

Metal Doped Green Zeolites for Waste Water Treatment: A Sustainable Remediation Model

¹Noshabah Tabassum, ¹Uzaira Rafique and ^{2,3}Muhammad Aqeel Ashraf

¹Department of Environmental Sciences, Fatima Jinnah Women University, The Mall,
Rawalpindi 46000, Pakistan.

²Department of Environmental Science and Engineering, School of Environmental Studies,
China University of Geosciences, 430074 Wuhan, P. R. China

³Water Research Unit, Faculty of Science and Natural Resources, University Malaysia Sabah
88400 Kota Kinabalu Sabah, Malaysia.
ashraf@ums.edu.my*

(Received on 22nd September 2015, accepted in revised form 15th February 2016)

Summary: The synthesis of zeolites from refused materials presents a greener model for environmental remediation. The present study offers a novel procedure to synthesize not only the basic framework but also Vanadium modified polymeric zeolites. The spent polythene bags, lunch boxes, and packaging are used as raw material for synthesis of zeolites. Characterization through EDX showed incorporation of vanadium is more than 35%, exhibiting FTIR frequencies in the range 601-995cm⁻¹. Thermogravimetric (TG) analysis revealed a stabilizing effect of zeolites on addition of dopant upto 320°C as determined by higher residue percentage (> 98%). Vanadium doped synthesized zeolites (MP1, MP2, MP3) were applied in batch adsorption experiments for in-situ (synthetic metal salt solution) and ex-situ (industrial effluents) removal of metals (Pb, Cr, and Cd). Adsorption results indicated the successful metal removal of more than 90% in the sequence Pb > Cd > Cr. The sequence follows, higher is the ionic radius of the metal cation, more is the adsorption on zeolites. Application of adsorption isotherms demonstrated fitness of Freundlich and Temkin models, whereas pseudo first order kinetics depicts metal removal. The study concludes that synthesized zeolites are suitable candidates with improvised green economy for industrial sector to treat effectively industrial discharges.

Keywords: Zeolites, Vanadium, Adsorption, Freundlich, Temkin

Introduction

A range of wastewater treatment processes are emerging in compliance to stringent requirements of environmental protection regulatory authorities for the industrial discharges. Due to the fast industrialization a huge quantity of wastewater has been discharged into the soils and water bodies. The wastewater released by textile industry is considered as most polluting among other industries depending on the volume and nature of effluents [1]. The waste water containing colored dyes and heavy metals, pose major hazard to the environment and the public health [2]. However, concerns are raised on the scope of conventional materials that make use of hazardous chemicals.

The microporous crystalline aluminosilicate minerals (zeolites) are broadly present in nature and are considered effective and low cost sorbent for environmental remediation. The growing interest in zeolites is due to ease in availability as natural mineral, simple preparation and extraction methods. The prepared zeolites are popular among scientists due to their ion exchange property and high surface area [3]. Different modifications in zeolite framework have been intensively investigated to improve their

adsorption capacity. The modification is either due to cation replacement [4] or incorporation of metals into the structure of zeolite [5].

Zeolites are considered next to clays, iron oxide coated sands and activated carbons as a low cost effective sorbent [6]. The utilization of zeolite for environmental remediation especially for pollution control, metal removal, and dyes has increased recently [7] and gained popularity among scientists due to ion exchange property and high surface area [3].

Internationally, millions of tones of mixed solid, liquid and gaseous waste materials such as household, commercial, industrial, agricultural, radioactive and clinical wastes are generated annually [8]. Zeolites emerged as strong candidates in the field of water purification for removal of metal cations like lead (Pb), copper (Cu), cadmium (Cd) and chromium (Cr) that can substitute into the structure of zeolite [5]. The successful removal of metals from wastewater using zeolite is reported by Savage and Diallo [9].

*To whom all correspondence should be addressed.

Modified zeolites showed higher uptake ability [10, 11] from single phase solution ion due to increased immobilization.

Incorporation of Cr^{5+} , Mo^{5+} and V^{4+} ions into zeolite cationic positions is reported on various supports like MgO , TiO_2 , ZrO_2 , Al_2O_3 and SiO_2 for the dispersal of vanadium [12-14].

The literature reports that Vanadium-containing silicates showed that vanadium species are linked to framework at defect sites [15] where Vanadium is not in tetrahedral positions. The presence of vanadium species in pores or internal positions is reported by [16]. However, the present study reveals that Vanadium oxide species incorporated in the zeolite framework form V^{5+} in a tetrahedrally coordinated environment. Literature also reports that the highly dispersed vanadium oxide species and the charge transfer excited state of this oxide species is well localized in the shorter $\text{V}=\text{O}$ bond [17, 18].

The present study reports at the synthesis of green zeolites from waste materials. The term 'green zeolite' is introduced as the synthesis is from the waste material following the 3R principle (reduce, reuse and recycle) and 12 principles of green chemistry [19].

The applicability of synthesized materials as adsorbents for the wastewater treatment is also assessed from synthetic and real industrial effluents. The specific objectives of study define:

- A novel method for the synthesis of zeolites through conversion of polymer refused materials into effective adsorbents following green principles.
- Complete characterization and modification of zeolites to introduce catalytic activity as well.
- To evaluate the effectiveness of synthesized zeolites as sorbents for the removal of metals from synthetic and industrial effluents for in-situ remediation model.

Experimental

Synthesis of zeolites from polymer products (PP):

Three polymer products were selected for the synthesis of zeolite. Commonly used plastic (polyethylene polymer) bags, packaging material (polystyrene polymer) and thermopole lunch boxes (polystyrene polymer) were collected from the local

market. Each sample was digested separately in solution of $\text{H}_2\text{SO}_4:\text{HNO}_3$ (1:3 v/v) on hot plate with stirring for 6 h at 250 °C. The acid digestion method developed for the present research is novel and reported for the first time for digestion of waste plastics. However, digestion method for the determination of inorganic contaminants in polyvinyl acetate is reported [20].

The solution was filtered, air dried, grounded and sieved through 40 μm mesh.

For the synthesis of zeolite, each digested powdered sample (one gram) was treated with 10 ml of 2M NaOH, 10ml of tetraethyl orthosilicate (TEOS) and 10 ml of alumina solution under stirring for 4 h at 200rpm. The solution was filtered and air dried. Same procedure was repeated for the synthesis of Zeolite from other two raw materials. So after synthesis three types of polymer based zeolites were synthesized, MP1(modified packaging material), MP2(modified polythene bags), MP3(modified polystyrene lunch box).

Modification of the Synthesized Zeolites with Metal Doping

The objective of the study was to synthesize zeolites that can conveniently be applied as adsorbents for environmental remediation. The literature reports are scarce in the application of zeolites as adsorbents. In order to further enhance the adsorptive ability, the incorporation of transition metal was attempted not only to provide the chelating metal in zeolite matrix, but also to provide thermal stability to the synthesized products.

Infect the transition metals have properties characteristic of metals; they are very hard and melt at very high temperature. So when they are incorporated into zeolite matrix than they can increase the thermal stability by transforming the zeolites into solid chelating ligands [21]. It is clearly indicated by the TG results (Table-5).

Each of the three synthesized zeolite was undertaken for modification. For this purpose, metal dispersion method was used [22]. General procedure is as follows:

An equal amount (w/w) of synthesized zeolite and Vanadium pentoxide, was mixed in agate mortar and calcined in furnace at 700°C, slightly above its melting temperature [23] for 5 h to ascertain the transition-metal oxides granule diffuse

into the micropore and vacancy of the zeolites. The calcined powder was passed through 250 μ m mesh.

Characterization Techniques

The synthesized and metal modified zeolites were characterized using different analytical techniques of FTIR, XRD, SEM/EDX and Particle size analysis.

Environmental Remediation Applications

Batch Adsorption Analysis

In the present investigation, Vanadium loaded zeolites were applied as adsorbent for the removal of metals (Pb, Cr, and Cd) from synthetic and real industrial aqueous solutions.

Adsorption analysis is conducted at different induced concentration of adsorbate as a function of time.

a) Removal of Metals from Synthetic Solution

The synthetic solution of Lead, Cadmium and Chromium were subjected to batch removal using zeolite synthesized from polythene bags, packaging material and thermopole lunch box. The stock solution of metals with the concentration of 1000mg/L was prepared and dilutions of 25, 50, 75 and 100 mg/L were made with distilled water. Then 1 mg dose of zeolite was placed in each solution of different concentrations. The solutions were placed

for 60 minutes. The samples were then filtered and results were analyzed on inductively coupled plasma optical emission spectrometry (ICP-OES).

b) Industrial Application for Removal of Metals

Industrial samples were collected from the textile and plastic industry of Faisalabad. GPS data of area of Faisalabad stands in the rolling flat plains of northeast Punjab, between longitude 73°74 East, latitude 30°31.5 North, with an elevation of 184 meters (604 ft) above sea level. Industrial effluents were collected from point source of Plastic factory located on Millet road (Sargodha road), Textile Industry located on Bawachuk, Manawala, Faisalabad showed in Fig. 1. For industrial waste water the batch experiments were done at ambient conditions with 1mg adsorbent dose and on equilibrium contact time.

For metal analysis in samples ICP-OES was used in the Geology Department of university of Malaya Kuala Lumpur Malaysia. ICP can determine the element ranges from Li-U except the atmospheric species (C, H, O, N) and noble gases. Its optimal Detection range is 50 ppmwt-50%wt. Percentage metal removal was calculated by using the formula:

$$Ci - Cf / Ci * 100$$

whereas;

Ci= Initial concentration

Cf=Final concentration



Fig. 1: Map showing the sampling area of industrial effluents.

Table-1: Physiochemical parameters of Effluents.

Physiochemical parameters	Effluents			
	Plastic industry	Textile industry	Standard value for Pakistan	WHO Standard (2010)
pH	9.37	8.92	6.5-8.5	6.5-8.5
E.C(ms/cm)	6.38	9.08	-----	-----
SO ₄ ²⁻ (mg/L)	500	550	600	500
Cl ¹⁻ (mg/L)	650	720	-----	-----
COD(mg/L)	160	190	150	-----
Lead (mg/L)	0.6791	6.862	0.05	0.01
Chromium(mg/L)	0.019	8.768	0.05	0.05
Cadmium(mg/L)	0.179	0.0455	0.01	0.003

Effluent Characterization

The physiochemical parameters, concentration of metals such as Lead, Cadmium and Chromium, in industrial effluents of Faisalabad city were investigated and are reported in Table-1. The physicochemical parameters like pH, EC, SO₄²⁻, Cl¹⁻, COD were determined by standard methods [24]. The potential pollutants (metals) in the industrial effluents were identified and evaluated by ICP-OES.

Result and Discussion

Characterization

Vanadium modified zeolites were characterized by standardized analytical techniques of FTIR, XRD, TG/DTA, SEM coupled with EDX, and Particle Size analysis.

Fourier Transform Infra Red Spectrophotometer (FT-IR)

FTIR was employed for the analysis of functional groups that might contribute in adsorption. The frequency range was measured as wave number from 500-4000cm⁻¹. The synthesized zeolites were characterized by Perkin Elmer Spectrum 100 FT-IR Spectrometer in Geology Department, University of Malaya Kuala Lumpur Malaysia.

Each modified zeolite was subjected to FT-IR analysis. The results are given in Table-2. FT-IR peaks in the range 601-995cm⁻¹ emerged upon the incorporation of V₂O₅ into zeolite matrix. This indicates the successful loading of modified zeolite. Literature reports shows that V₂O₅ displays three major peaks at 617 cm⁻¹, 827 cm⁻¹, 1022 cm⁻¹ [25].

These peaks are shifted upon interaction of metals with the matrix. It is interesting to note that Polymer based zeolites loaded with Vanadium indicate a shift of 617 cm⁻¹ in lower 587 cm⁻¹ MP1, 526 cm⁻¹ MP2, and 588 cm⁻¹ MP3 frequencies, respectively (Fig. 2).

Furthermore, loading of vanadium oxide is indicated by appearance of weaker and broader peaks at 942-953 cm⁻¹ in all modified zeolites. Literature assigns these peaks to V-O-V stretching modes [25].

It also suggests the small differences in the bond lengths of the terminal V=O bond on various supports. Fingerprint region of IR spectra is indicative of internal vibrations (920-1250 cm⁻¹) of the primary building units and vibration related to external linkage (500-650 cm⁻¹) of secondary building units in all zeolites. Present study results are also supported by Byrappa *et al.*, [26] and Flanigen, [27]. The presence of basic zeolite framework suggests that even upon loading, the structure remains intact. It is encouraging that adsorptive characteristics of zeolite framework and catalytic effect of loaded vanadium impacts a cumulative response to waste water treatment.

The bands around 500-650 cm⁻¹ are related to interaction between alumina tetrahedra and SiO₄ groups in the zeolites, confirming the basic formulae and suggests the Si:Al ratio in framework. These bands have been reported to be sensitive to the Si/Al ratio of the product [28].

All the synthesized zeolites show sharp peaks between 500-650 cm⁻¹ confirming the Si/Al ratio (Table-2). However, the sharp and weak signals in the range 1438 -1452 cm⁻¹ may be attributed to alumina containing entities with varying pore sizes [29]. The water molecules attached to frame work shows strong characteristic bending vibration at 1646 cm⁻¹ in all synthesized zeolites [30]

Scanning Electron Microscopy/Energy dispersive X-ray Analysis (SEM/EDX)

Surface morphology and elemental composition of all synthesized zeolites was determined by SEM/EDX JEOL JSM-7610F in the Physics Department, University of Malaya Kuala Lumpur Malaysia. JEOL JSM-7610F FEG-SEM combines two proven technologies – an electron column with semi-in-lens detectors and an in-the-lens Schottky field emission gun – to deliver ultrahigh resolution with wide range of probe currents for all applications (1pA to more than 200 nA). The JSM-7600F offers true 1,000,000X magnification with 1nm resolution and unmatched stability, making it possible to observe the fine surface morphology of nanostructures.

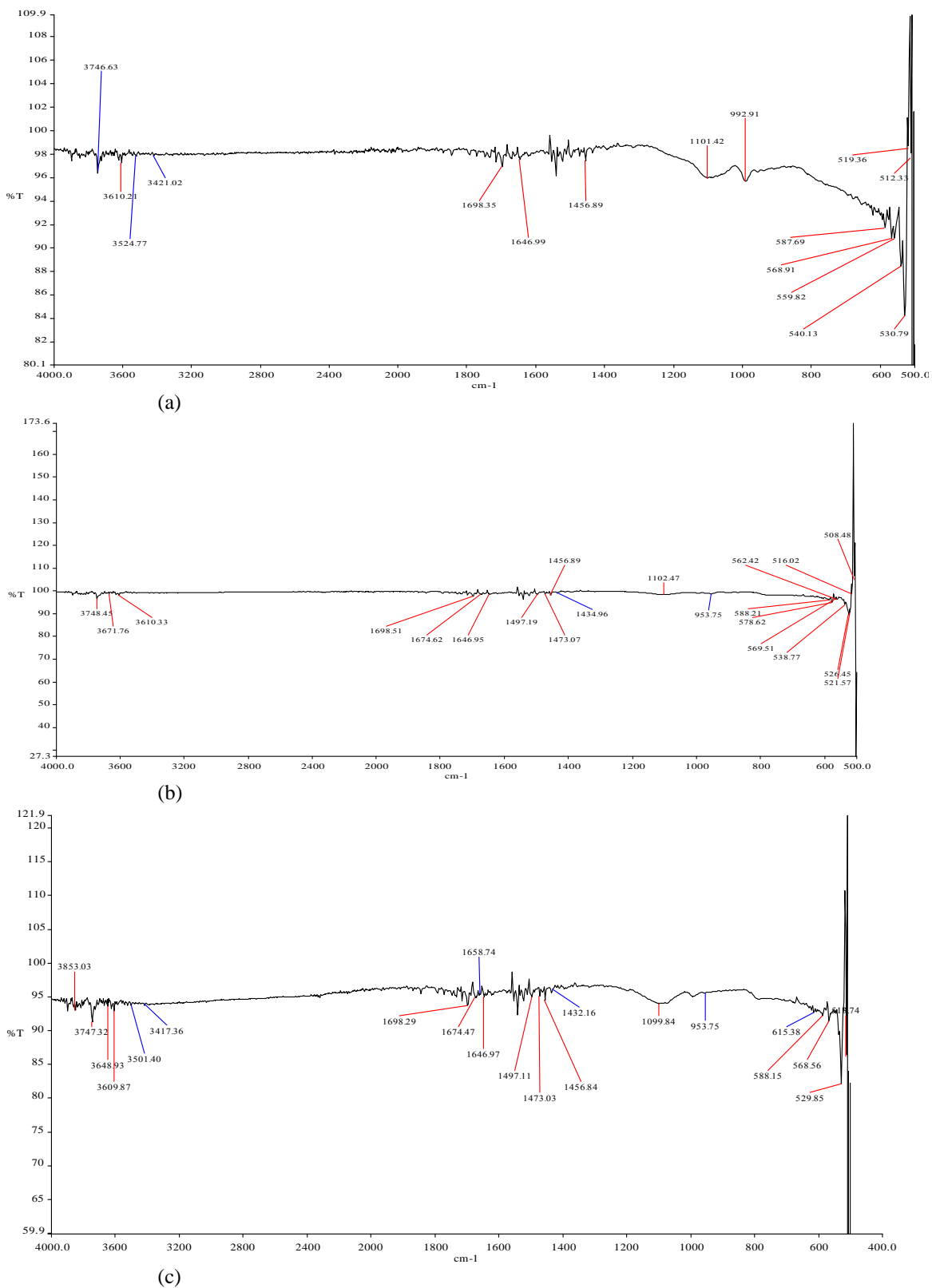


Fig. 2: An FTIR spectrum's of synthesized zeolites (a) MP1 (b) MP2(c) MP3.

Table-2: FT-IR characterization of synthesized zeolites.

Polymer based zeolites	
FTIR	
Important frequencies cm ⁻¹	Assignment

MP1	530,540,568,587	Si-O/ Al-O bend
	992,1101	V-O linkages
	992,1101	Tetrahedral SiO ₄ / AlO ₄ / ₂
	1456,	Aluminum containing entities;
MP2	1646,1698	Adsorbed H ₂ O
	3610,3746	OH group
	508,521,526,	Si-O/ Al-O bend
	953,1102	V-O linkages
MP3	1434,1456,1497	Tetrahedral SiO ₄ / AlO ₄ / ₂
	1646,1674,1698	Aluminum containing entities;
	3610,3748	Adsorbed H ₂ O
	529,568,588	OH group
MP3	615,953,1099	Si-O/ Al-O bend
	953,1099	V-O linkages
	1432,1456,1473,1497	Tetrahedral SiO ₄ / AlO ₄ / ₂
	1646,1658,1674	Aluminum containing entities;
	3609,3747	Adsorbed H ₂ O
		OH group

Scanning Electron Micrographs recorded for the synthesized Industrial and Polymer based modified zeolites are reproduced in Fig. 3 (a-f).

Packaging material (P1) is providing an outer lining of supporting framework with pores into

the central part of bed. In addition pores are small and uniform interlaced with polymeric outline. P2 and P3 show more resemblance to each other revealing clustering of particles in overlapping group formation. Therefore, channels are visible in each group space that is relatively deeper and wider. On the other hand, images of modified zeolites take different morphological features than the undoped. This is supported by Qian and Yan, [31] reporting significant change in the physical features of zeolites upon dispersion of metal oxides.

Longitudinal channels with multilayered formation evident in MP1, MP2, and MP3 is attributed to continuous polymeric framework with doped vanadium scattered on the surface of these zeolites (Fig. 3 b,d,f).

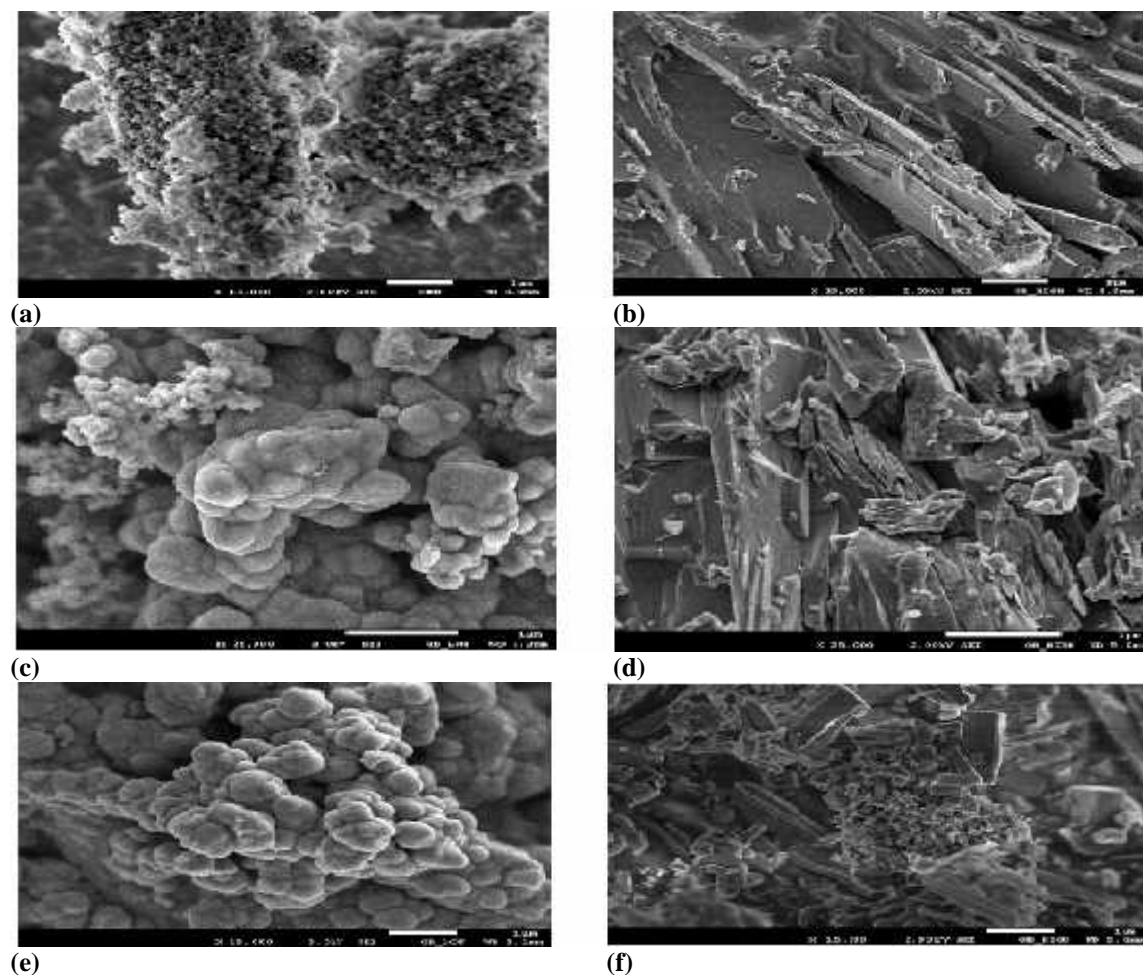


Fig. 3: SEM images for Polymer based zeolites (a) Unloaded P1 (b) Loaded MP1 (c) Unloaded P2 (d) Loaded MP2 (e) Unloaded P3 (f) Loaded MP3.

EDX analysis of undoped and vanadium loaded Industrial and Polymer based zeolites is summarized in Table-3

Table-3: Average Elemental composition (in percent) of synthesized zeolites.

Average Elemental Composition (in percent)						
Elements	Without Loading			Vanadium Loaded zeolites		
	P1	P2	P3	MP1	MP2	MP3
C	9.78	5.88	9.74	3.48	1.96	2.54
O	41.47	53.89	55.71	37.02	40.22	39.96
Na	4.79	8.23	6.23	2.36	4.03	2.64
Al	14.85	9.89	4.74	2.69	1.88	1.54
Si	27.60	20.25	15.05	11.30	8.44	18.19
K	-----	-----	-----	-----	-----	-----
Ca	1.52	1.86	-----	0.59	1.93	-----
Cl	-----	-----	-----	-----	-----	-----
V	-----	-----	-----	42.57	40.81	35.14

Alumina to Silica ratio is found to be 1:2, 1:2 and 1:3 in P1, P2, and P3, respectively and 1:4, 1:4, and 1:9 in doped MP1, MP2, MP3. The presence of silicon and aluminum in zeolites is also confirmed by other authors [32, 33]. Calcium content is significantly lower in polymer based zeolites as expected suggesting less contribution of Ca in binding or adsorptive properties.

The overall sequence of Vanadium in zeolites is MP1>MP2>MP3. Polymer based zeolites shows higher content of Vanadium which is related to the fact that polymer framework provide a continuous framework this is also confirmed by longitudinal channels in SEM images (Fig. 3 a-f).

XRD Analysis

Six modified adsorbents were characterized for surface structure and compositional features on Powder X-Ray Diffractometer of PANalytical Empyrean in the Geology Department of university of Malaya Kuala Lumpur Malaysia. Powder XRD was done at standard angular resolutions. Very high angular resolution scans helps to solve difficult problems in analysis. Through XRD we can determine the crystallographic orientation of samples up to 20 x 20 x 20 mms. The possible formulae for the adsorbents were also inferred from the data. Results are summarized in Table-4.

Polymer based zeolites also exhibited X-Ray data comparable Alumina to Silica ratio in MP1, MP2 and MP3. This suggests that the basic raw material belongs to same polymer class. This interpretation is further strengthened by comparable 2 value in three zeolites.

Table-4: X-Ray Diffraction analysis of Synthesized zeolites.

Zeolites	Polymer based zeolites			Proposed chemical formula
	2	Relative intensity	d-spacing	
MP1	12.7552	25.83	6.94035	H ₂₉ Al ₁₀ K _{13.5} O ₅₆ Si ₁₀
	18.5950	27.61	4.77181	
	27.7933	42.45	3.20995	
	30.8534	21.39	2.89820	
	25.5189	17.06	3.49064	
MP2	27.9130	44.86	3.19645	H ₂₉ Al ₁₀ K _{13.5} O ₅₆ Si ₁₀
	50.6094	17.45	1.80216	
	21.8819	38.72	4.06190	
	26.3817	12.63	3.37840	
	21.9075	73.63	4.05721	
MP3	27.8388	38.02	3.20480	H ₂₉ Al ₁₀ K _{13.5} O ₅₆ Si ₁₀
	29.0723	62.09	3.07157	
	50.5610	26.12	1.80377	
	41.3959	21.04	2.18123	
	26.3743	71.43	3.37933	

Thermogravimetric Analysis Thermogravimetric Analysis (TGA)

TGA of all samples was done by using Perkin Elmer Diamond Thermogravimetric/Differential Thermal Analysis (TG/DTA) system in Geology Department of university of Malaya Kuala Lumpur Malaysia. TG measurement technology providing property information for a variety of samples in the temperature range from ambient to 1500°C.

Thermogravimetric data of the synthesized zeolites with and without modification is reported in Table-5. It is noted that decomposition occurs in more than one step at varying temperature ranges. Decomposition pattern was studied from 0-950°C at rate of 10°C per minute. Polymer based zeolites (MP1, MP2 and MP3) interestingly showed similar thermogravimetric spectra. It is due to the fact that each zeolite is synthesized from the same class (polystyrene and polyethylene) of thermoplastic materials. However, doping has significantly reduced the weight loss in both steps inducing more stability. This might be attributed to the fact that metals are highly resistant (melting point of vanadium is 690°C). Upon its incorporation into the zeolite contributes strength to the matrix, thus inducing stabilizing effect as witnessed by TG decomposition pattern. It is noted that significant amount of residue is left in metal doped polymer in comparison to polymer alone (Table-5).

Particle Size Analysis

The particle size of synthesized material is imperative to be determined as it play significant role in the adsorption capacity. For this purpose, particle size analyzer Mastersizer 3000, Malvern Instruments is used. This service is provided by the Department

of Geology, University of Malaya, Kuala Lumpur, Malaysia.

Table-5: TG results for synthesized zeolites.

Zeolites	Dopant	%Wt Loss (Ist step)	%Wt Loss (2 nd step)	%Wt of Residue
P1	-----	10% 0-110°C	24% 110-300°C	66%
MP1	V ₂ O ₅	0.62% 0-110°C	1.36% 110-250°C	98.02%
P2	-----	10% 0-110°C	24% 110-300°C	66%
MP2	V ₂ O ₅	0.18% 0-220°C	1.1% 220-300°C	98.72%
P3	-----	10% 0-110°C	24% 110-300°C	66%
MP3	V ₂ O ₅	1.26% 0-245°C	0.3% 245-320°C	98.44%

Particle size distribution for each sample is measured using wet dispersion method [34]. The particles diameter and corresponding population density is calculated from the area under the curve (Fig. 4 a-c) and tabulated in Table-6.

It is noted that particle size ranges from 1 μm to greater than 100 μm with different population density. It clearly indicates polydispersity of each sample attributed to different ingredients and chemical composition of each polymer. The highest population density is found to have particle size of 100 μm for polymers. In addition the population density of these particles is comparable in samples with and without metal doping (Table-6). It suggests that metal doping has no significant contribution in defining the particle size and population density range. Further, it may be related to the fact that polymers comprise of a larger structural framework in comparison to vanadium contribution of synthesized zeolites. This is also witnessed and supported in SEM images of zeolites with little dispersion of the metal. However, a minor suppression of population density only for larger sized particles (>100 μm -1000 μm) in samples MP1, MP2, and MP3 may be a result of doping.

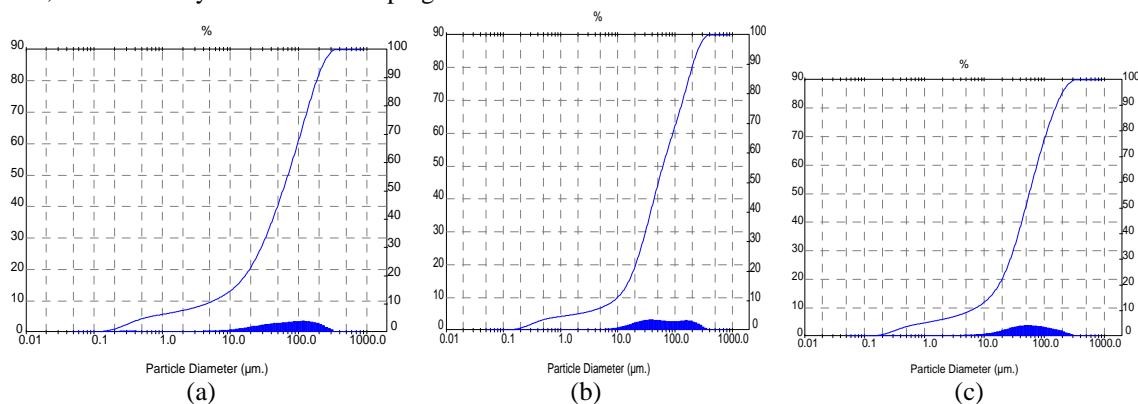


Fig. 4: Shows the particle size density (a)MP1 (b) MP2(c) MP3

It can generally be concluded that each synthesized zeolite belongs to macroporous (greater than 0.05 μm) family.

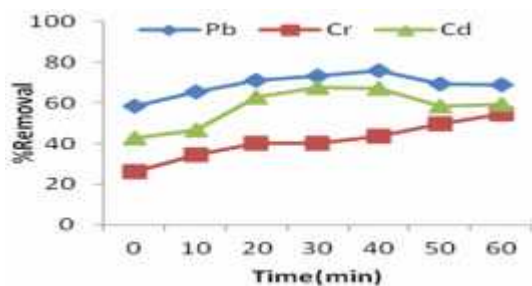
Table-6: Particle size and density (in percentage) of synthesized zeolites.

Size Range	Polymer based zeolites					
	P1	MP1	P2	MP2	P3	MP3
1 μm	2%	6%	4%	4%	5%	5%
10 μm	8%	13%	10%	10%	7%	12%
100 μm	55%	60%	61%	62%	73%	70%
>100 μm -1000 μm	35%	21%	25%	24%	15%	13%

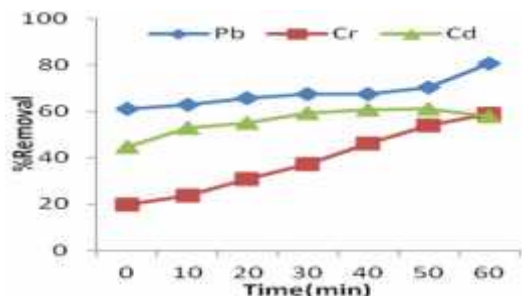
Batch Analysis as a Function of Time

Fig. 5 (a-c) depicts the removal efficiency of metals when polymer based synthetic zeolites are applied as a function of time. It is noted that a regular increase in adsorption is followed with increase in contact time. Fig. 2 shows that 60 minutes is the optimum time for optimum removal of Pb and Cr, whereas, Cd behavior is slightly different. Pandey *et al.*, [35] also reported that maximum metal adsorption is attained within 45 to 60 min. Equilibrium for Cd is attained more quickly and this is followed by clear desorption upon further contact. On the contrary, Pb and Cr shows a tendency of further increase in removal efficiency subject to more contact time is provided.

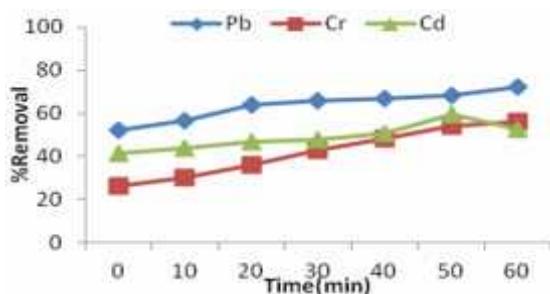
It is interesting to note that above mentioned behavior is applicable to zeolites of MP1, MP2 and MP3. It also suggests that each metal is less impacted by change in adsorbent. It may be explained that each zeolite has the same basic framework of polymer offering less dissociation and speciation of the metal ions. Overall performance of polymer based zeolites on the basis of contact time follow the sequence MP1 > MP2 > MP3. On the other hand, metal efficiency as a function of time remains the same irrespective of change in adsorbent.



(a)



(b)



(c)

Fig. 5: Removal of metals using zeolites (a) MP1 (b) MP2 (c) MP3 at variable Contact Time

Effect of Induced Concentration

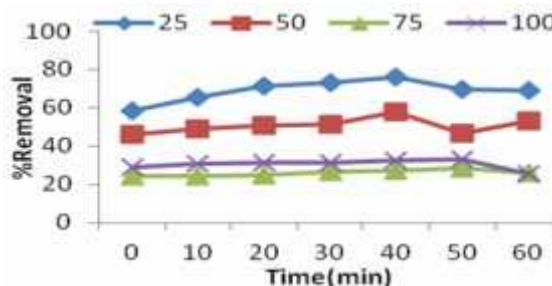
Four different concentrations (25 mg/L, 50 mg/L, 75 mg/L, 100 mg/L) of each metal solution were introduced in a batch mode to each synthesized zeolites. Change in induced concentration has significant impact on adsorption process.

It is observed that each zeolite has impacted to an appreciable extent in adsorbing metals. However, as the concentration is increased, tendency to adsorb metal solution decreases. A wide increase in Pb removal is depicted on concentration gap between 25 mg/L and 50 mg/L. Line of resemblance can be drawn for these two induced concentrations. However, this similarity is not applicable either to metal or zeolite type. It is also noted that the impact of higher concentrations (75 mg/L and 100 mg/L) is not significant for all metal types when adsorbed on

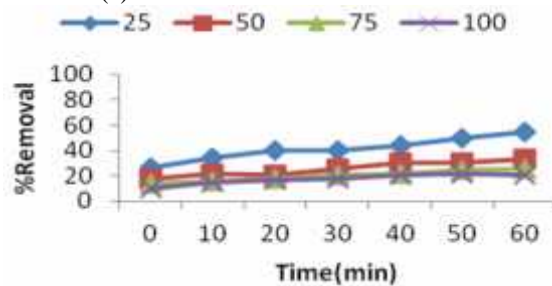
MP1 zeolite. During the course of time, an overlapping in percent removal is also observed (see Fig. 6)

MP2 zeolite is also following the indirect relation of metal removal and induced concentration. A significant and wider gap is noted between 25 mg/L and 50 mg/L for Pb and Cd, whereas less obvious gap for Cr. It may be Fig out due to more overlapping in case of last three concentrations (see Fig. 7).

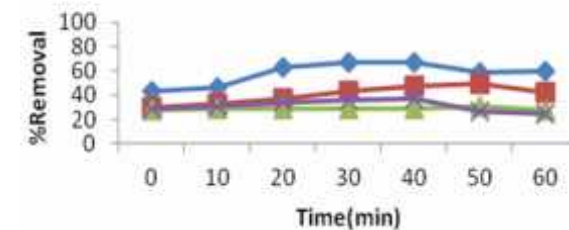
Polymer based MP3 zeolite was also subjected to metal removal at different induced concentrations. Results are shown in Fig. 8(a-c), showing no difference in trend of concentration. That is as the concentration is increased, percent removal of three metals decreases. A noteworthy change is the continuous overlapping of 75 mg/L and 100 mg/L over entire period of time.



(a)

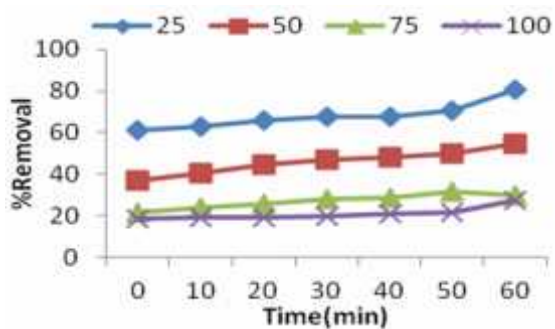


(b)

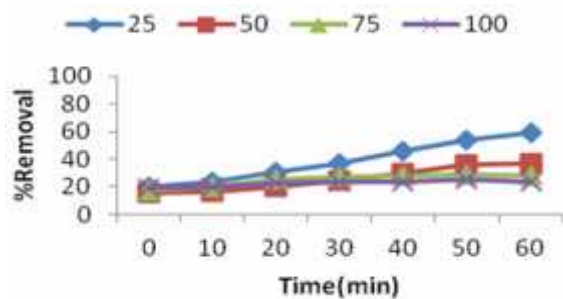


(c)

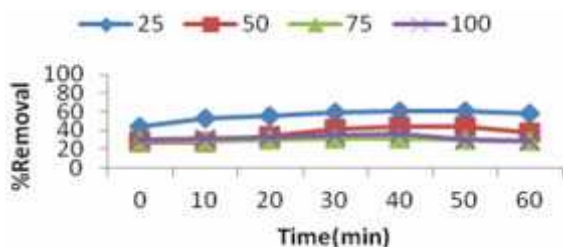
Fig. 6: Removal of Metals (a) Lead, (b) Chromium, and (c) Cadmium using MP1at different induced concentration.



(a)



(b)



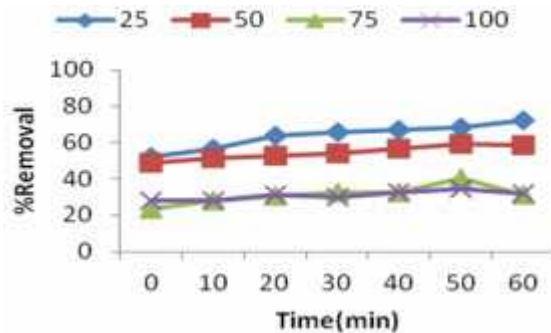
(c)

Fig. 7: Removal of Metals (a) Lead, (b) Chromium, and (c) Cadmium using MP2 at different induced concentration.

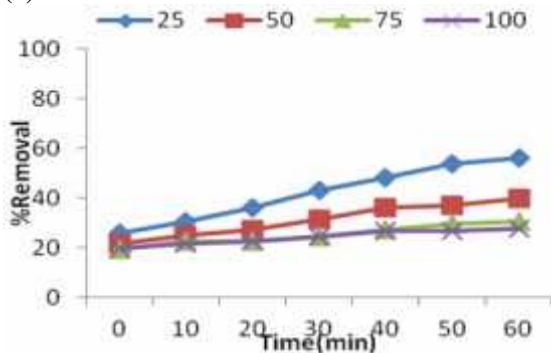
In Situ Batch Adsorption Analysis

Batch adsorption experiments were conducted on Real Industrial Effluents to determine the in situ removal of metals using the synthesized zeolites. The industrial effluents of plastic and textile industry were subjected to preliminary characterization to assess the background concentration of metals. A known mass of each zeolite was added to a known volume of effluent was subjected to batch for 60 minutes. In case desorption process started, the batch run was discontinued in that particular case. The filtrate was run and analyzed on ICP-OES.

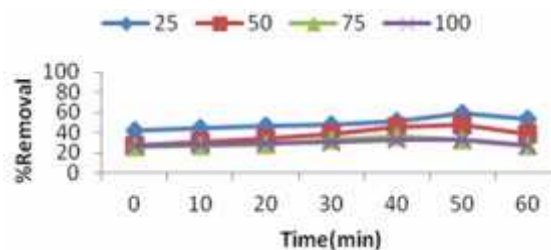
Results are presented graphically in Fig. 9 and 10.



(a)



(b)



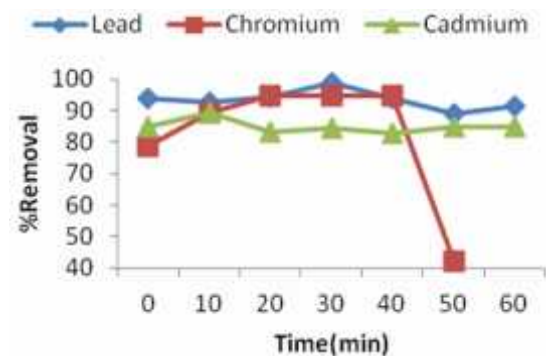
(c)

Fig. 8: Removal of Metals (a) Lead, (b) Chromium, and (c) Cadmium using MP3 at different induced concentration

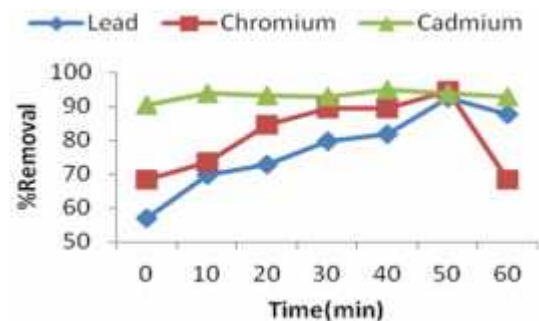
Graphical presentations elaborate the whole spectrum of adsorption batch as a function of time for the removal of metals. It is evident that there is a continuous adsorption process upto 60 minutes in most of the cases. In few instances, this adsorption is bisected with the desorption phenomenon justifying the efficiency of that particular zeolite as adsorbent. Further investigation reveals that polymer based zeolites showed a relatively wider gap in metal removal magnitude from plastic effluents (Fig. 9 (a-c)).

Comparison of metal removal from effluents of two industries shows significantly higher removal of Pb, Cd, and Cr from textile effluents using polymer based zeolite (Fig. 10(a-c)).The study concludes that metals can effectively be removed

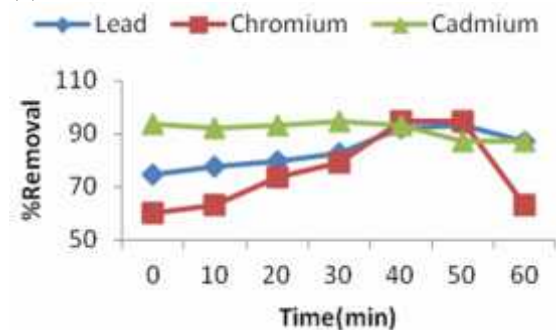
from effluents of textile using all the synthesized zeolites with removal capacity ranging from 95%-99.7%. This is also supported by other researchers work [36]. On the other hand, these zeolites show a tendency of metal removal from 79%-94% from plastic effluents.



(a)

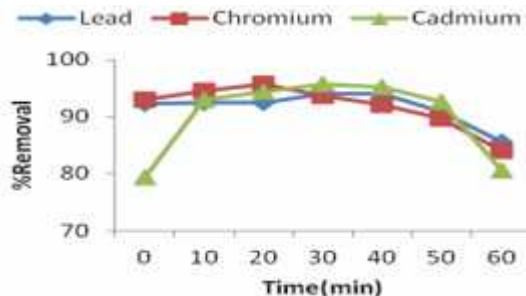


(b)

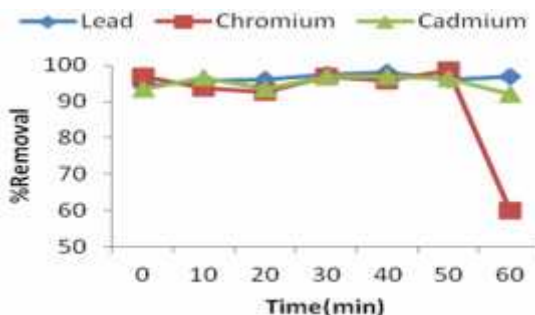


(c)

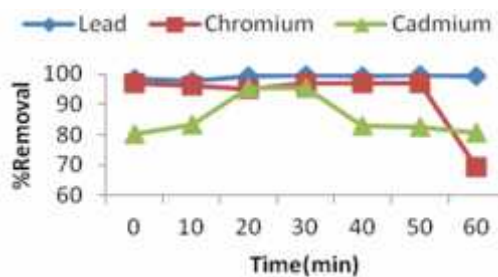
Fig. 9: Removal of Metals from Plastic industrial effluents by using Different zeolites (a) MP1, (b)MP2, (c)MP3.



(a)



(b)



(c)

Fig. 10: Removal of Metals from Textile industrial effluents by using Different zeolites (a) MP1, (b) MP2, (c) MP3.

Effect of Metal Modification on zeolites

Zeolites having metal cations in their framework have interesting and distinctive properties. Several vanadium silicates catalyst in which vanadium ions are incorporated into zeolite framework has been developed.

The present study is an attempt to synthesize Zeolites from the waste raw materials following the green chemistry principles. Each zeolites was then modified with metal oxide (V_2O_5) with the objective to determine whether the adsorptive properties of zeolite framework are coupled with the surface catalytic properties of transition metal.

The modification of the synthesized zeolites in the present investigation provides a spontaneous and feasible approach to monolayer dispersion into the basic framework. This is indicated by SEM/EDX analysis of the samples.

It was generally observed that incorporation of metal has significantly improved the adsorptive capacity of zeolites. The interest lies in the studies of possible additive effect for in-situ remediation of metals from industrial effluents. The results are encouraging reporting removal of greater than 90% of toxic pollutants like Pb, Cd and Cr.

The decomposition pattern of the modified zeolites was assessed through thermogravimetric analysis highlighting metal has greatly enhanced the stability. It also recommends that these zeolites can optimally work over a wide temperature range with no structural deterioration or change in adsorptive characteristics.

Adsorption Isotherms and Kinetics

In order to determine the Kinetics, Batch adsorption experiment was administered to models of pseudo-first order, pseudo-second order, first order, Elovich and intra-particle diffusion. Co-efficient of Regression (R^2) predicts the relationship between removal percentages of different metals as a function of time. It is generally observed that pseudo-first order kinetics show good relationship for the entire period of time on all the adsorbents. This is only significant for the removal of Chromium in comparison to other metals. On the other hand, each zeolite and each metal is found to be governed significantly by pseudo-second order kinetics with R^2 value from 0.96-0.99. Appreciable fitness of pseudo-second order is also reported in literature by a

Table-7: Adsorption kinetics of Synthesized Zeolites.

Zeolite	Parameters	Regression of Coefficient(R^2) for Adsorption Kinetics				
		Pseudo-first-order	Pseudo-second-Order	First Order	Intra-particle diffusion	Elovich
MP1	Pb	0.3528	0.996	0.3212	0.3714	0.7182
	Cr	0.9636	0.9626	0.9649	0.9261	0.8456
	Cd	0.3759	0.9865	0.3323	0.4239	0.6297
MP2	Pb	0.8179	0.9814	0.7465	0.8547	0.5251
	Cr	0.9899	0.8651	0.979	0.986	0.7122
	Cd	0.6837	0.997	0.69	0.6697	0.9232
MP3	Pb	0.9123	0.9961	0.935	0.8889	0.8906
	Cr	0.9893	0.9556	0.9903	0.9715	0.7762
	Cd	0.8514	0.983	0.8245	0.8833	0.6399

Table-8: Adsorption Isotherm of Synthesized Zeolites.

Zeolites	Parameters	Adsorption Isotherms		
		Freundlich	Langmuir	Temkin
MP1	Pb	0.9828	0.9321	0.992
	Cr	0.9588	0.8463	0.9934
	Cd	0.9828	0.9324	0.9942
MP2	Pb	0.9775	0.9178	0.989
	Cr	0.9473	0.805	0.9921
	Cd	0.9896	0.9594	0.997
MP3	Pb	0.9855	0.9416	0.994
	Cr	0.9722	0.893	0.9954
	Cd	0.9885	0.9547	0.9971

number of authors for the removal of metals using zeolite [37-39].

Intra-particle and first order kinetics is found in good agreement for the removal of Chromium on selected adsorbent MP1.

The evaluation of kinetic parameters on the basis of performance of synthesized zeolites reveal that only MP1, obey all the four Kinetic models with R^2 value greater than 0.926. It suggests that these adsorbents can be applied under wide variety of kinetics (Table-7).

Adsorption Isotherms are significant to assess the nature of adsorption process. The synthesized zeolites were applied as adsorbent to remove metals. The inter-relationship of adsorbate (metals) and adsorbent (zeolites) is tested to Freundlich, Langmuir, and Temkin models.

It is evident that Freundlich and Temkin are equally good for all the metals and all zeolites. Agreement to Freundlich indicates that metals through passive diffusion mechanism are incorporated to multilayered structure of zeolite. However, Temkin model depicts higher Regression of Co-efficient than Freundlich (Table-8).

It is also noted that Chromium does not obey Langmuir Isotherm. This gives an insight that monolayered adsorption is not a preferred option for selective adsorption of Chromium on zeolites.

Appreciable fitness of Tempkin and Freundlich is also reported in literature by a number of authors for the removal of metals using Zeolite [40, 41].

Conclusions

Following conclusions have been drawn from the present investigation:

- The present study reports the successful and efficient synthesis of zeolites characterized as Polymer based zeolites. It also employs green and environmental friendly approach using different wastes as starting materials for the synthesis.
- The doping of Vanadium pentaoxide into each zeolites enhanced the adsorptive and catalytic properties for removal of metals. Furthermore, addition of dopant showed a stabilizing effect as determined through TG studies.
- The average particle diameter places zeolites in macroporous range defining particles of 100 μm with population density of 50% or above.
- Modified zeolites through batch adsorption experiments showed removal capacity upto 99% from industrial effluents.
- MP2 is found the most effective adsorbents for the removal of toxic metals following the sequence of $\text{Pb} > \text{Cd} > \text{Cr}$.

Recommendation

The present study recommends the safe and successful application of modified zeolites as adsorbents for waste water treatment and in-situ remediation as well.

References

1. W. Shaobin, Z. H. Zhu., Characterisation and Environmental Application of an Australian Natural Zeolite for Basic Dye Removal from Aqueous Solution, *J. Hazard. Mater.*, 946 (2006).
2. W. Shaobin, M.Soudi, L. Li, Z. H. Zhu, Coal Ash Conversion into Effective Adsorbents for Removal of Heavy Metals and Dyes from Wastewater, *J. Hazard. Mater.*, 243 (2005).
3. M. R. T. Abreu, F. C. F. Barros, G. S. C. Raolino, C. P. Moura, R. F. Nascimento., Metal Ions Removal From Synthetic Solutions and Produced Water Using Activated Zeolite, *Int. J. Civil. Environ. Eng.*, 20 (2012).
4. T. Jean, P. P. Man, and J. Fraissard., Insertion of Vanadium or Molybdenum as Oxides in LaNaY Zeolite: Comparison with NaY, *J. Chem. Soc., Faraday Trans.*, **91**, 1037 (1995).
5. E. Erdem, N. Karapinar and R. Donat, The Removal of Heavy Metal Cations by Natural Zeolites, *J. Colloid Interface. Sci.*, **280**, 309 (2004).
6. Chojnacki, K. Chojnacka, J. Hoffmann, H. Gorecki, The Application of Natural Zeolites for Mercury Removal: from Laboratory Tests to Industrial Scale, *J. Miner. Eng.*, 933 (2004).
7. M. I. Panayotova, Kinetics and Thermodynamics of Copper Ion Removal From Waste Water by Use of Zeolite, *J. Waste Manage.*, 671 (2001).
8. K. S. Hui and C. Y. Chao, Effects of Step-Change of Synthesis Temperature on Synthesis of Zeolite 4A from Coal Fly Ash, *J. Microporous Mesoporous Mater.*, 145 (2006).
9. S. Nora, and M. S. Diallo, Nanomaterials and Water Purification: Opportunities and Challenges, *J. Nanopart. Res.*, **7**, 331 (2005).
10. P. Marinela, B. Velikov, Kinetics of Heavy Metal Ions Removal by Use of Natural Zeolite, *J. Environ. Sci. Health. Part A.*, **37**, 139 (2002).
11. C. Alberto, A. Mameli, A. M. Locci, R. Orru, G. Cao, Heavy Metals Uptake by Sardinian Natural Zeolites: Experiment and Modeling, *J. Ind. Eng. Chem. Res.*, **45** 1074 (2006).
12. N. Steinfeldt, D. Müller, and H. Berndt, VO Species on Alumina at High Vanadia Loadings and Calcination Temperature and their Role in the ODP Reaction, *J. Appl. Catal. A: General.*, **272**, 201 (2004).
13. G. Nishlan, H. B. Friedrich and M. J. van Vuuren., Controlling Factors in the Selective Conversion of Butane Over Promoted VPO Catalysts at Low Temperature, *J. Catal. Today.*, **97**, 315 (2004).
14. E. Elwathig, and H. B. Friedrich, Oxidative Dehydrogenation of Octane Using Vanadium-Magnesium Oxide Catalysts with Different Vanadium Loadings, *J. Appl. Catal. A: Gen.*, **373**, 122 (2010).
15. M. S. Rigutto and H. Van Bekkum, Synthesis and Characterization of A Thermally Stable Vanadium-Containing Silicalite, *J. Appl. Catal.*, **68**, L1 (1991).
16. G. Centi, S. Perathoner, F. Trifiro, A. Aboukais, C. F. Aissi, and M. Guelton, Physicochemical Characterization of V-Silicalite, *J. Phys. Chem.*, **96**, 2617 (1992).
17. Z. Shu Guo, M. Ariyuki, H. Mishima, S. Higashimoto, H. Yamashita and M. Anpo, Photoluminescence Property and Photocatalytic Reactivity of V-HMS Mesoporous Zeolites Effect of Pore Size of Zeolites on Photocatalytic Reactivity, *Microporous and Mesoporous Mater* **21**., no. **4**, 621 (1998).
18. T. Tsunehiro, H. Yamashita, R. Tsuchitani, T. Funabiki, and S. Yoshida, X-Ray Absorption (EXAFS/XANES) Study of Supported Vanadium Oxide Catalysts. Structure of Surface Vanadium Oxide Species on Silica and Alumina at a Low Level of Vanadium Loading, *J. Chem. Soc, Faraday Transactions 1: Physical*

- Chemistry in Condensed Phases* 84., no. 9, 2987 (1988).
19. A. Paul T, and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, p.30, (2000).
 20. M. Erika, and S. Cadore, Development of a Digestion Method for the Determination of Inorganic Contaminants in Polyvinyl Acetate (PVAc), *J. Braz. Chem. Soc.* **19**., 1284 (2008).
 21. F. Ramoa Riberio, A. E. Rodrigues, L. Deane Rollmann, and C. Naccache. "Zeolites: Science and Technology." In *NATO ASI Series E: Applied Sciences*, vol. 80. Nijhoff The Hague, 1984.
 22. P. A. Jacobs, E. M. Flanigen, J. C. Jansen, and H. Van Bekkum. *Introduction to Zeolite Science and Practice*. Elsevier, 2001.
 23. S. Atsushi, M. Katagiri, S. Kakimoto, S. Sugaya, and K. Shimizu, Effects of Calcination Temperature and Acid-Base Properties on Mixed Potential Ammonia Sensors Modified by Metal Oxides, *J. Sens.*, **11**, 2155 (2011).
 24. APHA, AWWA, and WEF, Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association, Washington, D.C. (2005).
 25. C. Wen, L. Q. Mai, J. F. Peng, Q. Xu, and Q. Y. Zhu, FTIR Study of Vanadium Oxide Nanotubes from Lamellar Structure, *J. Mater. Sci.*, **39**, 2625 (2004).
 26. K. Byrappa, S. Srikantaswamy, G. S. Gopalakrishna, and V. Venkatachalapathy, Infrared Spectra of Aluminium Orthophosphate Crystals, *J. Mater. Sci. Lett.*, **5**, 203 (1986).
 27. F. Edith M., Zeolites and Molecular Sieves: an Historical Perspective, *J. Stud. Surf. Sci. Catal.*, **137**, 11 (2001).
 28. F. Jiménez. Ana and A. Palomo, Mid-Infrared Spectroscopic Studies of Alkali-Activated Fly Ash Structure, *J. Microporous Mesoporous Mater.*, **86**, 207 (2005).
 29. N. O. Omisanya, C. O. Folayan, S. Y. Aku and S. S. Adefila, Synthesis and Characterisation of Zeolite a for Adsorption Refrigeration Application, *Adv. Appl. Sci. Res.*, **3**, 3746 (2012).
 30. S. Vandana, N. Agrawal, and R. Tomar, Sorption of Cr (VI) and As (V) on HDTMA-Modified Zeolites, *Int.J. Sci. Eng. Res.*, 1 (2011).
 31. L. Qian, and Z. F. Yan, Micropore Modification of Zeolites with Transition-Metal Oxides, *J. Colloids Surf., A.*, **180**, 311 (2001).
 32. S. Annie and V. Stoyanova, SEM-EDX and XRD Characterization of Zeolite NaA, Synthesized from Rice Husk and Aluminium Scrap by Different Procedures for Preparation of the Initial Hydrogel, *J. Porous Mater.*, **20**, 249 (2013).
 33. C. Jilin, G. Chang, H. Guo, and J. Chen, Synthesis and Characterization of Magnetic ZSM-5 Zeolite, *J. Trans. Tianjin Univ.*, **19**, 326 (2013).
 34. J. Cho, J. Park, Effect of CaO Addition on Properties of Ion-Induced Secondary Electron Emission of MgO films. *J. of Vacuum Science and Technology A.*, **18**, 329 (2007).
 35. P. K. Pandey, S. K. Sharma, and S. S. Sambhi, Kinetics and Equilibrium Study of Chromium Adsorption on Zeolite NaX, *Int. J. Environ. Sci. Tech.*, **7**, 395 (2010).
 36. H. Normala, and R. G. S. Yin, Removal of Heavy Metals from Textile Wastewater using Zeolit, *J. Environ. Asia.*, **3**, 124 (2010).
 37. F. Maryam, E. A. Mehrizi, M. Sadani, M. Karimaei, E. Ghahramani, K. Ghadiri, and M. S. Taghizadeh, Isotherms and Kinetics of Lead and Cadmium Uptake from the Waste Leachate by Natural Absorbent, *World. Appl. Sci. J.*, **15**, 1678 (2011).
 38. M. Syaifullah, and E. Munawar, Nanocrystalline Zeolite Y: Synthesis and Heavy Metal Removal, *J. Rekayasa Kimia. Lingkungan.*, **6**, 55 (2009).
 39. B. Wei-wei, H. F. Zou, S. C. Gan, X. C. Xu, G. J. Ji, and K. Y. Zheng, Adsorption of Heavy Metal Ions from Aqueous Solutions by Zeolite Based on Oil Shale Ash: Kinetic and Equilibrium Studies, *J. Chem. Res. Chin. Univ.*, **29**, 126 (2013).
 40. H. Mohsen, M. Kalbasi, M. Afyuni, H. Shariatmadari, P. E. Holm, and H. C. B. Hansen, Sorption Hysteresis of Cd (II) and Pb (II) on Natural Zeolite and Bentonite, *J. Hazard. Mater.*, **181**, 686 (2010).
 41. R. Purna Chandra, S. Satyaveni, A. Ramesh, K. Seshaiyah, K. K. S. N. Murthy, and N. V. Choudary. Sorption of Cadmium and Zinc from Aqueous Solutions by Zeolite 4A, Zeolite 13X and Bentonite, *J. Environ. Manage.*, **81**, 265 (2006).