ORIGINAL ARTICLE

Synthesis of zeolite/activated carbon composite material using custard apple shell for removal of heavy metal - Aqueous lead (II) and cadmium (II)

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Abstract

Aim: A composite material was prepared containing zeolite (ZSM-5) and activated carbon (AC) that was prepared from custard apple shell powder. **Materials and Methods:** The process consisted of the following steps: Preparation of AC and subsequent steam assisted dry gel conversion of tetraethyl orthosilicate and sodium aluminate to ZSM-5 and ZSM-5 AC composite. **Results:** The resulting material exhibited a hierarchical pore structure with high surface area and porosity as characterized by X-ray diffraction and nitrogen adsorption. The addition of AC enhanced the surface area and adsorption percentage of lead (Pb^{2+}) and cadmium (Cd^{2+}) from aqueous solution and further from industrial effluents. The coordination of the alumina incorporated was analyzed using Al magic angle spinning nuclear magnetic resonance. ZSM-5/AC composite with high crystallinity was obtained which exhibited high adsorption rates when compared to ZSM-5, AC individually and their mechanical mixtures. **Conclusions:** As a significant application, the modified adsorbents with the composite materials were tried out on an industrial effluent to check the capability of the adsorbents in the removal of Pb^{2+} and Cd^{2+}. It was observed that approximately 90% of the metal ions in question were removed by all the adsorbents tried out.

Key words: Activated carbon, Adsorption, Cadmium, Composite, Lead, Zeolite

INTRODUCTION

Adsorption is found to be superior and well-established technique over the years for the elimination of heavy metal ions from aqueous solution. The technique is found to be cost-effective, eco-friendly, and efficient. Various adsorbents such as agro waste, zeolites, resins, and nanosorbents are reported as potential adsorbents. The use of natural zeolite as an adsorbent has gained interest among researchers since its sorption properties provide a combination of ion exchange and molecular sieve properties which can also be easily modified.[1] Despite this interest, there is very little literature published on the kinetics of the process. Kinetic studies are important because the data obtained can be used for designing industrial adsorption systems through modeling and simulation.

Natural zeolites are crystalline hydrated aluminosilicates of alkali and alkaline earth cations. Due to their unique physicochemical properties, for example, high crystallinity, regular sub-nanometric cavities, and highly selective ion-exchange capacity, zeolites are being used as heavy metal ions sorbents, as chemical sieves, and as water softeners. In addition, zeolites are widely distributed in nature and are inexpensive and non-toxic sorbents. Besides the natural zeolite, the synthesized zeolite and zeolite/activated carbon (AC) composites are also active sorbents and play an important role in the adsorption of many metal ions. Several studies have been devoted to the synthesis protocols of zeolites/AC composites (particularly AC prepared from natural waste), proving that such materials are able to adsorb high concentrations of heavy metal ions in addition to their improved catalytic properties. It was found that the zeolite composite adsorbed higher amounts of Cu^{2+}, Cd^{2+}, and Pb^{2+} than the unmodified zeolite. Recently, in

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many studies, zeolites were used as substrates for modification, to improve the sorption of lead (Pb^{2+}) and cadmium (Cd^{2+}) in particular. The mixture of tetraethyl orthosilicate, sodium aluminate ($NaAlO_2$), and AC was used as starting material for the preparation zeolite material. In this study, the use of custard apple shell (CAS), a non-edible waste found in many coastal areas of India was used for preparing AC and then the same was used to prepare zeolite/AC composite material. Morphology control of zeolite is desirable since catalytic and adsorption properties are altered by morphology often, but it is a challenging task.[2-5] The current study is aimed to prepare a zeolite/AC composite material using activated CAS and further the impact of preparation parameters on textural characteristics and for its sorption capacity of Pb^{2+} and Cd^{2+} from aqueous and industrial effluent.

MATERIALS AND METHODS

Tetraethyl orthosilicate (TEOS) was added to $NaAlO_2$ in the molar ratio of 1:0.0390 (Si:Al) for the preparation of zeolite. The setup of steam-assisted dry gel conversion (SADGC) is shown in Figure 1.

Chemicals and Reagents

All chemicals and reagents used are analytical grade reagents procured from Sigma-Aldrich and other standard chemical suppliers. Milli-Q water was used in all the studies. 1000 mg/L stock solutions of Pb^{2+} and Cd^{2+} were prepared by dissolving the appropriate amount of nitrate salts in Milli-Q water. Phosphoric acid (H_3PO_4) was used as the activating agent. Adjustments of pH were carried out using 0.1 M HCl and 0.1 M NaOH solutions.

Experimental

Each experiment was repeated thrice, and average values have been reported. CAS was milled and sieved to segregate particles with a uniform size <100 mesh, and then 50 wt% of AC was added to it. The mixture of TEOS, $NaAlO_2$, and AC was stirred overnight followed by drying at 80°C for 12 h. After drying, a gel was obtained which was added to tetrapropylammonium hydroxide, mixed by stirring and dried overnight at 100°C. The dried gel was kept in a vial which was then placed in an autoclave containing 2 mL of water and that was kept in an oven at 170°C for 72 h. The 2 mL water that was added generated the steam which assisted in the dry gel conversion. The resulting dried sample was calcined in a tubular furnace at 550°C for 3 h under N_2 flow (150 mL/min). The mechanical mixture (MM) was prepared by adding AC in 50 wt% to the prepared ZSM-5 and was ground for 8–10 h. The resultant zeolite/AC composite was ZSM-5/AC; composite was characterized by Fourier transform infrared spectroscopy (FTIR), XRD (X-ray diffractometer), Al magic angle spinning nuclear magnetic resonance (Al MAS NMR), and scanning electron microscope (SEM).

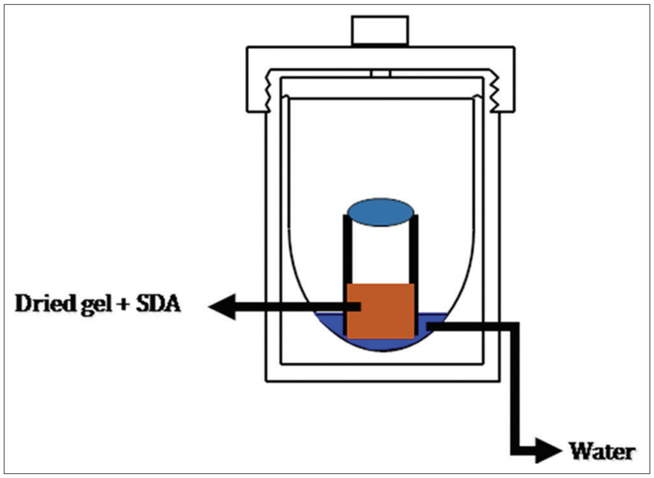

Figure 1: Set up of steam-assisted dry gel conversion

Batch Mode Adsorption Studies

Sorption experiments for prepared sorbents were studied individually at room temperature in a mechanical shaker with 250 mL conical flasks. Effect of parameters such as adsorbent dosage, contact time, pH, and initial metal concentration on the process of adsorption was studied. The sorption capacity of the prepared sorbents was determined by contacting optimized levels of the sorbent with 20 mL of known Pb^{2+} and Cd^{2+} metal ion solutions. The influence of pH on adsorption was evaluated by varying the pH from 2 to 8 using 0.1 M HCl and 0.1 M NaOH for pH adjustment. The influence of contact time was varied between 5 and 120 min. The residual metal ion concentration present in the supernatant was determined by atomic absorption spectrophotometer (AAS).[6] The amount of metal ions adsorbed to prepared adsorbents was determined from Equation 1 and percentage removal was evaluated by Equation 2.

$$q_e = (C_0 - C_1)\frac{V}{M} \quad (1)$$

$$\%\,Removal = \frac{(C_0 - C_1)}{C_0} \times 100 \quad (2)$$

where q_e is the metal uptake (mg/g) by adsorbents, C_o and C_1 are initial and final metal concentrations ($mg^{-1}L$), V is the solution Volume (L), and M is the mass of the adsorbent (g).[7,8]

Analytical Methods

The crystallinity of the samples was determined by XRD (Bruker D8 Advance). Textural characterization was determined by adsorption isotherms using Brunauer–Emmett–Teller (BET) using an automatic adsorption system (Micromeritics ASAP 2020). Before this measurement, the samples were degassed at 320°C for 4 h.[9-11] BET analysis revealed the surface area pore radius and pore volume was calculated, while surface functional groups of ZSM-5/AC composite were detected by FTIR (Shimadzu IR Affinity-1) from the scanning range of 4000 to 400 cm^{-1}.

RESULTS AND DISCUSSION

The ZSM-5/AC composite, ZSM-5, and MM were prepared to assess the effect of activation and the changes in the physical characteristics of the resulting adsorbents. The intercalation of H_3PO_4 in the carbon matrix and the SADGC method for the composite preparation results in the formation of new micropores, which increases the surface area and porosity, was observed from the BET analysis. However, the adsorption capacities of Pb^{2+} and Cd^{2+} by the ZSM-5/AC composite were considerably high in comparison with ZSM-5 and the MM.

XRD Analysis of the Prepared Sorbents

Although the preparation of the ZSM-5/AC composite was carried out under basic conditions, no significant change was observed in Si or Al content in ZSM-5 and ZSM-5/AC composite. Thus, the ZSM-5 and the ZSM-5/AC composite have active sites which are principally located in the structure channels and also on the external surface of the crystallites.[12,13] XRD patterns of the ZSM-5, ZSM-5/AC composite, and the MM are shown in Figure 2.

No crystalline phase was observed in AC when compared with ZSM-5/AC and ZSM-5 MM which was crystalline which also agrees well with the reported literature. It appears, therefore, that there is no drastic change in the crystal-chemistry of the ZSM-5 samples before and after composite formation. A general slight decrease of the diffraction peak intensity is observed for all the crystalline phases which were more pronounced for ZSM-5/AC composite. The data obtained composed with a conventional diffractometer, down with the polycrystalline nature of the samples, did not allow obtaining an elevated excellence in structure refinement of ZSM-5/AC composite aimed to prove the change in the extra-framework population between the ZSM-5 and ZSM-5/AC composite, respectively.[14]

SEM Analysis of Prepared Sorbents

The SEM micrographs of ZSM-5/AC and ZSM-5 sample are presented in Figures 3a and 3b. Except in AC, crystalline zeolite particles are visible in all other samples. SEM micrographs of the ZSM-5 and ZSM-5/AC composite crystals show a tabular morphology of the crystals of ZSM-5.[15-18] Form and size of the crystallites are preserved despite the basic composition of the composite [Figures 3c and 3d].

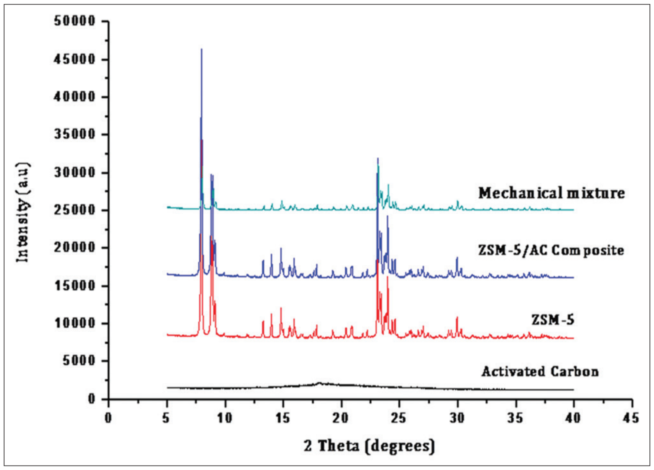

Figure 2: X-ray diffractometer patterns of activated carbon ZSM-5 with Si/Al ratio of 25, ZSM/activated carbon (AC) composite, and the mechanical mixture of ZSM-5/AC

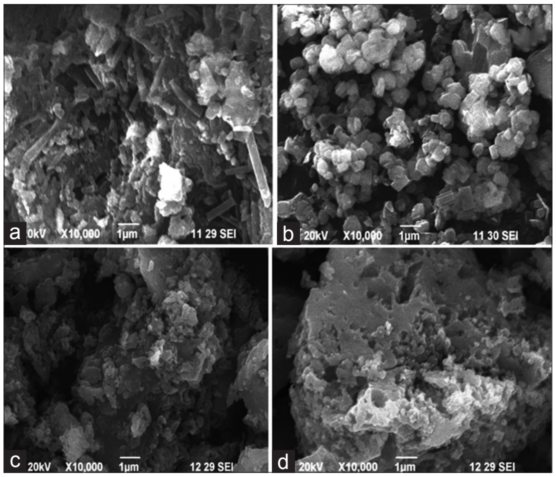

Figure 3: (a) Scanning electron microscope (SEM) micrographs of activated carbon (AC), (b) SEM micrographs of ZSM-5; (c) SEM micrographs of mechanical mixture; (d) SEM micrographs of ZSM-5/AC

Al MAS NMR and FTIR of Prepared Sorbents

Further structural configuration of Al atoms was investigated by Al-MAS NMR shown in Figure 4. A pronounced peak at around 56 ppm can be seen both in the ZSM-5 and ZSM-5/AC. It corresponds to tetrahedral geometry of the alumina. The absence of a peak at 0 ppm indicates clearly that Al is entirely incorporated in the framework of both ZSM-5 and ZSM-5/AC.[19] The FTIR spectra are shown in Figure 5, and significant ring structure of silica and the Double 5 ring of crystalline ZSM-5 can be clearly seen, and the same is presented in Table 1.

Surface Area of Prepared Sorbents using BET

The characteristics of ZSM-5, ZSM-5/AC, and MM prepared at optimum conditions were determined by BET analysis and date are summarized in Table 2. These result shows

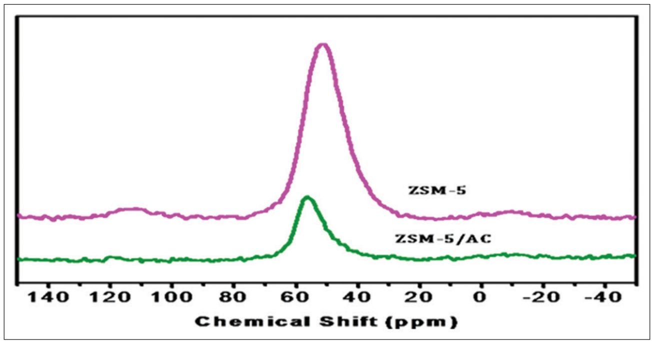

Figure 4: Al magic angle spinning nuclear magnetic resonance of ZSM-5 and ZSM-5/activated carbon

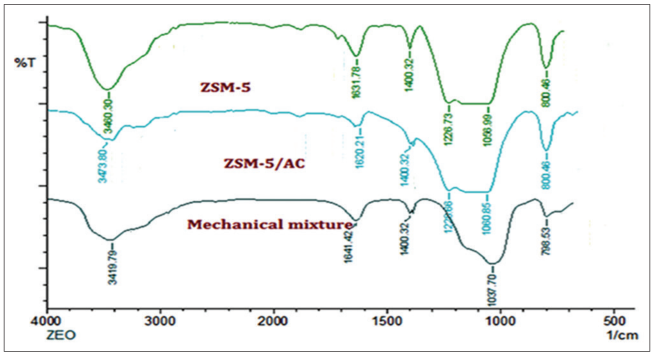

Figure 5: Fourier-transform infrared spectroscopy of ZSM-5, ZSM-5/activated carbon and mechanical mixture

that the surface areas of ZSM-5, ZSM-5/AC, and MM were 877.25, 1296, and 956.4 m^2/g, respectively. The high surface area of ZSM-5/AC helps in maximum Pb^{2+} and Cd^{2+} uptake when compared with ZSM-5 and MM. These micropores are preferable for adsorption of Pb^{2+} and Cd^{2+} ions since these ions also have smaller ionic radii similar to that of the micropores formed by ZSM-5/AC.[20-23]

Table 1: FT-IR of ZSM-5, ZSM-5/AC, and MM

Wavenumber (cm^{-1}) ZSM-5, ZSM-5/AC MM			Functional group
800	800	734	Ring structure of silica
547	549	550	Double five rings of crystalline ZSM-5

MM: Mechanical mixture, FT-IR: Fourier transform infrared spectroscopy, AC: Activated carbon

Table 2: Characteristics of the prepared adsorbents

Physical properties	ZSM-5	ZSM-5/AC	MM
Surface area (m^2/g)	877.25	1296	956.4
Total pore volume (cc/g)	9.4	4.2	7.4
BJH average pore diameter (nm)	4.4	2.5	4.6

MM: Mechanical mixture, AC: Activated carbon

Table 3: Effect of pH on the removal Pb^{2+} and Cd^{2+}

	Removal percentage of ions by					
pH	ZSM-5/AC (%)		MM		ZSM-5	
	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
2	54.56	52.5	51.23	57.18	66.54	68.22
3	65.5	65.30	65.8	61.45	72.45	72.21
4	69.78	74.58	69.51	69.78	82.12	81.81
5	98.56	96.34	77.13	73.44	88.62	86.40
6	91.45	89.65	95.78	95.65	97.18	96.15
7	85.34	76.45	92.12	91.10	93.90	88.95

MM: Mechanical mixture, AC: Activated carbon

Batch Mode Adsorption Studies

Effect of pH on adsorption

The effect of pH on the process of adsorption is of great importance since it influences chemical speciation of the metal in solution and also on the ionization of chemically active sites on the sorbent surface. The pH at which sorbent surface charge takes a zero value is defined as the pH point of zero charges (pHpzc). The knowledge of pHpzc allows one to get some knowledge on the ionization of functional groups at the sorbent surface and their interactions with metal species in solution; at pHs higher than pHpzc, sorbent surface is negatively charged and could interact with metal species, while at pHs lower than pHpzc, solid surface is positively charged and could interact with negative species. The obtained pHpzc of ZSM-5/AC was pH 6 ± 0.1 while pHpzc was 5.5 ± 0.1 for the ZSM-5. This important and crucial parameter for batch adsorption process was studied, as it affects the surface charge of the adsorbents and the degree of ionization of adsorbate during the adsorption process. pH influences metal ion sorption due to the competition between metal ions and H^+ ions for active sorption sites and hence the effect of H^+ ion concentration on the removal of Pb^{2+} and Cd^{2+} by ZSM-5, ZSM-5/AC, and MM was studied at different pH ranging from 2 to 7 [Table 3]. It could be observed that the adsorption of Pb^{2+} and Cd^{2+} increases as the pH increased from 2 to 6. Beyond pH 6, the removal efficiency was found to decrease for both the adsorbents. Similar observations were reported for removal of Cd^{2+} ions by watermelon rind. Hence, further sorption experiments were carried out at pH 6 for ZSM-5, ZSM-5/AC, and MM.[24,25]

Kinetics of Adsorption

Kinetics of the adsorption process was studied for all the three adsorbent with respect to contact time. Sorption experiments were conducted at different time intervals (10–120 min) for removal of Pb^{2+} and Cd^{2+} ions onto ZSM-5, ZSM-5/AC, and MM. The uptake of Pb^{2+} and Cd^{2+} was rapid initially, and equilibrium had been achieved within 60 min. To analyze the mechanism and rate of adsorption of Pb^{2+} and Cd^{2+} ions onto prepared sorbents, experimental data were fitted to pseudo first-order and pseudo second-order models.

Table 4: Pseudo first- and second-order kinetic data for Pb^{2+} and Cd^{2+} parameters with experimental values obtained at 30°C

Model	Constants	ZSM-5/AC		ZSM-5		MM	
		Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
Experimental	q_e (mg g^{-1})	118.56	105.41	105.4	101.14	95.10	78.26
Pseudo first-order	q_e (mg g^{-1})	61.71	51.35	41.53	39.35	43.51	38.89
	k_1 (min^{-1})	0.081	0.091	0.031	0.059	0.032	0.045
	R^2	0.956	0.917	0.915	0.952	0.955	0.993
Pseudo second-order	q_e (mg g^{-1})	105.25	101.15	101.15	99.83	91.54	71.59
	k_2 (g mg^{-1} min^{-1})	0.015	0.012	0.062	0.056	0.075	0.035
	R^2	0.999	0.999	0.998	0.999	0.998	0.999

MM: Mechanical mixture, AC: Activated carbon

Pseudo first-order kinetic model

The linear form of pseudo-first order equation is given as

$$In\left(q_e - q_t\right) = Inq_e - \kappa_1 t \quad (3)$$

q_e is the amount of metal adsorbed at equilibrium (mg/g), q_t is the amount of metal adsorbed at time t and k_1 is the first order reaction rate constant. The theoretical (q_e) values found from the pseudo first-order kinetic model calculated from Equation 3 were observed to have large difference compared to experimental values, and further, the low correlation coefficients (R^2) also suggest a poor pseudo first-order fit of the experimental data.

Pseudo second-order kinetic model

The kinetic data were also analyzed using pseudo second-order kinetic model as per Equation 4. Equilibrium capacity of pseudo second-order model is shown in Table 4. Pseudo second-order kinetic for Pb^{2+} and Cd^{2+} parameters with experimental values obtained at 30°C is given. The values and correlation coefficients (R^2) for pseudo second-order model are also represented. It was observed that the theoretical q_e values were very close

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

to the obtained experimental values which fit the model better supported by the respective R^2 values. These observations suggest that sorption by ZSM-5, ZSM-5/AC MM follows pseudo second-order kinetic reaction, which suggests that the process controlling the rate, maybe chemical sorption involving valence forces through sharing or exchanging of electrons between adsorbate and adsorbent.

In general, the experimental data that fits pseudo second-order model indicate that the rate-limiting step for the process involves a chemical reaction, that is, chemisorption. A number of conditions must be met if the rate of removal of heavy metals from solution is controlled by chemical reactions. These conditions are

- The rate constant should be constant for all values of initial concentration of counterions,
- The rate constant should not change with adsorbent particle size, and
- The rate constant is sometimes independent of the degree of agitation (stirring rate).

If any of these conditions is not satisfied, chemical reaction kinetics is not rate controlling even if the rate data are successfully fitted to pseudo second-order model.[26] To test whether the rate of removal of Pb^{2+} and Cd^{2+} ions is controlled by reactions, kinetic experiments were conducted at two different initial metal ion concentrations. From Table 4, it is seen that rate constant k, for the removal of Pb^{2+} and Cd^{2+} ions was not constant for different initial metal ion concentrations. This lack of consistency in the rate constants is proof that even though the results provide an excellent fit to the pseudo second-order kinetic model, the rate-limiting step is not chemisorptions.

Adsorption Isotherms

Evaluation of the maximum loading capacity of ZSM-5, ZSM-5/AC, and MM was carried out through sorption experiments conducted at different initial metal ion concentrations (50–300 mg/L) of Pb^{2+} and Cd^{2+} ions at equilibrium.

Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption process and linear form of Langmuir isotherm after rearrangement is given as,

$$\frac{C_\mathrm{e}}{q_e} = \frac{1}{bV_\mathrm{m}} + \frac{C_\mathrm{e}}{V_\mathrm{m}} \quad (5)$$

where C_e is the concentration of metal solution at equilibrium (mg^{-1}), q_e is the amount of metal adsorbed per unit mass of adsorbent (mg/g), V_m is the amount of adsorbate at complete monolayer coverage (mg/g), and b is a constant that relates to the heat of adsorption (L/mg). The maximum uptake of Pb^{2+} and Cd^{2+} by ZSM-5/AC, ZSM-5, and MM prepared at optimum conditions calculated from Equation 4. The calculated constants of the Langmuir isotherm equation for the two samples along with R^2 values are presented in Table 5. This table shows that the maximum uptake of Pb^{2+} and Cd^{2+} by ZSM-5, ZSM-5/AC, and MM mixture. The uptake of Pb^{2+} and Cd^{2+} of ZSM-5/AC at a given metal ion concentration is higher than that of ZSM-5, MM, and AC which may be due to the high surface area exhibited by ZSM-5/AC through SADGC and may be due to the ability of ZSM-5/AC to produce a highly microporous structure as compared to that ZSM-5 and MM.

Removal of Pb^{2+} and Cd^{2+} from Industrial Effluent

In an effort to examine the practical utility of prepared ZSM-5, ZSM-5/AC, and MM out to remove Pb^{2+} and Cd^{2+} from the industrial effluent after optimizing conditions of Pb^{2+} and Cd^{2+} removal from aqueous solution, effluent samples collected from industrial areas of Vellore district were tried out for removal of the two metal ions. The collected effluent was filtered to remove all the insoluble portions, and the filtrate was taken for study. The Pb^{2+} and Cd^{2+} concentration in the effluent was measured to be 25.5 and 21.3 mg/L, and the pH of the effluent was 1.5 [Table 6]. For the treatment of this effluent by ZSM-5, ZSM-5/AC, and MM, the optimized condition was used. It can be observed that approximately 98% and 90% of Pb^{2+} and Cd^{2+} by ZSM-5/AC; 92% and 90% of Pb^{2+} and Cd^{2+} by ZSM/5; and 80% 88% of Pb^{2+} and Cd^{2+} by MM. Since the prepared adsorbents are biodegradable, it can be easily disposed of after recovering Pb^{2+} and Cd^{2+} from the biosorbent by desorption.

Removal of Pb^{2+} and Cd^{2+} in the Presence of other Bivalent Metal Ions

The effect of other bivalent metals in the removal of Pb^{2+} was studied, and the data are reported in Table 7. The data suggest there was a marginal decrease of 1–3% in the presence of Cu^{2+}, Zn^{2+}, and Co^{2+}. In the presence of Cd^{2+},the decrease noticed was 9%, and in the multiple metal system, 8.9% was noticed. This proves that the sorbents had preferential adsorption of Pb^{2+} ions and no significant decrease in the sorption with the interferences of other metal ions. The other bivalent metal ions role in the removal of Cd^{2+} ions was studied, and the data are reported in Table 8. As observed from the data, 2–8% decrease was noticed in the sorption of Cd^{2+} in the presence of Cu^{2+}, Zn^{2+}, and Co^{2+} ions. In the presence of Pb^{2+} ions, the decrease noticed was 12.84%, and in the multiple metal ion system, 27.53% was noticed.

The preferential uptake exhibited by the sorbents toward Pb^{2+} ions is due to the smaller ionic radius and larger electro-negativity compared to other cocations. Similarly, Cd^{2+} ions also exhibited higher sorption capacity among the other investigated cations except for Pb^{2+} ions. Compared to Pb^{2+} and Cd^{2+} ions, as evidenced from Table 7, Pb^{2+} ions exhibit higher sorption capacity, and this might be due to smaller ionic radii and higher electro-negativity. Similar observations were reported earlier for the sorption of Pb^{2+} and Cu^{2+} ions by watermelon rind.

Desorption Studies

The revival of the adsorbent is of essential significance for reducing the cost of the remov al process. Desorption and

Table 5: Pb^{2+} and Cd^{2+} equilibrium isotherm results

Sample	q_m (mg/g)		B (l/mg)		R^2	
	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
ZSM/AC	131.55	121.24	0.341	0.213	0.999	0.999
ZSM	121.22	109.53	0.294	0.214	0.999	0.998
MM	108.54	101.52	0.215	0.185	0.998	0.999

MM: Mechanical mixture, AC: Activated carbon

Table 6: Raw characteristics of industry wastewater

Parameter	Value before adsorption	Value after adsorption		
		ZSM-5/AC	ZSM-5	MM
pH	1.5	5.1	6.1	6.5
Pb^{2+} (mg/L)	29.8	2.8	3.1	4.2
Cd^{2+} (mg/L)	18.1	3.7	4.1	5.1

MM: Mechanical mixture

Table 7: Effect of other bivalent metals on removal of Pb^{2+}

Sorption system	q_e (mg/g) ZSM 5-AC	% decrease in q_e ZSM-5/AC
Pb^{2+}	131.55	-
Pb^{2+}-Cd^{2+}	118.67	9.7
Pb^{2+}-Cu^{2+}	127.60	2.22
Pb^{2+}-Co^{2+}	128.97	0.33
Pb^{2+}-Zn^{2+}	127.56	0.15
Pb^{2+}-Cd^{2+}-Cu^{2+}-Co^{2+}-Zn^{2+}	118.45	8.99

AC: Activated carbon

Table 8: Effect of other bivalent metals on removal of Cd^{2+}

Sorption system	q_e (mg/g) ZSM 5-AC	% decrease in q_e ZSM-5/AC
Cd	121.24	-
Cd^{2+}-Pb^{2+}	105.67	12.84
Cd^{2+}-Cu^{2+}	118.78	2.02
Cd^{2+}-Co^{2+}	113.67	6.24
Cd^{2+}-Zn^{2+}	111.76	7.81
Cd^{2+}-Pb^{2+}-Cu^{2+}-Co^{2+}-Zn^{2+}	87.86	27.53

AC: Activated carbon

Table 9: Data on desorption for prepared adsorbents

ZSM-5/AC		ZSM-5		MM	
Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
93.45	91.34	92.33	92.32	82.35	81.34
89.45	85.34	85.34	83.25	75.44	71.23
65.34	64.14	54.34	45.33	65.34	43.23

MM: Mechanical mixture, AC: Activated carbon

regeneration potential of prepared adsorbents was studied using 0.1M HCl as a desorbing agent. 0.1 g of Pb^{2+} and Cd^{2+} loaded adsorbents were kept in contact with 20 mL of 0.1M HCl for 30 min and desorbed acidic solution was analyzed by AAS to determine the metal ion concentration. Desorption of Pb^{2+} and Cd^{2+} from the metal loaded ACs is presented in Table 9. It can be seen that the adsorbents can be effectively recycled for two cycles without affecting efficiency. The adsorption efficiency is observed to reduce in the subsequent cycles.[27,28]

CONCLUSIONS

Zeolite with MFI structure ZSM-5 and its composite with AC ZSM-5/AC have been prepared successfully by SADGC method, and their textural properties have been studied. The FTIR results confirm the presence of ring structures of silica and double 5 rings of crystalline ZSM-5. The XRD patterns of ZSM 5, ZSM-5/AC, and MM show the presence of crystalline peaks except for the AC which was amorphous. The structural configuration of alumina atoms was investigated by Al MAS NMR. A pronounced peak at 56 ppm can be seen both in the ZSM-5 and ZSM-5/AC which corresponds to tetrahedral alumina species. The absence of a peak at 0 ppm demonstrates that alumina is entirely incorporated in the framework of both ZSM-5 and ZSM-5/AC. The SEM micrographs of ZSM-5/AC and ZSM-5 sample were taken, and except in AC in all other samples, crystalline zeolite particles were visible. BET analysis indicates the presence of both micropores and mesopores in both ZSM-5 and the composite. The results show that the prepared materials ZSM-5, ZSM-5/AC, and MM could efficiently remove around 100 mg/g of Pb^{2+} and Cd^{2+} from aqueous solution at an equilibrium time of 60 min. As a significant application, the modified adsorbents with the composite materials were tried out on an industrial effluent to check the capability of the adsorbents in the removal of Pb^{2+} and Cd^{2+}. It was observed that approximately 90% of the metal ions in question were removed by all the adsorbents tried out. The sorption capacity of the composite was tried in binary and multiple systems, and it was observed that the composite has preferential adsorption over Pb^{2+} and Cd^{2+} in comparison with other bivalent metals. Desorption of Pb^{2+} and Cd^{2+} from the metal loaded composite materials resulted in 80–90 % of Pb^{2+} and Cd^{2+} release for the first two cycles and showed a marked decrease in the third cycle.

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