International Journal of Research in Advent Technology, Vol.7, No.3, March 2019
E-ISSN: 2321-9637
Available online at www.ijrat.org

Synthesis and application of hybrid organic–inorganic composite material: Polyaniline Zirconium (IV) Iodosulfosalicylate

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Abstract- Today the contamination of water is becoming a serious health issue all over the world. Water is being polluted by the industrial waste, sewage waste, etc. The presence of heavy metals is making water adulterated. There are assorted approaches for the de adulteration of water like- chemical precipitation, ultra filtration, reverse osmosis etc. But these approaches are not agreeable for the deportation of heavy metals in trace amount form the adulterated water. So it was hurting for the advancement of techniques for the distillation of water. And hence ion exchange technique was made known. Many metals based ion exchanger were generated but the influential ion exchanger is an inorganic ion exchanger based on zirconium metal for the reason of their admirable ion exchange properties. In the present study we have elucidate the synthesis of novel hybrid Inorganic-organic Zirconium-based ion exchangers and discuss its analytical applications in the waste water treatment by the determination of ion exchange capacity.

Keywords- Ion exchange resin, organic inorganic hybrid materials, Polyaniline Zirconium (IV) Iodosulfosalicylate, heavy Metals

1. INTRODUCTION

The adulteration of groundwater, which is a major source of water, is a serious health and environmental problem all over the world. Pollution of ground water is principally due to industrial effluent and municipal waste [1-3]. Due to rapid development and industrialization the levels of industrial pollution have been rising rapidly. Adulteration of water by heavy metals through discharge of industrial waste water is a very serious environmental problem because of their toxicological and physiological effects [4-7]. So the problem of pollution due to industrial wastewater is becoming serious in the world. Therefore , the treatment of polluted industrial waste water remain a topic of global concern since waste water collected from municipalities, communities and industries must ultimately be returned to receiving waters or to the land [8-11]. Industrial waste pour toxic metals that makes the water polluted has attracted great attention. A number of regulatory agencies have aspire to restrict the discharge of untreated metal-containing effluents into public sewers, rivers, sea and onto land. Heavy metals are of special concern because of their persistence [12-15]. Heavy metals are non biodegradable and tend to accumulate in living organisms. Many heavy metal ions are known to be toxic or carcinogenic [16].

Heavy metals are those metals and their compounds that harm human health when absorbed or inhaled. Generally in small amounts, some heavy metals support life, but when taken in large amounts, they become toxic. Chemically Heavy metals are defined as chemical elements with a specific gravity that five times more than the specific gravity of water. Some well-known toxic metallic elements with a specific gravity that is 5 or more than that of water are Arsenic, Cadmium, Iron, Lead, and Mercury [17-19]. Heavy metals are non-degradable in the environment and can cause harm to living species.

2. EXPERIMENTAL

2.1. *Reagents and instruments*

The important chemicals and reagents which are used for the synthesis of our selected ion exchange resins are Zirconium (IV) oxychloride (Loba Chemie Pvt. Ltd., Mumbai, India), potassium iodate (RFCL Limited, New Delhi, India), 5-sulfosalicylic acid (Sisco Research Pvt. Ltd., Maharashtra, India), polyaniline (sigma alderic, India). The chloride and nitrate salts of metal ions were used of analytical grade. Solutions of metal salts were prepared in doubly distilled water and standardized according to the appropriate methods.

A digital pH meter (Cyberscan pH 2100), FTIR spectrophotometer (Interspec 2020, Spectrolab, UK), an automatic thermal analyser (DTG, 60 H Shimadzu) water bath, incubator and shaker were used.

2.2 *Synthesis of polyaniline zirconium (iv) iodosulfosalicylate ion exchange resin:*

Polyaniline zirconium(IV) iodosulfosalicylate resin was prepared by adding 0.1M solution of zirconium oxychloride to a mixture of 0.1M solution of 5-sulfosalicylic acid, 0.1 M solution of potassium iodate and polyaniline .(in the ratio 1:2:2:3) at pH 1. The resulting solution was stirred vigorously on a magnetic stirrer for 8 hours.The resulting product was filtered out and washed with distilled water and dried n a hot plate at 40°C on a hot plate. The product formed is cracked into small granules and kept for further analysis.

2.3. *Characterisation of ion exchanger:*

FTIR spectrum of polyaniline zirconium (IV) iodosulfosalicylate dried at 50 °C was recorded using the KBr pellet method. Simultaneous TGA and DTA studies of polyaniline zirconium (IV) iodosulfosalicylate were carried out by DTG. 60 H Shimadzu Thermal analyser between 20°C and 800°C at the rate of 20°C per minute in a nitrogen atmosphere. The microphotographs of polyaniline zirconium (IV) iodosulfosalicylate and metals sorbed polyaniline zirconium (IV) iodosulfosalicylates were obtained by scanning electron microscope at various magnifications.

2.4 Chemical stability:

Chemical stability of the synthesized polyaniline zirconium (IV) iodosulfosalicylate was determined by equilibrataing 0.5 g of the sample with 20 ml of different concentrations of H_2SO_4, HNO_3, HCl, acetic acid and bases .

3. RESULTS AND DISCUSSION:

In the present study an attempt has been made to explore the synthesis of hybrid ion exchange resin polyaniline zirconium (IV) iodosulfosalicylate and its application for removal of heavy metals from synthetic solution and waste water samples. Various samples of hybrid cation exchanger were prepared by sol-gel mixing of inorganic precipitate of zirconium(IV) iodosulfosalicylate and different molar concentrations of aniline (0.1-0.4M). The ion exchange capacity of synthesized ion exchange resin for different metal ions was determined by column process and the result is shown given tables 1-5.

Table 1 Conditions of synthesis of different samples and Ion exchange capacity for Pb^{2+}Ion

SAMPLE	Volume ratio(v\v)	Zr (IV)	IO_3^-	Sulfosalicylic acid	Polyaniline	IEC(meg/g) for Pb^{+2}
PZ-1	1:1:1:1	0.1M	0.1M	0.1M	0.1M	1.98
PZ-2	1:1:1:1	0.1M	0.1M	0.1M	0.2M	2.16
PZ-3	1:1:1:1	0.1M	0.1M	0.1M	0.4M	3.25

Table-2 Conditions of synthesis of different samples and Ion exchange capacity for sr^{2+}Ion

SAMPLE	Volume ratio(v\v)	Zr(IV)	IO_3^-	Sulfosalicylic acid	Polyaniline	IEC(meg/g) for Sr^{+2}
PZ-1	1:1:1:1	0.1M	0.1M	0.1M	0.1M	0.98
PZ-2	1:1:1:1	0.1M	0.1M	0.1M	0.2M	1.23
PZ-3	1:1:1:1	0.1M	0.1M	0.1M	0.4M	2.23

Table-3 Conditions of synthesis of different samples and Ion exchange capacity for Cd^{2+}Ion

SAMPLE	Volume ratio(v\v)	Zr(IV)	IO_3^-	Sulfosalicylic acid	Polyaniline	IEC(meg/g) for cd^{+2}
PZ-1	1:1:1:1	0.1M	0.1M	0.1M	0.1M	2.03
PZ-2	1:1:1:1	0.1M	0.1M	0.1M	0.2M	2.76
PZ-3	1:1:1:1	0.1M	0.1M	0.1M	0.4M	3.98

Table-4 Conditions of synthesis of different samples and Ion exchange capacity for K^+ Ion.

SAMPLE	Volume ratio(v\v)	Zr(IV)	IO_3^-	Sulfosalicylic acid	Polyaniline	IEC(meg/g) for Na^+
PZ-1	1:1:1:1	0.1M	0.1M	0.1M	0.1M	0.64
PZ-2	1:1:1:1	0.1M	0.1M	0.1M	0.2M	1.56
PZ-3	1:1:1:1	0.1M	0.1M	0.1M	0.4M	1.83

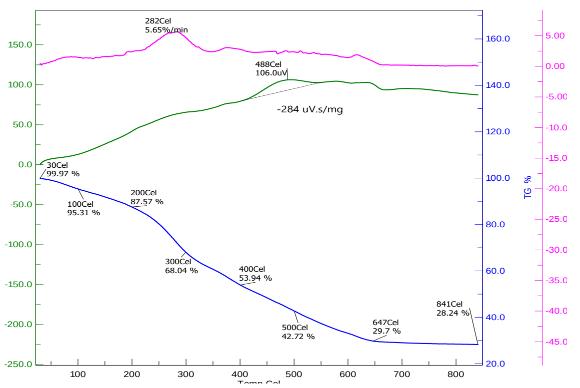
Table-5 Conditions of synthesis of different samples and Ion exchange capacity for Na^+Ion

SAMPLE	Volume ratio(v\v)	Zr(IV)	IO_3^-	Sulfosalicylic acid	Polyaniline	IEC(meg/g) for k^+
PZ-1	1:1:1:1	0.1M	0.1M	0.1M	0.1M	0.93
PZ-2	1:1:1:1	0.1M	0.1M	0.1M	0.2M	1.05
PZ-3	1:1:1:1	0.1M	0.1M	0.1M	0.4M	1.98

The maximum capacity was obtained with 0.4M polyaniline. Therefore polyaniline zirconium (IV) iodosulfosalicylate was synthesized using 0.4 polyaniline for further studies(PZ-3).this material appears to be promising hybrid material with good ion exchange capacity, mechanical and chemical stability in comparison to inorganic ion exchange, zirconium(IV) iodosulfosalicylate. The improvement in these characteristics may be due to the binding of polyaniline with inorganic moiety i.e. zirconium (IV) iodosulfosalicylate.

Chemical stability of any ion exchange materials is an important parameter that is required for their suitability for analytical applications [20]. In view of this the chemical stability of polyacrylamide zirconium (IV) iodate has been evaluated in different concentrations of HCl, HNO_3, H_2SO_4, CH_3COOH and NaOH. It was found that the material is fairly stable in 1 M HCl, 1 M HNO_3, 1M H_2SO_4, 1M CH_3COOH and 0.10 M NaOH

The FTIR spectrum (Fig. 1) of polyaniline zirconium (IV) iodosulfosalicylate revealed the presence of external water molecule, metal-oxygen and metal-OH

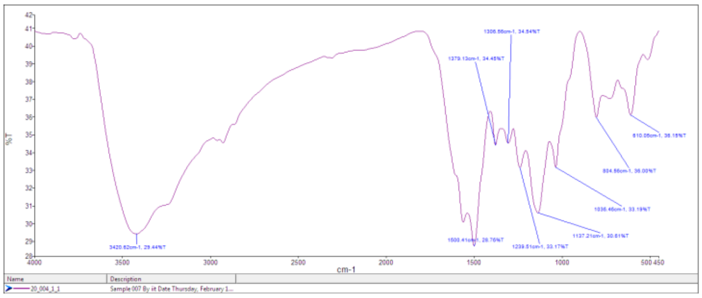


stretching bands. The bands at 1671.82 cm−1 and 1624.5 cm−1 are attributed to C=N and C=C stretching modes for the quinoid and benzenoid rings, the peaks at about 1379 cm^{-1} and 1306 cm^{-1} are attributed to C–N stretching mode for benzenoid ring, and the peak at 1137 cm^{-1} is assigned to the plane bending vibration of C–H, and out-plane bending vibrations of polyaniline are reported to occur at about 804 cm^{-1}.

Figure 1: FTIR spectrum of polyaniline zirconium (IV) iodosulfosalicylate.

TGA curve for polyaniline zirconium (IV) iodosulfosalicylate hybrid ion exchanger in nitrogen atmosphere are shown in Fig. 2. The results reveal a typical three-step weight loss behaviour. For polyaniline, in the first step, weight loss is seen up to 200 °C. This is attributed to the loss of water molecules from the nanocomposite mate-rial. The second weight loss starts at around 265 °C and ends at around 629 °C. This is attributed to possibly decomposition of the backbone of polyaniline as well as the low molecular weight fragments of the polymer and the decomposition of the polymer has been completed. The third step, starting from 300 °C onwards, rep-resents degradation and large weight loss above 500 °C and the formation of metal oxide residue.

Figure 2: TGA- curves of polyaniline zirconium (IV) iodosulfosalicylate



4. CONCLUSION:

The results of the investigation performed implies that polyaniline zirconium(IV) iodosulfosalicylate can be suggested a promising and effective hybrid cation exchanger. The reason to develop hybrid ion exchange resin was that, earlier the resins used were not that effective in the removal of heavy metal ions from the adulterated water. And as adulteration of water is becoming a serious health issue, hence to improve the quality of water for drinking purpose hybrid ion exchange resins were developed. To determine the characteristics of the resin the FTIR and TGA analysis were carried out. Different sample of resins were

(A.1)

prepared by varying the concentration of polyaniline i.e. 0.1M, 0.2M, 0.4M. Determination of ion exchange capacity of all the samples of resin was carried out by column method, hence it was found that the ion exchange capacity of 0.4M concentration resin was the highest and that of 0.1M resin was the lowest. Hence from this it was concluded that as the concentration of the polyaniline in the samples of resins increases, the sample becomes more effective. Many metal salts like KCl , NaCl , $SrCl_2$, $CdCl_2$, $Pb(NO_3)_2$, were used for detection of ion exchange capacity of resins, and the resins showed the highest affinity towards Pb(II). Hence it can be concluded that the hybrid resin prepared can be used for the removal of heavy metal ions from water specially in the removal of Pb(II).

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