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Characterization and ion-exchange behavior of thermally stable nano-composite polyaniline zirconium titanium phosphate: Its analytical application in separation of toxic metals

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ABSTRACT

A 'polymeric-inorganic' advanced nano-composite cation-exchanger has been synthesized via sol–gel technique by incorporating polyaniline into inorganic ion-exchanger, zirconium titanium phosphate, a class of mixed material of tetravalent bimetallic acid salts (TMA). The composite shows extraordinary high ion-exchange capacity of 4.52 meq g^{-1} as well as good chemical and thermal stability than other polyaniline composites prepared so far. The physico-chemical property of the composite, polyaniline zirconium titanium phosphate (PAZTP) was determined using AAS, TEM, SEM, FTIR and TGA-DTA studies. Ion-exchange behavior was also observed to characterize the material. On the basis of distribution studies, the material was found to be highly selective for toxic heavy metal ions Hg(II) and Pb(II). The analytical applications of the material have been explored by achieving some binary as well as ternary separations of heavy metal ions. A comparative study of the ion-exchange properties of PAZTP with other polyaniline composites has been done.

1. Introduction

Human exposure to heavy metals has risen dramatically in the last 50 years, however, as a result of an exponential increase in the use of heavy metals in the industrial processes and products. The most often implicated in human poisoning are mercury, nickel, lead, arsenic, cadmium, aluminum, chromium and copper. Mercury and lead fulfil no essential function in the human body, it can merely do harm after uptake from food, air or water. In today's industrial society, many occupations involve daily heavy metal exposure, and over 50 professions entail exposure to mercury alone like physicians, pharmaceutical workers, any dental occupation, cosmetic workers, etc. Toxicity studies confirm that these metals can directly influence human behavior by impairing mental and neurological functions, influencing neurotransmitter production and utilization and altering numerous metabolic body processes.

So every possible care should be taken to keep them isolated from getting mixed into air, water and soil. For this purpose, various competent technologies including membrane process, precipitation, adsorption, electrosorption and ion-exchangers were developed to remove the heavy toxic metal ions from the polluted water [1–9]. In the last decade, ion-exchangers have been used extensively in the chemical decontamination process for metal ion recovery, regeneration of decontaminants, removal of the formulation chemicals from the coolant [10] and aqueous effluents [11–18]. Advancement of inorganic ion-exchangers is not only due to high thermal stability and resistivity but also for unusual selectivity for ionic species and versatility in separation sciences [19,20]. Organic–inorganic hybrid materials are hi-tech because they can present simultaneously both the properties of an inorganic molecule besides the usual properties of polymer (an organic molecule). Nowadays, nano-composites lead to unexpected new properties exhibiting a vast application potential [21] which are often not exhibited by individual compounds and thus open a new avenue for chemists, physicists and materials scientists [22].

Aryl amine polymers have been intensively studied, for instance polyaniline has received great attention since its rediscovery by Shirakawa et Al. [23], due to its wide range of proposed application [24] such as actuators [25], electrochromic and photovoltaic devices [26], secondary batteries [27], fuel cells [28], supercapacitors [29], ionic sensors [30], biosensors, [31] electro catalysis [32] and corrosion protection [33]. All of the previously reported polyaniline conducting polymers are based on its interesting and unique electrical conductivity (metallic) and electroactivity. This paper deals with the new potential application of aryl amine polymer, polyaniline, as a composite cation exchange material useable for environmental protection in water and wastewater treatment, some of them have been prepared successfully and used in environmental analysis [34–39].

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An effort has been done to compare the ion-exchange properties of PAZTP with other polyaniline based organic–inorganic hybrid composites prepared so far [40–44].

2. Experimental

2.1. Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, Loba Chemie, E-merck and Qualigens (India Ltd., used as received). All other reagents and chemicals were of analytical grade. The following instruments were used during the present research work: A FTIR spectrophotometer (Perkin Elmer, U.S.A, model Spectrum-BX); digital pH-meter (Elico Li-10, India); Rigaku X-ray diffractometer — Phillips (Holland), model PW 1148/89; UV/VIS spectrophotometer — Elico (India), model EI 301E; a double beam atomic absorption spectrophotometer (GBC 902, Australia); a thermal analyzer — V2.2A DuPont 9900; Carlo-Erba, model 1108; a digital potentiometer (Equiptronics EQ 609, India; accuracy $\pm$0.1 mV with a saturated calomel electrode as reference electrode; an electronic balance (digital, Sartorius-21OS, Japan) and an automatic temperature controlled water bath incubator shaker — Elcon (India).

2.2. Synthesis of composite cation-exchanger polyaniline zirconium titanium phosphate (PAZTP)

The composite cation-exchanger was prepared by sol–gel mixing of polyaniline (an organic polymer) into the inorganic precipitate of zirconium titanium phosphate (ZTP) with varying mixing ratio as indicated in Table 1. The preparation method for the inorganic precipitate of zirconium titanium phosphate (ZTP) was very similar to that of Alberti and Constantino [45], with slight modification [46]. Dark green color polyaniline gel was prepared by oxidative coupling using ammonium persulphate in an acidic aqueous medium. The precipitate of polyaniline was added into the white inorganic gel of ZTP with a constant stirring. Black colored precipitate obtained was allowed to settle overnight and then filtered off and washed thoroughly with DMW to remove excess acid and any adhering ions (chloride and sulphate). The washed gel was dried over P_4O_{10} at 30 °C in an oven. The dried product was immersed in a 1 M HNO_3 solution for complete replacement of counter ions by the H^+ form. The excess acid was removed after several washing with DMW then dried at 40 °C and sieved to obtain shiny black granules of PAZTP. On the basis of the Na^+ exchange capacity (I.E.C) and yield percentage, sample PA-7 was selected for further studies.

2.3. Ion-exchange properties of polyaniline zirconium titanium phosphate (PAZTP)

2.3.1. Ion-exchange capacity

1 M alkali and alkaline earth metal nitrates were used as eluants to elute the H^+ ions completely from one gram (1 g) of the dry cation-exchanger by the column method, maintaining a very slow flow rate (~0.5 ml min^{-1}). The effluent was titrated against a standard (0.1 M) NaOH solution for the total ions liberated in the solution using phenolphthalein as indicator and the I.E.C. (meq g^{-1}) values were noted.

2.3.2. Elution behavior and effect of eluant concentration

The optimum concentration of the eluants for the complete elution of the H^+ ions was determined by passing a fixed volume (250 ml) of sodium nitrate ($NaNO_3$) solution of varying concentrations through the column containing 1 g of the exchanger in the H^+ form with a minimum flow rate. The effluent was titrated against a standard alkali solution (0.1 M NaOH). The efficiency of the column was determined by eluting different 10 ml fractions of $NaNO_3$ solution with a minimum flow rate and each fraction of 10 ml effluent was titrated against a standard alkali solution for the H^+ ions eluted out.

2.3.3. pH Titration

The Topp and Pepper method [47] was employed for pH titration studies of PAZTP (PA-7) in equimolar solutions of alkali metal chlorides and their hydroxides. 500 mg portions of the sample in the H^+ form was treated with 50 ml of the solution concerned. The pH of the solution was recorded every 24 h until equilibrium was attained.

2.4. Chemical stability and thermal stability

The chemical stability also plays an important role in the elucidation of properties of the ion-exchangers. Portions of 250 mg of composites in the H^+ form were treated with 20 ml of varying concentration of acids, bases, organic solvents and also in DMW for 24 h with occasional shaking.

To study the effect of temperature on the I.E.C., 1 g material (PA-7) in the H^+ form was heated at various temperatures in a muffle furnace for 1 h and the Na^+ ion-exchange capacity was determined by the column process after cooling them at room temperature.

2.5. Chemical composition

To determine the chemical composition of polyaniline zirconium titanium phosphate (PAZTP), 200 mg of the sample was dissolved in 20 ml of concentrate H_2SO_4. The material was analyzed for

Table 1
Conditions of the preparation and the ion-exchange capacity of various samples of the PAZTP composite cation-exchanger.

Sample	Mixing volume ratio (v/v)			Mixing volume ratio (v/v) Volume ratio (v/v)			Appearance of the beads after drying	Na^+ ion-exchange capacity (meq/gm)
	$TiCl_4$ in H_2SO_4	$ZrOCl_2$ in H_2SO_4	Na_2HPO_4 in DMW	% Aniline in 1 M HCl	Aniline in 1 M HCl	0.1 M $(NH_4)_2S_2O_8$ in 1 M HCl		
PA-1	1(1 M)	1(1 M)	1(2 M)	0.5	1	1	Black shiny granules	3.7
PA-2	1(0.1 M)	1(4 M)	2(1 M)	0.2	2	1	Black shiny granules	1.12
PA -3	1(0.1 M)	1(2 M)	2(0.2 M)	1	1	2	Dark blackish purple granules	1.6
PA-4	1(1 M)	1(1 M)	2(1 M)	0.12	1	1	Greenish granules	0.72
PA-5	1(1 M)	1(1 M)	1(2 M)	1	1	1	Dull purple crystal	0.72
PA-6	1(1 M)	1(2 M)	2.5(2 M)	5	1	1	Greenish granules	0.512
PA-7	**1(0.2 M)**	**1(0.1 M)**	**2(0.2 M)**	**0.5**	**1**	**2**	**Black shiny granules**	**4.52**
PA-8	1(0.2 M)	1(0.1 M)	2(.2 M)	1	0.25	2	Black shiny granules	4.2
PA-9	1(0.1 M)	1(0.1 M)	2(0.2 M)	1	1	2	Blackish purple crystal	3
PA-10	1(0.1 M)	1(0.1 M)	2(1 M)	0.1	1	1	Dark green crystal	2.8
PA-11	1(0.2 M)	1(0.1 M)	2(0.2 M)	0.5	1	1	Greenish granules	2.5
PA-12	1(0.2 M)	1(0.1 M)	2(0.2 M)	–	–	–	White granules	3.36
PA-13	–	–	–	0.5	1	1	Dark green granules	0.20

Bold signifies the selected sample, on the basis of high ion exchange capacity, for carrying out further experimental studies mentioned in the manuscript.