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Synthesis of zeolite from crop waste and its application for pesticide removal

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ABSTRACT

Sustainable development is renowned as promising culture and multifaceted methodology comprising environmental, ecological, scientific, economic, social and political issues of global significance. The key aspects of sustainable development from an energy and chemical perspective are to develop more renewable forms of energy and products to reduce pollution. Agricultural residues attract widespread attention for renewable energy generation and also for their large scale combustion. The combustion of these products results in the generation of ashes which is a source of silica for the synthesis of adsorbents like zeolites. The present study aims at synthesis of zeolite from waste of agricultural areas to propose a system of waste management. To achieve the objectives, waste wheat (straws) and chemically (Cetyl trimethylammonium bromide CTAB) modified wheat was mixed with spent aluminium foil solution, separately to obtain Si-Al zeolites.

The synthesized product is characterized by Fourier transform infra-red spectroscopy (FTIR) and X-ray diffraction (XRD). The adsorption efficiency of synthesized zeolite was assessed by removal of pesticide (2, 4-Dichlorophenoxyacetic acid).

FTIR peaks of Si-O-(Si) and Si-O-(Al) at 1200-400 cm-1 confirmed the synthesis of aluminosilicate zeolite. Characterization of materials under XRD revealed crystalline morphology and nano-sized particles (0.24 nm) of synthesized zeolites.

The two newly synthesized zeolites were applied as adsorbents for the removal of selected pesticides (2, 4-D (herbicide) and carbaryl (insecticide)) used on agricultural fields. The results indicated that modified zeolites are better adsorbents with percent removal of 5 and 15 orders higher for carbaryl and 2,4-D, respectively. This is attributed to the enhanced surface area and porosity due to surfactant (CTAB) addition.

The sequence of removal on Zeolites suggests that basic insecticide (carbaryl) is less efficiently removed than acidic 2, 4-D. The study proposes novel agro-based adsorbents for management of pesticides in agricultural settings.

KEYWORDS

Aluminosilicate;
2.4-D;
Carbaryl;
CTAB.

INTRODUCTION

Zeolites are mostly crystalline in nature and known as hydrated alumino-silicate minerals composed of tetrahedral units of silica (Si) and alumina (Al) bonded together by oxygen atoms. The characteristic properties of zeolites such as ion exchange capacity are determined by the main units Si and Al. The ion exchange properties of zeolite are mostly used for environmental remediation[6]. Zeolite can be modified for organic and anion adsorption processes by varying the cation nature or introduction of surfactant[14]

The ion exchange capacity, molecular sieve properties, porosity, large surface area and further valuable properties allow them to utilize as catalysts, binder, adsorption and other processes[5, 3, 11]. The adsorption capacity of zeolite has been increased by using different activation methods such as acid activation[1], heat activation[4], and modification.

In all over the world different kinds of zeolite are originated out of them 40 are in their natural forms while more than 100 forms are being synthesized. The main advantages of natural zeolites are their low price and availability and these are widely applied in industry, environmental remediation, farming, pharmaceuticals, and numerous other areas[20]. But synthetic zeolites have several advantages compared to natural zeolites like transparency, consistent pore volume, size and enhanced ion exchange capabilities and these are synthesized in laboratory. Zeolites are synthesized in laboratory with reduced time and we can also obtain over desire pore size and uniform structure as compared to natural crystallization. The synthesis of zeolites from synthetic chemical salts of silica and alumina is expensive. This can be reduced by the use industrial by-products such as fly ash or paper sludge ash and agricultural waste like rice husks.

In this study zeolite is synthesized from agricultural waste like wheat straws (WS). The utilization of WS is limited and so discovering and recovering value added products or materials from WS are desirable. Several studies have been done on the synthesis of zeolite from RH but in this study we are using dual waste as raw materials. For example, the ashes of agricultural waste (WS) as silica source and spent aluminum foil as alumina source for the synthesis. This will benefit the environment by utilizing waste and reduce disposal and landfill problems.

MATERIAL AND METHODS

Experimental

The present research is designed to synthesize low cost Si-Al Zeolites by utilizing the waste of crops towards greener approach. For this purpose wheat straw is used as silica natural precursor. Whereas, aluminum foil (spent) is accepted as alumina source. The synthesized materials are also subjected as adsorbents for the removal of pesticides.

Synthesis of zeolites

The procedure for the synthesis of Zeolites follows the layout of[12], and is briefly described below:

Wheat straws collected from agricultural field was rinsed thoroughly with distilled water to remove adhering dirt, oven dried, and sieved through 100 mesh (to obtain particle size of 150mm). The material was pre-treated for acid leaching in 3M HCl and digested at 90^0C for 3-4 hours. The excess acid was washed with plenty of distilled water. The digested husk was dried in oven at 100°C for 24 hours and calcined in muffle furnace at 550^0C for 6 hours. The ash obtained was coded as WSA.

A known mass (3g) of WSA was treated with 3M NaOH solution on magnetic stirrer and heated till boiling. The solution was filtered and the filtrate (Sodium silicate) was kept as feedstock (Filtrate A).

Similarly, spent aluminum foil (2g) was dissolved in 3M NaOH solution, filtered and filtrate (Sodium aluminate) was regarded as Filtrate B.

Si-Al zeolite was synthesized by mixing equimolar volume of Filtrate A and B. The mixture was homogenized through heating and stirring. The thick gel obtained was aged in Teflon beaker for 24h till complete crystallization. The crystals were rinsed with distilled water and dried in oven. The product obtained was coded as ZWS.

Modification of synthesized zeolites

The synthesized zeolite (WSZ) was subjected to modification with the objective to enhance the surface characteristics of the materials[9]. A known mass of the zeolite was vigorously stirred with 0.5 molar aqueous solution of cetyl trimethylammonium bromide (CTAB), filtered and oven dried. The dried modified zeolite was coded as WSZ_m.

Characterization

The synthesized zeolites were characterized to study the bulk and surface characteristics using different standardized techniques by Fourier Transform Infrared (FTIR) spectroscopy and powder X-Ray Diffraction (XRD).

Batch Adsorption Experiment

The synthesized Zeolites, before and after modification, were applied as adsorbent for the elimination of selected pesticides. The removal (in percentage) of pesticides was calculated using the following relation:

$$\%R = \frac{Ci - Ce}{Ci} * 100$$

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy (FTIR)

FTIR analysis scans over 4000-400 cm^{-1} as pressed KBr pellets of each zeolite to determine surface functional groups and chemical structure. Important frequencies recorded are composed in TABLE 1.

IR spectra of silica sources (WS) show symmetric and asymmetric stretching vibrations, in respective order, of C–H bonds (Kordatos et al., 2013) at 2960 cm^{-1} and 2850 cm^{-1}. On the other hand, these peaks diminish in the calcined products of WS, confirming the successful conversion into ash. Further, band at 800 cm^{-1} corresponds to the Si–O bonds vibration in silicon oxygen network (Javed et al., 2011). The presence of broad band of (O–H) peak at 1658 cm^{1} due to bending mode of absorbed water or zeolitic water (Markovic et al., 2003) and silanol groups (Si– OH) at 3430-3460 cm^{-1} (Kordatos et al., 2013). The absorption band at 668 $cm^{"1}$ appeared in zeolite product is known to assignable to Si-O-M where M is the exchangeable Na^+ ion metal species[23]. The initiation of crystallization process in a synthesized zeolite (product) is determined by the band in the range 500–550 cm^{-1}[2]. This is also supported by other researcher[21]. The bonding of surfactant in wheat straw modified zeolites appears at 2850 cm^{-1} and 2922 cm^{-1}, also supported by[16].

X-ray diffraction (XRD)

Zeolites synthesized from wheat straws are subjected to XRD for structural characteristics and to predict geometrical arrangements. Particle size was also determined using mathematical calculations as proposed by Debye-Scherrer. Results of XRD are summarized in TABLE 2.

The diffraction peaks of modified and unmodified zeolites demonstrate that its constituents behave similarly in scattering the incoming X-Rays. This diffraction to some appreciable extent is limited to (21^0-34^0) degrees. Similar pattern is also noted for

TABLE 1 : Important frequencies which confirm the synthesis of zeolite

Assignments	Sample codes			
			Zeolite products	
	Raw WS	WSA	Unmodified WSZ	Modified WSZ_m
Asymmetric T-O(T= Si/Al) stretching	**1060.88**	**1120.6**	**977.94**	**1012.6**
Symmetric T-O	808.20	800.49	800.49	-
stretching	-	-	669.32	669.32
Bending vibrations of T-O	-	470.65	466.79	464.88
		-	553.59	555.16
Si-C stretching	2362.88	-	-	2359
C-H stretching	2962.76	-	-	2960.7
	2854.74			2850.7

TABLE 2 : XRD data along with particle size of the zeolite

Pos.[°2Th.]	Height[cts]	FWHM[°2Th.]	d-spacing[Å]	Rel.Int.[%]	Particle size (d = nλ/$\beta cos\theta$)
			WSZ		
21.6127	460.11	0.0984	4.11189	59.71	1.499448
23.9373	648.44	0.1230	3.71758	84.14	1.20447
27.0675	633.48	0.1230	3.29435	82.20	1.2211939
29.8890	770.63	0.1476	2.98949	100.00	1.01628
34.1221	579.25	0.1722	2.62768	75.17	0.880.76
			WSZ_m		
21.6532	507.73	0.1722	4.10428	56.61	0.856885
23.9667	821.74	0.1476	3.71307	91.63	1.00378
27.0964	662.26	0.1476	3.29090	73.84	1.010011
29.9086	896.84	0.1722	2.98757	100.00	0.871137
34.1500	560.33	0.1476	2.62560	62.48	1.027182

the surfactant modified Zeolite and this is in agreement in literature[15]. However, the peak intensity is reduced when diffracted at 23^0 and 29^0 upon modification. The diffraction pattern observed for presently synthesized zeolites drags its similarity from the synthesis carried out from fly ash by[22]. (see Figure 1).

Batch Experiment

Close batch experiment was conducted in order to find out the adsorption capacity of zeolite.

Application of synthesized zeolites for adsorption of pesticides by UV analysis

The synthesized zeolites were applied as adsorbents for the removal of pesticides (2, 4-D and Carbaryl) belongs to herbicide and carbamate family. For this purpose, a known concentration (0.03mg/L) of pesticide solution was induced on a known mass (10mg) of each adsorbent and calculated as a function of time. The consequences are graphically presented in Figure 2.

The results showed that surfactant modified zeolites, synthesized from crop waste (WS) are effective in removing pesticides. The mechanism of modification with cationic templating (CTAB) can be explained on the basis of narrowing down of pore size distribution[19], thus providing more surface area for adsorption.

It is also noted that adsorption increases with increase in time. However, the rate of adsorption is relatively high at initial stages. It might be due to available of active sites[8] followed by slower degree with increasing time. Similar trends in adsorption were studied by researcher[7].

It is evident from the Figure that equilibrium is attained upon contact of adsorbate with adsorbent in 20-25 minutes. It suggests that synthesized adsorbents are effective and efficient in removing pesticides from aqueous media. However, further increase in contact time, did not significantly increase the pesticide uptake. It may be due to deposition/saturation of ion on available sites.

The adsorption capacity for 2, 4-D is more than for carbaryl. 2, 4-D is more soluble as compare to carbaryl and according to general performance of adsorption mechanism, the 2, 4-D should adsorb to less than carbaryl, however, reverse of it has been observed experimentally. This is due to low solubility difference and also smaller size and presence of two chloro and one acid group in 2, 4-D it contribute more adsorption than carbaryl. It can be elucidated on the basis of donor–acceptor complex mechanism[18]. The electron-withdrawing groups present on the exterior surface of adsorbent disengage the ring and promote adsorption through complex formation via donor–acceptor mechanism. It is known that chloride and acid substituent's deactivate the ring due to inductive effect. Thus the order of deactivation in 2, 4-D is more than carbaryl, and adsorption too.

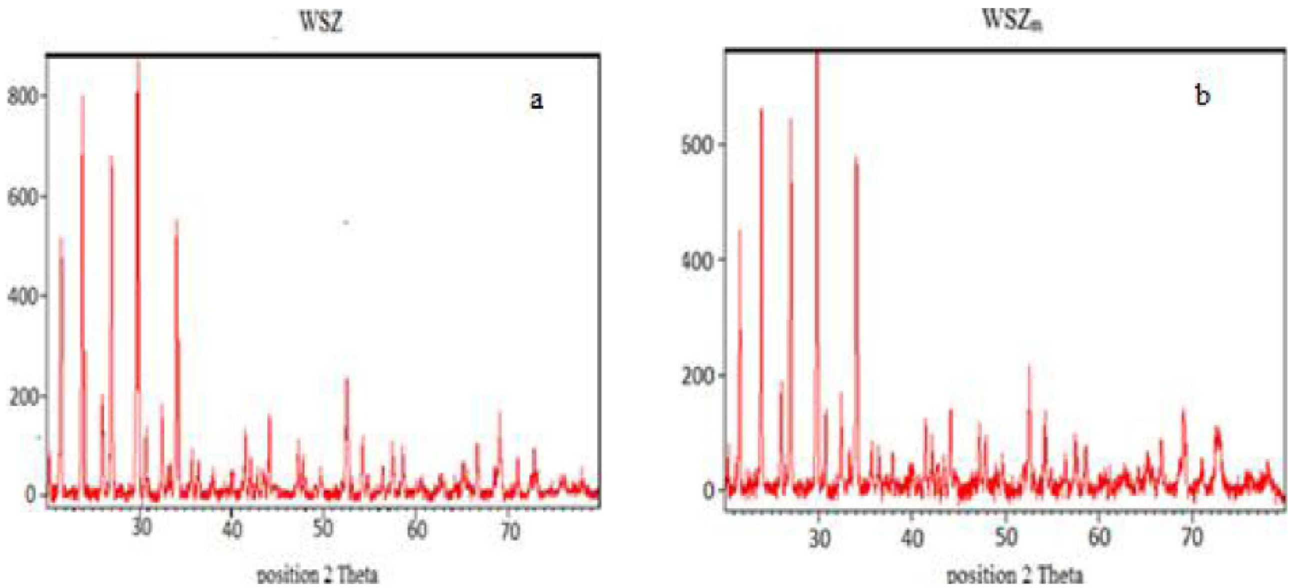

Figure 1 : XRD patterns of (a) unmodified and (b) modified zeolites from wheat straw ash

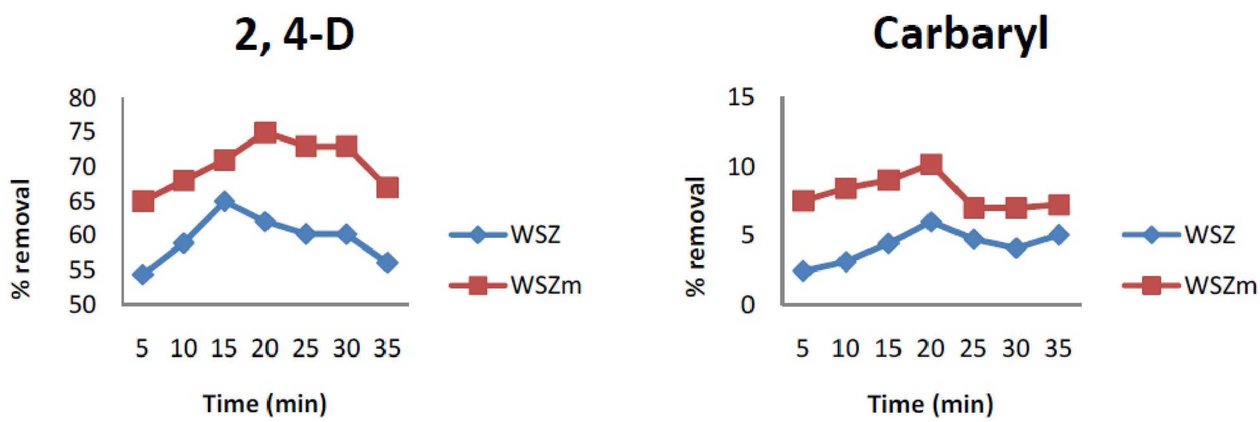

Figure 2 : Removal of pesticides with respect to time

CONCLUSION

The present study is designed on the green route synthesis of Si-Al Zeolites by utilizing the waste of crops towards sustainable development. Wheat straw is used as silica natural precursor. Whereas, aluminum foil (spent) is accepted as alumina source. Zeolite is synthesized by hydrothermal process and later on modified by cationic surfactant cetyl trimethyl ammonium bromide (CTAB). The synthesized zeolites were characterized to study the bulk and surface characteristics using different standardized techniques of FTIR and XRD for identification of elements, crystallinity and surface morphology of the obtain product. The synthesized materials are subjected as adsorbents for the removal of different pesticides (2, 4-D and carbaryl) and the results indicated that modified zeolites are better adsorbents with percent removal of 5 and 15 orders higher for carbaryl and 2,4-D, respectively.

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