International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.9 pp 424-432, 2015

Ion exchange, adsorption and antimicrobial properties of tin(IV) molybdovanadosulphosalicylate composite material and its application in environmental remediation

Vinisha Valsaraj P.*[1] and Janardanan C.

Post Graduate and Research Department of Chemistry, Sree Narayana College, Kannur-670 007, Kerala, India

Abstract: A new composite tin(IV) molybdovanadosulphosalicylate was synthesized, where properties of organic and inorganic components combined together which leads to the formation of a new solid state structure with new features. The composite materials exhibit good ion exchange capacity, higher stability, reproducibility and selectivity for heavy metals. The distribution coefficient of different metal ions on the composite is in the following order; Pb(II) > Cd(II) > Co(II) > Cu(II) > Zn(II) > Bi(III) > Ni(II) > Mn(II) > Mg(II). On the basis of difference in K_d values some important binary separations of metal ions were achieved. Separations of heavy metal ions from synthetic mixtures were achieved with this composite material. UV-Visible spectrophotometric studies revealed the enhanced adsorption ability of this material towards dyes. The carbon dioxide adsorption ability of the material was studied. The antibacterial activity of tin(IV) molybdovanadosulphosalicylate was explored against *staphylococcus aureus*. The results confirmed the bacteriostatic nature of the tin(IV) molybdovanadosulphosalicylate. On the basis of good ion exchange capacity, adsorption ability and antimicrobial activity, tin(IV) molybdovanadosulphosalicylate can be considered as an excellent material for the environmental remediation.

Keywords : Adsorption, Antimicrobial activity, Binary separation, Distribution coefficient, Ion exchange capacity.

Introduction

The synthesis of composite material has attained a great deal of attention because it provided new material with advanced properties by encomposing both organic and inorganic characteristics within a single molecular scale. The intrinsic multifunctional character of these materials makes them potential candidate in different fields such as corrosion chemistry, membrane chemistry, separation chemistry, biochemistry, environmental chemistry, material chemistry and so forth. Thus the synthesize and study of different properties of such hybrid ion exchangers with good ion exchange properties, high stability, reproducibility, and selectivity for heavy toxic metal ions were explored by Khan et al. [1]. Anchoring of organic molecules bearing ionogenic groups, such as –OH, –COOH, SO_3H, etc. onto inorganic ion-exchangers has been reported [2-4].

The limitless growth in industrialization has depleted the natural habitat of living beings due to uncontrolled pollution. Effluent from the dyeing and finishing processes contain highly coloured species, high amounts of surfactant, dissolved solids and harmful heavy metals. The heavy metals present even at trace levels in natural waters has been proven toxic for humans and animals causing major health problems [5]. Highly coloured wastes are not only aesthetically displeasing but also hinder light penetration and may in consequence disturb biological processes in water-bodies. Moreover, the organic dyes are toxic to some organisms and hence disturb the ecosystem [6-9]. To solve this problem, industrial waters must be treated to remove the toxic metal ions and colour before they are discharged into the water bodies. The ion exchange is simple and effective technique for separation and recovery of heavy metals from waste water.

Recently, global warming resulted from greenhouse gases has received a prime attention. Carbon dioxide (CO_2) has occupied more than 60% of the total content of greenhouse gases that emitted in the atmosphere which induces to the global warming effects [10]. Based on this fact, efforts to reduce the concentration of CO_2 emitted to the atmosphere should be implemented actively and vigorously. Therefore, one of the strategies to reduce the concentration of CO_2 that emitted to the atmosphere is by executing carbon capture and storage (CCS) method [11]. A variety of adsorbents have been proposed by considering their structures and compositions as well as adsorption and regeneration mechanisms. Currently, the selection of a green–based material as solid adsorbent is seen as an attractive method to replicate the development of the existing adsorbent technology based on its high availability, inexpensive and environmental–friendly material.

In this present paper we introduced the synthesis of a novel composite ion exchange material and is characterized using various physiochemical techniques. Ion exchange and antimicrobial activity of this material was studied. Along with these properties we tried to understand the adsorption capability of this material towards dye and carbon dioxide.

Materials & Methods

Stannic chloride (E.Merck), Sodium molybdate (E.Merck), sodium vanadate and 5-sulphosalicylic acid (Loba Chem) were used for the synthesis of the exchangers. All other reagents and chemicals used were of analytical grade.

The precipitate of tin(IV) molybdovanadosulphosalicylate (SnMoVS) was prepared by adding gradually the solution of 0.1 M stannic chloride into the mixture of 0.05 M sodium vanadate, 0.05 M 5-sulphosalicylic acid and 0.05 M sodium molybdate solution with constant stirring at room temperature for 1 hr whereby a gel type slurry was obtained. The resulting precipitate was kept overnight in the mother liquor for digestion. After decanting off the supernatant liquid, the remaining precipitate was washed and filtered with demineralized water to remove any excess reagent. The material was dried in an oven at $50 \pm 2^{\circ}C$. In order to convert the material in H^+ form, it was subsequently treated with 1.0 M HNO_3 solution for 24 hrs with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess of acid was removed by washings with demineralized water and finally dried in an oven at $50 \pm 2^{\circ}C$. The material was sieved and kept in a desiccator.

The ion exchange capacity of the material was determined by column method [12] and the effect of temperature on ion exchange capacity was studied. Selectivity studies were carried out for various metal ions in demineralized water by batch process [12]. The effect of temperature on distribution value of metal ions was studied. Quantitative separations of some important metal ions were achieved on tin zirconium tungstate-polyaniline columns [12].

The adsorption study was conducted in a batch system in which 200 mg tin(IV) molybdovanadosulphosalicylate adsorbent was mixed with 50 mL of Crystal violet (CV) dye solution of 20 mgL^{-1} for 2hrs in a 100 mL conical flask and the mixture was shaken in an electrical shaker at a constant agitation speed. The sample solution withdrawn from each flask after 1 hr were then analysed by using UV-Visible diffuse reflectance spectrophotometer with 1 cm path length quartz cell by measuring absorbance at λmax of dyes (MB – 663 nm).

The experiments were repeated by varying the following parameters: contact time, temperature, adsorbent concentration, pH and dye concentration.

The dye removal percentage can be calculated as follows:

$$\text{Removal (\%)} = \frac{Ci - Ce}{Ci} \text{ X } 100$$

Where C_i and C_e are the initial concentration and equilibrium concentrations of dye solution (mgL^{-1}), respectively, V is the volume of solution (L) and W is the mass of adsorbent (mg).

Carbon dioxide adsorption-desorption experiments were conducted at at room temperature (298 K) using Quantachrome Quadrasorb automatic volumetric instrument. Ultrapure H_2 (99.95%) was purified further by using calcium aluminosilicate adsorbents to remove trace amounts of water and other impurities before introduction into the system. The weight of material, SnMoVS used for CO_2 adsorption-desorption experiment was 0.12 g.

The newly synthesized tin(IV) molybdovanadosulphosalicylate was examined in antibacterial activities against *Staphylococcus aureus* bacterial strains. Petriplates containing 20ml Muller Hinton medium were seeded with 24 hrs culture of bacterial strains such as *E coli* and *Staphylococcus aureus,* Wells of approximately 10mm were bored using a well cutter and 25 µL, 50 µL and 100µL of sample was added to the well from a stock concentration of 0.1g/1mL. The plates were then incubated at 37 °C for 24 hrs. The antibacterial activity was assayed by measuring the diameter of the inhibition zone formed around the well (NCCLS, 1993). Gentamycin was used as a positive control.

Results & Discussion

The composite, tin(IV) molybdovanadosulphosalicylate (SnMoVS) obtained as brownish orange solid having Na^+ ion exchange capacity of 1.89 $meqg^{-1}$ at room temperature.

FT-IR spectra of tin(IV) molybdovanadosulphosalicylate (SnMoVS) (Figure 1a) composite ion exchanger shows a broad band in the region ~3429 cm^{-1} which is attributed to symmetric and asymmetric –OH stretching, while the band at ~1622 cm^{-1} is attributed to H-O-H bending. A band in the region ~1378 cm^{-1} is attributed to the presence of δ (MOH). This indicates the presence of structural hydroxyl protons in SnMoVS. The band at 1160 cm^{-1} is attributed to the SO_3 asymmetric stretching vibrations of sulphosalicylic acid salts [13]. Bands at 805 cm^{-1} and ~496 cm^{-1} may be due to the presence of Mo-O-Sn and Sn-O bonds.

No observable peaks in the X-ray diffraction pattern of SnMoVS (Figure 1b) indicate the amorphous nature of the material. Scanning electron microscopy (SEM) study was performed to examine the surface morphology of composite material. SEM photograph of TSM depicted its irregular shape (Figure 1d) and the rough surface with pleats.

The thermogram of SnMoVS cation exchanger (Figure 1c) exhibit the weight loss of 10% up to ~ 100 °C which is due to the removal of free external water molecules. Further, a gradual mass loss (about 6%) up to 500 °C may be on account of the condensation of hydroxyl groups. There is no sudden decrease in the weight which indicates that there is no structural change in this material. Thus thermogravimetric analysis clearly reveals that the samples are quite stable at high temperatures up to 600 ºC and can be used in high temperature applications.

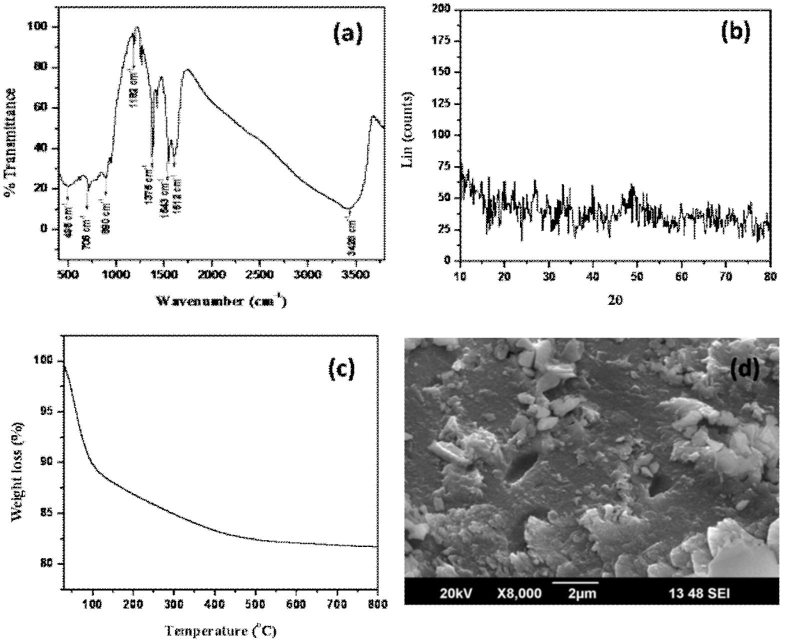

Fig. 1. a. FT-IR, b. XRD , C. TGA and d. SEM image of SnMoVS

In order to explore the potentiality of the new hybrid cation exchange material in the separation of metal ions, distribution studies for metals ions were performed in different solvent systems (Table 1). It is clear that the K_d values vary with the composition and nature of the contacting solvents. The selectivity for metal ions is in the order of Pb(II) > Cd(II) > Co(II) > Cu(II) > Zn(II) > Bi(III) > Ni(II) > Mn(II) > Mg(II). It was observed from the K_d value studies that the uptake of Pb(II) and Cd(II) is exceptionally high in all solvents, while the remaining metal ions are poorly sorbed. Thus, the composite cation exchanger can be very well utilized for the separation of lead and cadmium ions from waste effluents.

Table 1. K_d values of various metal ions in different electrolyte

Metal ion	Dimeneralized water	0.001M HNO_3	0.01M HNO_3	0.1M HNO_3	0.001M NH_4NO_3	0.01M NH_4NO_3	0.1M NH_4NO_3
Pb(II)	449.86	356.00	200.00	166.00	288.00	201.00	156.00
Zn(II)	37.20	15.00	NS	NS	15.00	NS	NS
Mn(II)	21.51	11.90	NS	NS	12.00	NS	NS
Ni(II)	24.60	11.12	NS	NS	15.00	NS	NS
Hg(II)	NS	NS	NS	NS	NS	NS	NS
Ca(II)	NS	NS	NS	NS	NS	NS	NS
Cd(II)	300.78	250.12	198.89	45.65	260.12	100.00	64.54
Co(II)	84.91	64.12	34.00	9.01	50.12	19.00	4.12
Cu(II)	51.90	26.99	3.70	NS	20.01	9.90	NS
Mg(II)	15.45	4.55	NS	NS	3.55	NS	NS
Al(III)	NS	NS	NS	NS	NS	NS	NS
Bi(III)	30.77	7.12	NS	NS	12.34	3.90	NS

NS: No observable Sorption

The separation capability of the material has been demonstrated by achieving some analytically important binary separations of some important metal ions viz. Mg(II)–Cd(II), Mg(II)–Pb(II), Ni(II)–Cd(II) and Ni(II)-Pb(II) (Table 2). Table 2 summarizes the salient features of these separations. The separation was based on sequential elution of ions through the column depending upon the metal-eluting ligand (eluent) stability. It was also observed that Pb(II) as well as Cd(II) retained strongly on the cation exchanger column. The weakly retained metal ions get eluted first, followed by the stronger one. It is evident from data that the separations are quite sharp, quantitative and reproducible.

Table 2. Binary separation of metal ions on SnMoVS

Separation achieved	Separation factor	Eluent	Metal ion (mg) Loaded	Metal ion (mg) Eluted	% Efficiency
Mg(II)		0.01M NH_4NO_3	2.80	2.75	98.96
Cd(II)	19.47	0.4 M HNO_3 + 0.4 M NH_4NO_3	1.92	1.87	97.40
Mg(II)		0.01 M NH_4NO_3	2.80	2.72	97.14
Pb(II)	29.12	0.5 M HNO_3 + 0.5 M NH_4NO_3	2.80	2.71	96.77
Ni(II)		0.01 M HNO_3	3.20	3.18	99.38
Cd(II)	12.23	0.5 M HNO_3 + 0.5 M NH_4NO_3	1.92	1.88	97.92
Ni(II)		0.01 M HNO_3	3.20	3.17	99.06
Pb(II)	18.29	0.5 M HNO_3 + 0.5 M NH_4NO_3	2.80	2.70	96.43

The practical utility of the composite material was demonstrated by separating lead and cadmium from synthetic mixtures (Table 3 & 4).

Table 3. Selective separation of Pb(II) from synthetic mixtures containing Pb(II), Cu(II) [2.57 mg], Mg(II) [2.97 mg], Hg(II) [4.70 mg] and Ni(II) [1.93 mg]

Amount of metal ion loaded (mg)	Amount of metal ion found (mg)	Recovery (%)	Eluent used	Volume of eluent (mL)
4.10	4.03	98.29	0.5 M HNO_3	70
3.92	3.85	98.21	0.5 M HNO_3	50

Table 4. Selective separation of Cd(II) from synthetic mixtures containing Cd(II), Cu(II) [2.57 mg], Mg(II) [2.97 mg], and Hg(II) [4.70 mg]

Amount of metal ion loaded (mg)	Amount of metal ion found (mg)	Recovery (%)	Eluent used	Volume of eluent (mL)
2.68	2.54	94.78	0.5 M HNO_3	70
2.29	2.16	94.32	0.5 M HNO_3	50

Crystal Violet, belonging to triphenylmethane group, is widely used in animal and veterinary medicine as a biological stain, for the purpose of identification [14]. Crystal Violet is harmful by inhalation, ingestion and skin contact, and has also been found to cause cancer and severe eye irritation in human beings [15,16]. It is poorly degraded as recalcitrant molecule by microbial enzymes, and can persist in several environments. Tin(IV) molybdovanadosulphosalicylate showed adsorptivity towards this harmful dye in aqueous solution.

The contact time between the dye (CV) and the adsorbent is of significant importance in the wastewater treatment by adsorption. In physical adsorption, most of the adsorbate species are adsorbed within a short interval of contact time. However, for strong chemical binding of the adsorbate with adsorbent, a longer contact time is required for the attainment of equilibrium. A large number of vacant surface sites are available for adsorption during the initial stage, and after certain contacting time, the remaining vacant surface sites are difficult to occupy due to repulsive forces between the solute molecules on the solid and bulk phases. The adsorption of CV was analysed as a function of contact time on 10 mgL^{-1} concentration of 50 mL dye solution with 200 mg exchanger at neutral pH and 30 °C (Figure 2c). The study shows that the equilibrium is attained within 2 hrs and it is selected as equilibrium time for further study. The effect of adsorbent dosage on the removal of CV was studied at 10 mgL^{-1} concentration of 50 mL dye solution (Figure 2a) for 2 hrs at neutral pH and 30 C°. Removal of dye increased with increasing adsorbent dosage which is due to the greater availability of reactive sites [17]. The percentage of CV removal ranged from 75.6 to 99 % within 2 hrs when treated with different amounts of exchanger.

Figure 2b shows the percentage sorption of dyes at different concentration of dyes in the presence of 200 mg of exchanger at neutral pH and 30 °C for 2 hrs. The percentage of removal decreases with the increase in dye concentration which may be due to the non availability of active site. The enhanced removal of dye at low dye concentration could be due to the faster movement of dye into the activated sites of composite [18]. However, at higher concentration (40 mgL^{-1}) the removal rate is decreased to 81.07% because the dye molecules need to diffuse to the adsorbent sites by intra particle diffusion. In addition to these factors, steric repulsion between the dye molecules could slow down the adsorption process at higher concentration of dye and thereby decrease the removal rate.

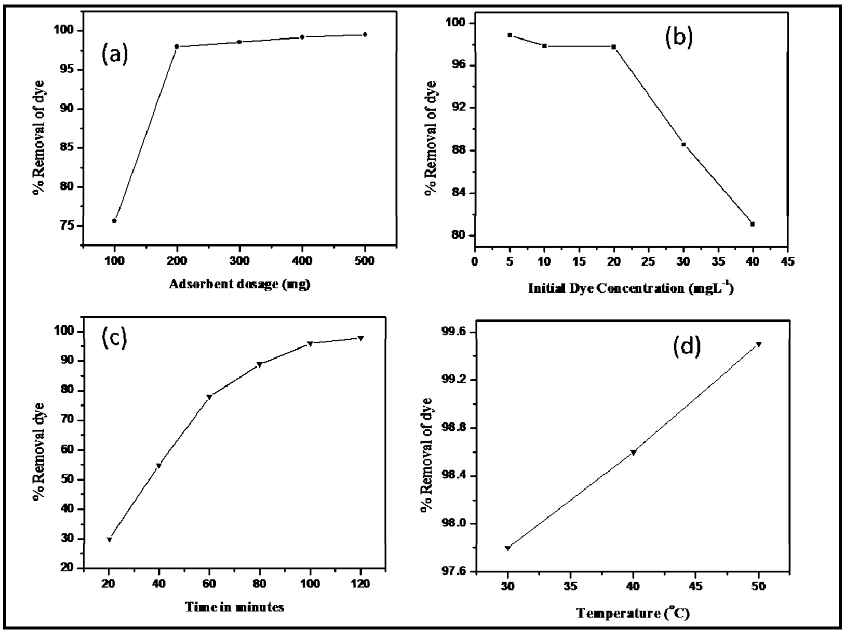

Fig. 2. a. effect of adsorbent dosage, b. effect of dye concentration, c. effect of time and d. effect of temperature on the removal of CV by SnMoVS

The effect of temperature on adsorption of dye was studied using 200 mg exchanger with 10 mgL^{-1} dye solution at neutral pH at different temperature (Figure 2d). The temperature effect on dye removal clearly indicates that dye uptake increases with increase in temperature. This may be explained on the basis of the fact that increase in temperature enhances the rate of diffusion of the adsorbate molecules across the external boundary layer and to the internal pores of the adsorbent particles as a result of the reduced viscosity of the solution [19]. In addition, the mobility of sorbate molecules also increases with temperature, thereby facilitating the formation of surface monolayers.

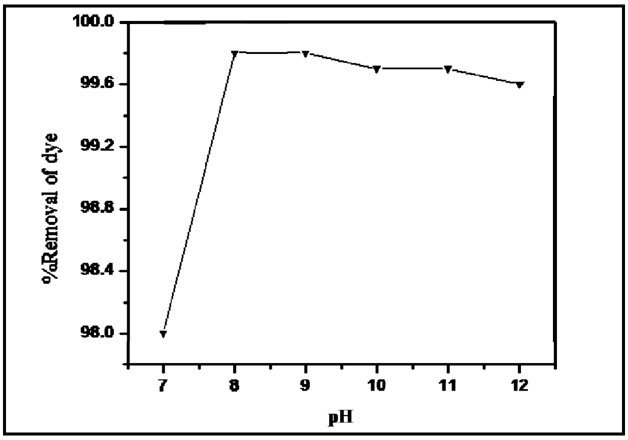

Fig. 3. Effect of pH on the removal of CV by SnMoVS

The effect of pH of the solution is important when the adsorbing molecules are capable of ionizing in response to pH [20]. Hence, the effect of pH of solution on dye removal efficiency of exchanger was analysed using 200 mg in 10 mgL^{-1} dye solution at different pH at 30 °C and the result is drawn in Figure 3. In the acidic medium the colour of the dye disappeared. Because of this reason it was impossible to study the adsorption capability of exchanger in the acidic medium. So here we studied the dye removal efficiency of material in the pH range of 7 to 12. The result shows that at pH 8 almost 100% of the dye can be removed from aqueous solutions. When solution pH increases, OH^- ions accumulate on the adsorbent surface [21]. Thereby the electrostatic interaction between negatively charged adsorbent surface and cationic dye molecules increases the adsorption [22]. Furthermore, when the solution has pH 8, the negative charge density of the surface of exchanger increases which favors the adsorption of cationic dye [23]. The cation exchanger can be easily regenerated by treating the material with 1.0 M HNO_3 and reuse for the practical purposes. After five series of sorption- desorption cycle, the loss in the sorption capacity is only 7-15%.

SnMoVS composite ion exchanger also acts as absorbent for CO_2. The main factor which makes the material suitable for adsorption is its high surface area. The nitrogen sorption isotherm at 77 K exhibits a type I character with a saturated adsorption capacity of about 53 cm^3 (STP) g^{-1}, corresponding to a pore volume of 0.075 cm^3 g^{-1} for the material (Figure 4a). The Brunauer–Emmett–Teller and Langmuir surface areas are calculated to be 177 m^2g^{-1} for SnMoVS.

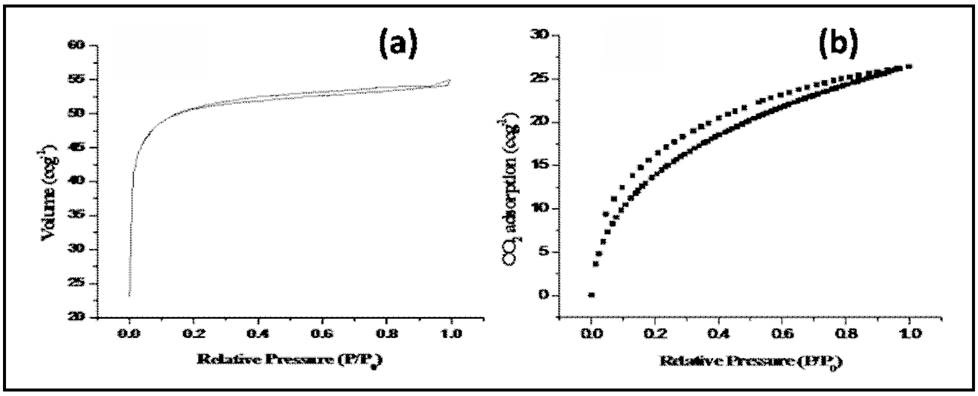

Fig. 4 (a). BET adsorption isotherm and (b) CO_2 adsorption isotherms of SnMoVS

For finding out the gas adsorption ability of this material, we studied the carbon dioxide adsorption isotherms (Figure 4b). The CO_2 uptakes at 1 atm are 26 cm^3 (STP) g^{-1} (1.16 mmol g^{-1}, 4.8 wt %) at 77 K for the material. The carbon dioxide adsorption studies show that the material has reasonably good ability for the adsorption of carbon dioxide. The adsorption isotherms are plotted below. The CO_2 adsorption experiment reveals the advantages of these exchangers for CO_2 adsorption. Some improvement in its structure will make it a potential candidate as carbon dioxide storage material.

SnMoVS showed a promising antimicrobial activity at all concentrations (50, 100 µL) for inhibiting the growth of Staphylococcus aureus bacteria. The analysis data are described in the table 5. Area of zone of inhibition is used as a criterion to ascertain the biocidal activity. According to this criterion, 10 mm to 17 mm zone of inhibition zone would represent significant activity. The photographic image of antibacterial study (*Staphylococcus aureus*) of SnMoVS is shown in Figure 6. The mechanism responsible for antimicrobial activity involves the rupturing of bacterial cell wall due to the binding of composite which release ions that react with the thiol groups (-SH) present on the bacterial cell surface to the outer membrane of *Staphylococcus aureus*. The heavy metal present in composite also inhibits the active transport and retards the enzyme activity, thus deactivating the proteins, rupturing the cell membrane and eventually causing the cell lysis [24]. The presence of *staphylococcus aureus* was found in the wastewater plant. By using the tin(IV) molybdovanadosulphosalicylate along with other ion exchangers used in the wastewater treatment plant we can control the growth of the bacteria *staphylococcus aureus* in the wastewater plant.

Table 5. Organism: Staphylococcus aureus

Sample	**Volume of Sample (µL)**	**Zone of inhibition (mm)**
Gentamycin		27
	25µL	Nil
	50 µL	11
	100 µL	16

Note: 0.1 gm in 1 mL DMSO

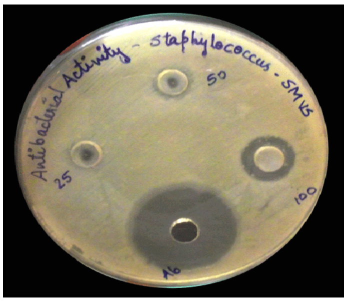

Fig. 6. Photographic images of zone of inhibition for *staphylococcus aureus* SnMoVS

Conclusion

Tin(IV) molybdovanadosulphosalicylate composite material showed good ion exchange capacity having high selectivity for the Pb(II) and Cd(II). It is evident from the results that the quantitative and efficient separations of lead and cadmium from various metal ions are feasible on SnMoVS column. The composite showed adsorptive properties towards dye and CO_2 gas. Composite material has an effective antimicrobial agent against *staphylococcus aureus* bacteria. In view of all these outcomes, it may be concluded that SnMoVS composite ion exchanger could be a potential candidate for the environmental remediation.

Acknowledgments

Author gratefully acknowledges the Council of Scientific and Industrial Research (CSIR), New Delhi, for the award senior research fellowship. Instrumental support received from STIC, Kochi, Biogenix, Trivandrum is also gratefully acknowledged.

References

1. Khan AA, Inamuddin and Alam MM, 2005 Determination and separation of Pb^{2+} from aqueous solutions using a fibrous type organic-inorganic hybrid cation-exchange material: polypyrrole thorium(IV) phosphate. Reactive and Functional Polymers., 2005, 63; 119–133.
2. Beena B, Chudasama U, A comparative study of the catalytic activity of $[Cu(NH_3)_4]^{2+}$ sorbed on zirconium phosphate and zirconium phenylphosphonate. Trans. Met. Chem., 1995, 20; 166–169.
3. Pandit B, Chudasama U, A new inorgano-organic ion exchanger: chromotropic acid anchored onto zirconium molybdate. Colloids Surfaces; Psysicochem. Eng. Aspects., 1998, 132; 145–151.
4. Pandit B, Chudasama U, Synthesis, characterization and application of an inorgano organic material: p-chlorophenol anchored onto zirconium tungstate. Bull. Mater. Sci., 2001, 24; 265–271.
5. Davidson PW, Myers GJ, Weiss B, Mercury exposure and child development outcomes. Pediatrics, 2004, 113; 1023–1029.
6. Garg VK, Amita M, Kumar R, Gupta R, Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. Dyes Pigments, 2004, 63; 243–250.
7. Wang S, Booyjoo Y, Choueib A, A comparative study of dye removal using fly ash treated by different methods. Chemosphere, 2005, 60; 1401–1407.
8. Hamdaouik O, Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. J. Hazard Mater., 2006, B135; 264–273.
9. Ozer A, Dursan G, Removal of methylene blue from aqueous solution by dehydrated wheat bran carbon. J. Hazard Mater., 2007, 146; 262–269.
10. Albo A, Luis P, Irabin A, Carbon Dioxide Capture from Flue Gases using a Cross–Flow Membrane Contactor and the Ionic Liquid 1–Ethyl–3–Methylimidazolium Ethylsulfate. Ind.Eng. Chem. Res., 2010, 49; 11045–11051.
11. An H, Feng B, Su S, CO_2 Capture Capacities of Activated Carbon Fibre–Phenolic Resin Composites. Carbon., 2009, 47; 2396–2405.
12. Vogel AI, A text book of quantitative inorganic analysis. (Longman Group Limited, London) (1975).
13. Socretes G, Infrared Characteristic Group Frequencies, John Wiley & Sons, New York, (1980) 115.
14. Saeed A, Sharif M, Iqbal M, Application potential of grapefruit peel as dye sorbent: Kinetics, equilibrium and mechanism of crystal violet adsorption. J. Hazard. Mater., 2010, 179; 564-572.
15. Ahmad R, Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP). J. Hazard. Mater., 2009, 171; 767-773.
16. Wu Q, Shan Z, Shen M, Li SJ, Chen H, Biosorption of direct scarlet dye on magnetically modified Saccharomyces cerevisiae cells. Chin. J. Biotechnol., 2009, 25; 1477-1482.
17. Hamad BK, Noor AM, Afida AR, Asri MNM, High removal of 4-chloroguaiacol by high surface area of oil palm shell-activated carbon activated with NaOH from aqueous solution. Desalination., 2010, 257; 1-7.
18. Ashtoukhy ESZE, Loofa egyptiaca as a novel adsorbent for removal of direct blue dye from aqueous solution. J. Environ. Manage., 2009, 90; 2755-2761.

19. Unnithan MR, Vinod VP, Anirudhan TS, Ability of iron(III)-loaded carboxylated polyacrylamide-grafted sawdust to remove phosphate ions from aqueous solution and fertilizer industry wastewater: Adsorption kinetics and isotherm studies. J. Appl. Polym. Sci., 2002, 84; 2541-2553.
20. Hameed BH, Spent tea leaves: a new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions. J. Hazard. Mater., 2009, 161; 753-759.
21. Ahmad R, Kumar R, Adsorption studies of hazardous malachite green onto treated ginger waste. J. Environ. Manage., 2010, 91; 1032-1038.
22. Santhi T, Manonmani S, Smitha T, Removal of malachite green from aqueous solution by activated carbon prepared from the epicarp of *Ricinus communis* by adsorption. J. Hazard. Mater., 2010, 179; 178-186.
23. Janoš P, Buchtová H, Rýznarová M, Sorption of dyes from aqueous solutions onto fly ash. Water Res., 2003, 37; 4938-4944.
24. Cook G, Costerton JW, Darouiche RO, Direct confocal microscopy studies of the bacterial colonization in vitro of a silver-coated heart valve sewing cuff. Int. J. Anti. Agent., 2000, 13; 169-173.

*****