genetic diversity and antimicrobial resistance of *E. coli* from human and animal sources uncovers multiple resistances from human sources. *Carbohydrate Polymers*, *10*, 760–767.

Gupta, V. K., Agarwal, S., Pathania, D., Kothiyal, N. C., & Sharma, G. (2013). Use of pectin–thorium (IV) tungstomolybdate nanocomposite for photocatalytic degradation of methylene blue. *Carbohydrate Polymers*, *96*, 277–283.

Gupta, V. K., Agarwal, S., & Saleh, T. A. (2011). Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes. *Water Research*, *45*, 2207–2212.

Gupta, V. K., Ali, I., & Saini, V. K. (2007). Defluoridation of wastewaters using waste carbon slurry. *Water Research*, *41*(15), 3307–3316.

Gupta, V. K., Ali, I., Saleh, T. A., Nayak, A., & Agarwal, S. (2012). Chemical treatment technologies for wastewater recycling – A review. *RSC Advances*, *2*, 6380–6388.

Gupta, V. K., Chandra, S., & Lang, H. (2006). A highly selective mercury electrode based on a diamine donor ligand. *Talanta*, *66*, 575–580.

Gupta, V. K., Chandra, S., & Mangla, R. (2002). Dicyclohexano-18-crown-6 as active material in PVC matrix membrane for the fabrication of cadmium selective potentiometric sensor. *Electrochimica Acta*, *47*, 1579–1586.

Gupta, V. K., Gupta, B., Rastogi, A., Nayak, A., & Agarwal, S. (2011). A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye-acid blue 113. *Journal of Hazardous Materials*, *186*, 891–901.

Gupta, V. K., Jain, A. K., & Kumar, P. (2006). PVC-based membranes of N,N′-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane as Pb(II)-selective sensor. *Sensors and Actuators, B: Chemical*, *120*, 259–265.

Gupta, V. K., Jain, R., Radhapyari, K., Jadon, N., & Agarwal, S. (2011). Voltammetric techniques for the assay of pharmaceuticals – A review. *Analytical Biochemistry*, *408*, 179–196.

Gupta, V. K., Jain, R., & Varshney, S. (2007). Electrochemical removal of the hazardous dye Reactofix Red 3 BFN from industrial effluents. *Journal of Colloid and Interface Science*, *312*, 292–296.

Gupta, V. K., Mittal, A., Malviya, A., & Mittal, J. (2009). Adsorption of carmoisine A from wastewater using waste materials – Bottom ash and deoiled soya. *Journal of Colloid and Interface Science*, *335*, 24–33.

Gupta, V. K., Rastogi, A., & Nayak, A. (2010). Biosorption of nickel onto treated alga (Oedogoniumhatei): Application of isotherm and kinetic models. *Journal of Colloid and Interface Science*, *342*(2), 533–539.

Gupta, V. K., Pathania, D., Agarwal, S., & Singh, P. (2012). Adsorptional photocatalytic degradation of methylene blue onto pectin-CuS nanocomposite under solar light. *Journal of Hazardous Materials*, *243*, 179–186.

Gupta, V. K., Pathania, D., Singh, P., Kumar, A., & Rathore, B. S. (2014). Adsorptional removal of methylene blue by gum-cerium (IV) tungstate hybrid cationic exchanger. *Carbohydrate Polymers*, *101*, 684–691.

Gupta, V. K., Pathania, D., Singh, P., Rathore, B. S., & Chauhan, P. (2013). Cellulose acetate–zirconium (IV) phosphate nano-composite with enhanced photocatalytic activity. *Carbohydrate Polymers*, *95*, 434–440.

Hassan, S. S. M., Marei, S. A., Badr, I. H., & Arida, H. A. (2001). Novel solid-state ammonium ion potentiometric sensor based on zirconium titanium phosphate ion exchanger. *Analytica Chimica Acta*, *427*, 21–28.

Innamuddin, S. A., Khan, W. A., Siddiqui, A. A., & Khan, A. A. (2007). Synthesis, characterization and ion-exchange properties of a new and novel 'organic-inorganic' hybrid cation-exchanger: Nylon-66 Zr(IV) phosphate. *Talanta*, *71*, 841–847.

Islam, M., & Patel, R. (2008). Polyacrylamide thorium (IV) phosphate as an important lead selective fibrous ion exchanger: Synthesis, characterization and removal study. *Journal of Hazardous Materials*, *156*, 509–520.

Jain, A. K., Gupta, V. K., Bhatnagar, A., & Suhas. (2003). A comparative study of adsorbents prepared from industrial wastes for removal of dyes. *Separation Science and Technology*, *38*, 463–481.

Khan, A. A., Alam, M. M., & Inamuddin. (2005). Preparation, characterization and analytical applications of a new and novel electrically conducting fibrous type polymeric-inorganic composite material: Polypyrrole Th(IV) phosphate used as a cation exchanger and Pb(II) ion selective membrane electrode. *Materials Research Bulletin*, *40*, 289–305.

Khan, A. A., Niwas, R., & Alam, M. M. (2002). Ion-exchange kinetics on styrene supported zirconium(IV) tungstophosphate: An organic–inorganic type cation exchanger. *Journal of Chemical Technology*, *9*, 256–260.

Khan, A. A., & Paquiza, L. (2011). Characterization and ion-exchange behavior of thermally stable nano-composite polyaniline zirconium titanium phosphate: Its analytical application in separation of toxic metals. *Desalination*, *265*, 242–254.

Mittal, A., Gupta, V. K., Malviya, A., & Mittal, J. (2008). Process development for the batch and bulk removal and recovery of a hazardous, water-soluble azo dye (Metanil Yellow) by adsorption over waste materials (Bottom Ash and De-Oiled Soya). *Journal of Hazardous Materials*, *151*, 821–832.

Mittal, A., Mittal, J., Malviya, A., & Gupta, V. K. (2009). Adsorptive removal of hazardous anionic dye "Congo red" from wastewater using waste materials and recovery by desorption. *Journal of Colloid and Interface Science*, *340*, 16–26.

Mittal, A., Mittal, J., Malviya, A., & Gupta, V. K. (2010). Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials. *Journal of Colloid and Interface Science*, *344*, 497–507.

Mittal, A., Mittal, J., Malviya, A., Kaur, D., & Gupta, V. K. (2010). Adsorption of hazardous dye crystal violet from wastewater by waste materials. *Journal of Colloid and Interface Science*, *343*, 463–473.

Mojumdar, S. C., Varshaney, K. G., & Agarwal, A. (2006). Hybrid fibrous ion exchange materials: Past, present and future. *Research Journal of Chemistry and Environment*, *10*(1), 89–97.

Nabi, S. A., & Naushad, Mu. (2008). Synthesis, characterisation and analytical application of a new composite cation exchanger cellulose acetate–Zr (IV) molybdophosphate. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *316*, 217–225.

Nabi, S. A., Naushad, Mu., & Bushra, R. (2009a). A new hybrid EDTA-zirconium phosphate cation exchanger: Synthesis, characterization and adsorption behavior for environmental monitoring. *Adsorption Science & Technology*, *27*, 423–437.

Nabi, S. A., Naushad, Mu., & Bushra, R. (2009b). Synthesis and characterization of a new organic–inorganic Pb^{2+} selective composite cation exchanger acrylonitrile stannic (IV) tungstate and its analytical applications. *Chemical Engineering Journal*, *152*, 80–87.

Nabi, S. A., Naushad, Mu., & Inamuddin. (2007). Synthesis and characterization of new inorganic cation exchanger-Zr(IV) tungstomolybdate: Analytical application for metal content determination in real sample and synthetic mixture. *Journal of Hazardous Materials*, *42*, 404–411.

Nabi, S. A., Shahadat, M., Bushra, R., Oves, M., & Ahmed, F. (2011). Synthesis and characterization of polyaniline Zr(IV) sulphosalicylate composite and its applications (1) electrical conductivity and (2) antimicrobial activity studies. *Chemical Engineering Journal*, *173*, 706–714.

Nabi, S. A., Shahadat, Md., Bushra, R., Shalla, A. H., & Ahmed, F. (2010). Development of composite ion-exchange adsorbent for pollutants removal from environmental wastes. *Chemical Engineering Journal*, *165*, 405–412.

Park, B. D., & Kadla, J. F. (2012). Thermal degradation kinetics of resole phenol-formaldehyde resin/multi-walled carbon/cellulose nanocomposite. *Thermochimica Acta*, *540*, 107–115.

Pathania, D., Singh, P., & Siddiqi, Z. M. (2013). Separation and estimation of heavy metals on zeolitic material synthesized from fly ash by chemical modification. *Ion Exchange Letters*, *1–4*, 1–6.

Reilley, C. N., Schmid, R. W., & Sadek, F. S. (1959). Chelon approach to analysis: I. Survey of theory and application. *Journal of Chemical Education*, *36*, 555–564.

Rekha, K., Nirmala, M., Nair, M. G., & Anukaliani, A. (2010). Structural, optical, photocatalytic and antibacterial activity of zinc oxide and manganese doped zinc oxide nanoparticle. *Physica B*, *405*, 3180–3185.

Sanghavi, B. J., Mobin, S. M., Mathur, P., Lahiri, G. K., & Srivastava, A. K. (2013). Biomimetic sensor for certain catecholamines employing copper(II) complex and silver nanoparticle modified glassy carbon paste electrode. *Biosensors and Bioelectronics*, *39*, 124–132.

Sanghavi, B. J., Sitaula, S., Griep, M., Karna, S., Ali, M., & Swami, N. (2013). Real-time electrochemical monitoring of adenosine triphosphate in the picomolar to micromolar range using graphene-modified electrodes. *Analytical Chemistry*, *85*, 8158–8165.

Sanghavi, B. J., & Srivastava, A. K. (2010). Simultaneous voltammetric determination of acetaminophen, aspirin and caffeine using an in situ surfactant-modified multiwalled carbon nanotube paste electrode. *Electrochimica Acta*, *55*, 8638–8648.

Sanghavi, B. J., & Srivastava, A. K. (2013). Adsorptive stripping voltammetric determination of imipramine, trimipramine and desipramine employing titanium dioxide nanoparticles and an Amberlite XAD-2 modified glassy carbon paste electrode. *Analyst*, *138*, 1395–1404.

Siddiqui, W. A., Khan, S. A., & Inamuddin. (2007). Synthesis, characterization and ion exchange properties of a new and novel organic–inorganic hybrid cation exchanger: Poly(methyl methacrylate) Zr(IV) phosphate. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *295*, 193–199.

Siddiqi, Z. M., & Pathania, D. (2003b). Studies on titanium(IV) tungstosilicate and titanium (IV) tungstophosphate. II. Separation and estimation of heavy metals from aquatic environments. *Acta Chromatographica*, *13*, 172–185.

Siddiqi, Z. M., & Pathania, D. (2003a). Titanium (IV) tungstosilicate and titanium (IV) tungstophosphate: Two new inorganic ion exchangers. *Journal of Chromatography A*, *987*, 147–158.

Topp, N. E., & Pepper, K. W. (1949). Properties of ion-exchange resins in relation to their structure. Part I. Titration curves. *Journal of the Chemical Society*, 3299–3303.

Vilhera, C., Goncalves, M. L., & Mota, A. M. (2004). Binding of copper (II) to pectin by electrochemical methods. *Electroanalysis*, *16*, 2065–2072.

Yang, Z., Chen, S., Hu, W., Yin, N., Zhang, W., & Xiang, C. (2012). Flexible luminescent CdSe/bacterial cellulose nanocomposite membrane. *Carbohydrate Polymers*, *88*, 173–178.

Zeng, T., Pan, L. T., & Gao, H. W. (2008). Heterodinuclear replacement complexation for sensitive determination of iron ion in surface water with dibromocarboxyarsenazo. *Journal of the Chinese Chemical Society*, *55*, 79–87.

Zhao, X. T., Zhao, H. P., Le, Y. Q., Zeng, T., & Gao, H. W. (2007). Determination of cobalt at ng ml^{-1} level in water using the electrophilic substitution complexation between Co(II) and chlorophosphonazo-p-Cl-Cu(II) complex. *Annali di Chimica*, *97*, 251–263.