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Synthesis and characterization of zeolite NaY using local rice husk as a source of silica and removal of Cr(VI) from wastewater by zeolite

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Abstract

The Zeolite NaY in pure phase was synthesized from rice husk (RH) following a three step synthetic route. In the preliminary step seed gel was prepared from a mixture of silicate and Na-acetate solution. This step was then followed by the preparation of feedstock gel. The third or final step involved the mixing of seed gel (5%) and feedstock gel (95%) which produced the zeolite of desired phase, NaY. The synthesized zeolite was characterized by FT-IR, XRD, SEM and DLS particle size analyzer and used to treat wastewater containing Cr (VI). The adsorption of Cr(VI) was monitored as a function of pH of the solution, contact time and initial concentration of Cr(VI). The adsorption results revealed that after scaling up the methodology, the synthesized zeolite NaY could be used as a promising cost-effective adsorbent for the treatment of wastewater containing chromium.

Keywords: Rice Husk; Silica; Aluminosilicate; Zeolite NaY; Chromium

Introduction

Rice husk (RH) is an agricultural waste and during milling of paddy *ca.* 22 % of the weight of paddy is left as husk (Aderolu *et al.*, 2007). The husk contains about 70 - 75 % volatile organic matters while the rest is hydrated silica (Park, 2003; Williams *et al.*, 2000). Rice husk is generally used in rural areas as a source of fuel for cooking and as animal feeds. However, due to the presence of significant percentage of silica in RH, considerable attention has been given to utilize RH for producing pure silica (Riveros *et al.*, 1986), silicon carbide and zeolites (Jan-Jerrel *et al.*, 2011) as well as a pozzolanic material (Ramezaniapour *et al.*, 2009), as an adsorbent (Wahab *et al.*, 2005) etc.

Rice husk ash (RHA) produced during controlled burning of husk at a temperature of $\sim 550^{\circ}\text{C}$ (Wittayakun *et al.*, 2008) is enriched with amorphous silica (*ca.* 85 - 90 %). The utilization of RHA as an alternative source of silica towards the synthesis of zeolites has been reported nearly 24 years ago (Bajpai *et al.*, 1978). They have synthesized mordenite type zeolite using silica from RHA. However, in addition to this, researchers throughout the world have made a significant contribution in synthesizing different types of zeolites *e.g.* MOR, NaX, Beta, ZSM-5, ZSM-48, and FSM-16 using this

silica source (Wang *et al.*, 1998; Katsuki *et al.*, 2005; Prasetyoko *et al.*, 2005; Dalal and Rao, 1985).

Zeolite is a microporous crystalline material which consists of hydrated aluminosilicates composed of tetrahedral TO_4 units (T = Si or Al) which are inter linked by oxygen atoms. According to (Jobic, 1992): "A zeolite is an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement permitting ion exchange and reversible dehydration". The general formula of zeolite is represented by $\text{M}_a^{n+}[\text{Si}_x\text{Al}_y\text{O}_z]\cdot m\text{H}_2\text{O}$ where M^{n+} is the cation; $[\text{Si}_x\text{Al}_y\text{O}_z]$ is zeolite framework while $m\text{H}_2\text{O}$ is water molecule present in sorbed phase (Roberie, 2001). Both natural and synthesized zeolites find use as molecular sieves (Haggerty and Bowman, 1994). Zeolites exhibit high sorption capacity for inorganic cations including heavy metals (Curkovic *et al.*, 1997 and Mier *et al.*, 2001) and ammonium (Semmens and Goodrich, 1977).

Bangladesh is a developing country where discharge of industrial waste is a major problem. Particularly, the tannery industries are playing a major role in polluting the surface water through direct release of the toxic, hazardous wastes

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(containing excess chromium salts) into the rivers and/or in nearby ponds. Although the tannery sector is the fourth largest foreign exchange earner of the country and contributes about six per cent of total export earnings, it is also responsible for significant water pollution. Tanneries in the city's Hazaribagh area discharge huge amount of liquid toxic wastes containing chromium everyday. Hence, considering the wastewater scenario of tannery industries of Hazaribagh in Bangladesh, an attempt has been made to remove chromium (VI) from waste water using the zeolite, synthesized from RHA. Such an attempt is expected to be beneficial in two ways: (i) A cost effective and easy approach will be facilitated to remove Cr(VI) from tannery wastewater and (ii) utilization of RHA will be a promising material recycling technology for future waste management.

Materials and methods

Chemicals

Analar grade NaOH, NaAlO₂, K₂Cr₂O₇ were purchased either from BDH, UK or E. Merk Germany and used as received. RH was collected from Biswas Rice Mill, Sutrujtpur, Magura. All the solutions of desired concentrations were prepared using double distilled water.

Method

The experimental method comprised the following three steps: (a) Preparation of amorphous Si from RH; (b) Synthesis of zeolite, NaY using prepared silica (Si); and (c) Treatment of wastewater containing chromium using the synthesized zeolite NaY.

(a) Preparation of amorphous Si from RH

Prior to burning, the rice husk was washed three times by distilled water and then soaked in 1% H₂SO₄ for 24 hours. Rice husk was then washed repeatedly with distilled water to remove acid and it was dried at normal temperature and pressure. The dried rice husk was then burnt in a Tube Furnace at a constant temperature of 650°C under usual atmospheric pressure for an hour to ensure that the product is in amorphous silica phase. The product was obtained in the form of blackish powder. It was then further burnt in a Muffle Furnace at 650°C for six hours to obtain the white ash. The rice husk ash was ground using a mortar to homogenize and to obtain a powdered form of the material.

(b) Synthesis of zeolite, NaY using prepared silica

Sodium aluminate, sodium hydroxide (NaOH) pellets and silica from RHA were used as the raw materials to synthesize zeolite NaY. The synthesis was accomplished by following the method of Ginter, D. M. (Ginter *et. al.*, 1992) but the compositions and types of raw materials were different. The overall method comprised three steps; at first seed gel was prepared which was followed by the second step feedstock gel while the final step was the preparation of overall gel.

Preparation of seed gel

Seed gel was prepared from a mixture of aluminate and silicate solution. At first NaOH solution was prepared by dissolving a requisite amount of the pellets in deionized water. This NaOH solution was then mixed with the sodium aluminate, NaAlO₂ solution to prepare the aluminate solution. The mixture was then heated gently under continuous stirring condition until it turned into solution. On the other hand, silicate solution was prepared by dissolving the silica (obtained from RHA) in NaOH solution. It was then stirred and heated in the water bath maintaining the water at boiling temperature. The aluminate and silicate were then mixed in a Teflon beaker and stirred until it became homogeneous. At this stage, the mixture was transferred into an airtight Teflon bottle and kept for ageing at room temperature for 24 hours. After 24 hours of ageing, the loose brown gel appeared which was used as seed gel. Seed gel contributed 5% of the overall gel composition.

Preparation of feedstock gel

The second step was the preparation of feedstock gel which comprised 95% of the whole gel composition. The preparation step was similar to that of the seed gel but different in the quantity of starting materials used. Moreover no ageing step was followed, *i.e.* it was used immediately after the preparation.

Preparation of overall gel

Finally, the overall gel was prepared by mixing the feedstock gel (95%) and seed gel (5%). The feedstock gel was stirred magnetically and at the same time the seed gel was added slowly and the mixture was continuously stirred for 2 hours. The mixture was then transferred into the airtight Teflon bottle and left for ageing for 24 hours at room temperature. After the completion of the ageing step the mixture was kept

in an oven at 100°C for 24 hours. The Teflon bottle was then taken out and the cap was quickly opened to cool it at room temperature. At this stage, the solid product formed was separated by suction filtration and followed by washing with hot deionized water and then dried overnight in the oven at 100°C. The flowchart of the entire preparation procedure is shown in Fig. 1. This synthesized zeolite NaY was then characterized using x-ray diffractometer (XRD), fourier transform infrared spectrometer (FT-IR), scanning electron microscope (SEM) equipped with energy dispersive system and particle size analyzer. After completing the characterization, zeolite NaY was used to treat the chromium containing water.

Prestige 21 (SHIMADZU). Sample to KBr ratio of 1:100 was used to obtain experimental spectra and the sample was scanned in the mid-infrared wave number range of 4000-400 cm^{-1} with an average of 25 scans. The resolution of the spectrometer was 2 cm^{-1} .

SEM images were recorded by JEOL - JSM 6490OLA scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). The sample was mounted with double sided tape and electrically conducted by coating with metal in AGAR AUTO Sorption COATYER.

Particle size distribution of the zeolite NaY was determined by the Zetasizer Nano Series equipment (Malvern

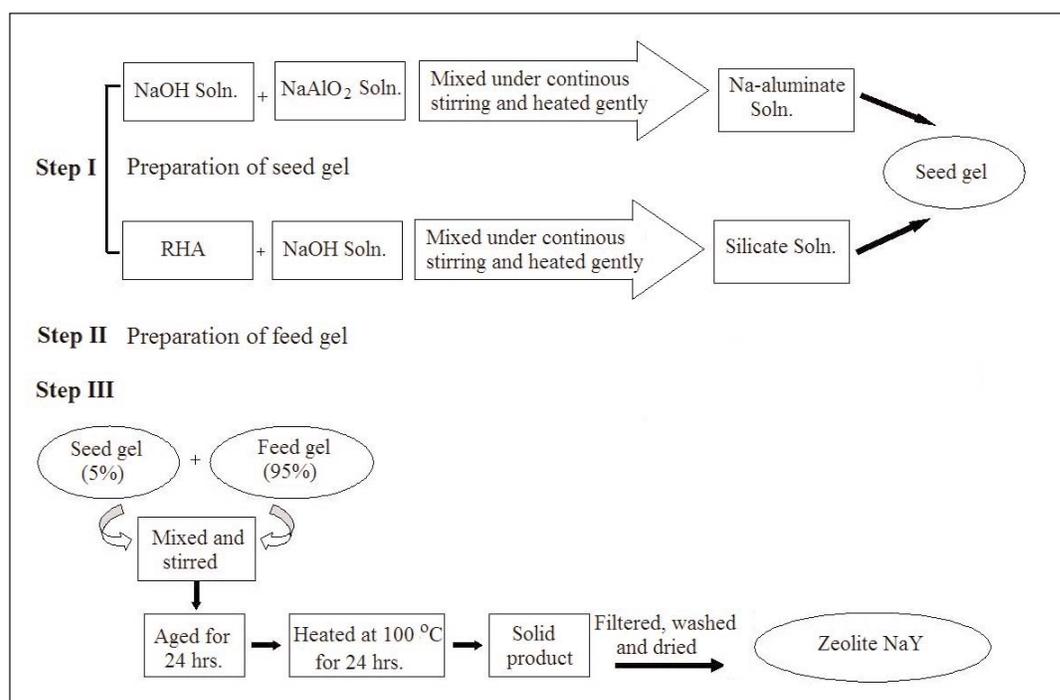


Fig. 1. Flowchart of the zeolite NaY synthesis procedure from RHA

Characterization of the synthesized zeolite NaY

Phase analysis of the synthesized zeolite NaY was performed by X-ray diffraction spectrophotometer (PANalytical X'Pert PRO XRD PW 3040). The intensity data was collected in 0.02° steps at the scanning range of $2\theta = 10^\circ$ to 90° using $\text{CuK}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) radiation source. The sample was ground to fine powder and loaded into the stainless steel (SS) sample holder. The observed data was compared with the standard data.

The functional groups present in the synthesized zeolite NaY were identified by recording the FT-IR peaks using FT-IR

Instrument Ltd., England) based on Dynamic Light Scattering (DLS).

Treatment of chromium containing wastewater using zeolite NaY

The stock solution (1,000 mg L^{-1}) of Cr (VI) was prepared by dissolving requisite amount of $\text{K}_2\text{Cr}_2\text{O}_7$ in deionized water and diluted to the desired concentration range (2-100 mg L^{-1}). The concentrations of Cr (VI) were measured by Atomic absorption spectrophotometer (AAS, PERKIN ELMER USA; Model - A Analyst 800). The adsorption effi-

ciency of the synthesized zeolite NaY was then examined by monitoring the concentration of Cr(VI) in the substrate solution as a function of adsorbent-solution contact time, initial concentration of Cr(VI) and pH of the of the substrate solution.

Effect of adsorbent-solution contact time

Six reagent bottles were charged with 50 mL Cr (VI) solution of 10 mg L⁻¹ concentration and the pH of each sample was adjusted at 2.0. A fixed amount (0.5 g) of zeolite NaY was added to each bottle and shaken well at room temperature. After different time intervals (0, 10, 30, 60, 180 and 360 min), the reaction mixtures were separated by filtering and the concentrations of residual Cr (VI) in the supernatant solutions were measured by the AAS.

Effect of initial Cr(VI) concentration

Effect of initial Cr(VI) concentration on the removal of Cr(VI) was investigated at room temperature with initial concentrations of Cr (VI) as 2.0, 11.0, 21.0 and 106.0 mg L⁻¹ using 0.5 g zeolite NaY as adsorbent. The pH was adjusted at 2.0. The adsorption was allowed for 180 mins.

Effect of pH

The effect of pH was studied by varying the initial pH ranges from 2.0 - 7.0 by adjusting the pH with 0.1 M NaOH and 0.1 M HCl. A fixed amount (0.5 g) of the synthesized zeolite NaY was added to 50 mL Cr (VI) solution having the desired pH. The concentration of each Cr (VI) solution was maintained at 10 mg L⁻¹. The solutions were shaken well in the reagent bottles and after 60 min each of the reaction mixture was filtered. The concentration of Cr(VI) in the filtered solutions were measured by AAS.

However in each case the adsorption efficiency of zeolite NaY was calculated by using the following equation.

$$\% \text{ of Adsorption} = \frac{A_0 - A_t}{A_t} \times 100 \quad (1)$$

where A_0 is the initial concentration of Cr (VI) solution and A_t is the concentration after treatment.

Results and discussion

Characterization of prepared RHA by XRD and SEM

A typical XRD pattern of pure RHA is shown in Fig. 2. A broad peak at 2θ position $\sim 22^\circ$ is clearly observed in the

diffractogram (Fig. 2.) which is characteristic of amorphous silica (Wittayakun *et. al.*, 2008). This form of silica is suitable for Zeolite synthesis because it dissolves easily in NaOH to form sodium silicate (Wittayakun *et. al.*, 2008). The SEM image ($\times 100$ magnifications, Fig. 3) of the prepared RHA shows that the particle size of the RHA was not uniform.

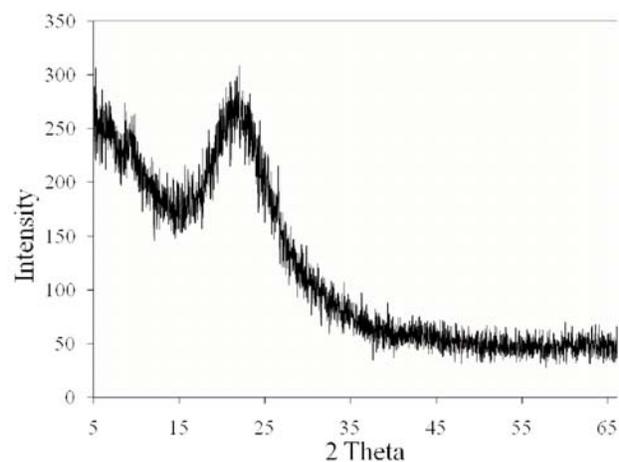


Fig. 2 XRD pattern of RHA



Fig. 3. SEM image of RHA

Characterization of the synthesized zeolite NaY by EDX, XRD, FT-IR and SEM

The recorded EDX spectrum of the synthesized zeolite NaY is shown in Fig. 4, which clearly shows the presence of the expected elements Si, Al, Na and O. However, the XRD diffractogram validated the presence of the desired phase in the prepared zeolite.

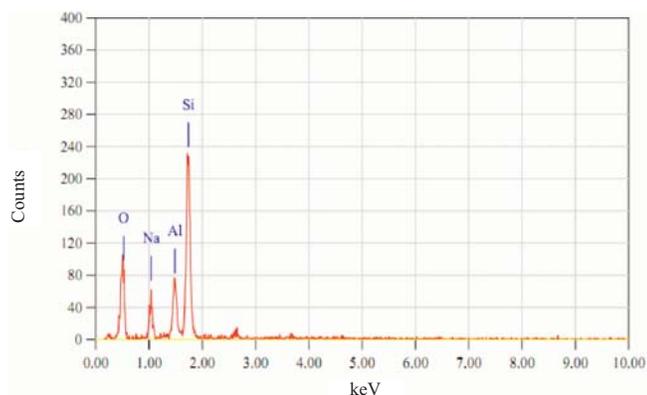


Fig. 4. EDX spectrum of zeolite NaY

The diffractogram (Fig. 5) of the zeolite NaY synthesized by the seeding and ageing techniques exhibit prominent peaks at 2θ positions $5^\circ - 70^\circ$ which are characteristic of zeolite NaY. However, the observed result revealed that the synthesized zeolite NaY has formed in mixed phases; *i.e.* both amorphous and crystalline phase are present.

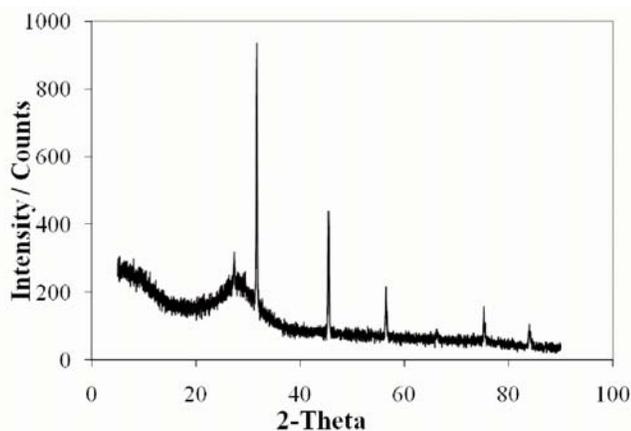


Fig. 5. XRD image of Zeolite NaY

The FT-IR spectrum of the zeolite NaY is illustrated in the Fig. 6 which shows the presence of strong IR absorption bands in the spectral region below 1200 cm^{-1} . Since the mid FT-IR region of zeolite NaY exhibits the fundamental vibrations of $(\text{Si,Al})\text{O}_4$ tetrahedra framework, so the mid FT-IR region of the spectrum was considered (1300 to 400 cm^{-1}) for analysis of NaY. Vibration frequencies of the zeolite lattice result from stretching and bending modes of the T-O bands and are observed in the range 400 to 1200 cm^{-1} (457.13 cm^{-1} and 1029.99 cm^{-1}). This observation confirmed that SiO_4 or AlO_4 are linked (Rahman *et al.*, 2009). The broad bands observed at 3446.79 cm^{-1} and 1648.27 cm^{-1} are

due to tortuous vibration and covalent vibration respectively (Liu *et al.*, 2003).

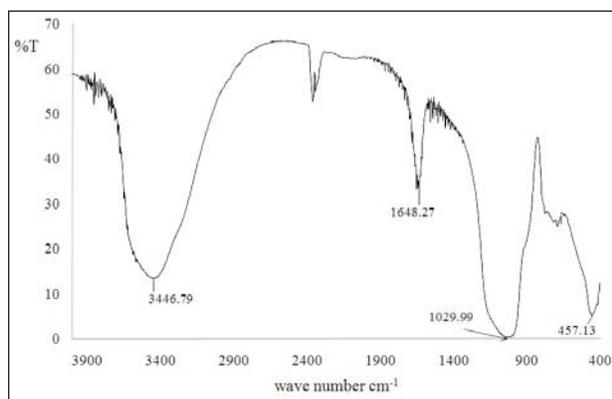


Fig. 6. FT-IR spectrum of Zeolite NaY

The SEM image of synthesized Zeolite NaY with magnification of $\times 200$ is illustrated in Fig. 7 which shows irregular morphology having various sizes and shapes (*i.e.* octahedral, twined etc.). It appears that, several crystals are fused together in agglomerated form.

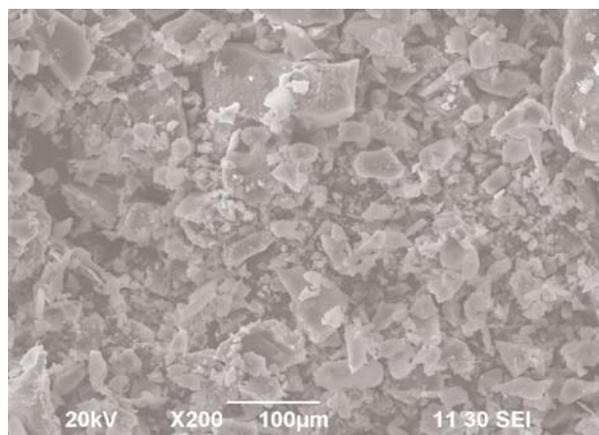


Fig. 7. SEM image of prepared zeolite NaY

Determination of particle size distribution of zeolite NaY

The particle size distribution and the statistics of distribution of the zeolite NaY is given in (Fig. 8). The major population (56.2%) had a particle size in the range 255-295 nm. There are smaller particles of sizes 190 nm (3%), 220.2 nm (15.4%), 342 nm (19.2%) and 396.1 nm (6.2%). It may, however, be pointed out that the particle sizes determined from the Dynamic Light Scattering (DLS) measurements represent the size and distribution of bulk particles that might be composed of aggregates of smaller particles, as well.

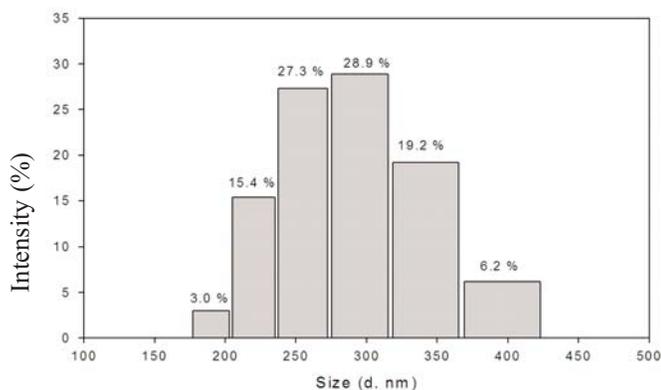


Fig. 8. Particle size distribution of zeolite NaY

Treatment of chromium containing wastewater using zeolite NaY in relation to contact time, initial Cr(VI) concentration and pH

Effect of adsorbent-solution contact time

Fig. 9 shows that the initial rate of adsorption of Cr(VI) is rapid and gradually increases till 180 min. After reaching the equilibrium position it tends to be steady. During the initial stage of adsorption, a large number of vacant surface sites are available for adsorption. After the lapse of some time, the remaining vacant surface sites had the difficulty to become occupied due to repulsive forces between the adsorbent molecules on the solid surface and in the bulk phase. Besides, the metal ions are absorbed into the mesopores that get almost saturated with Cr (VI) ions during the initial stage of adsorption.

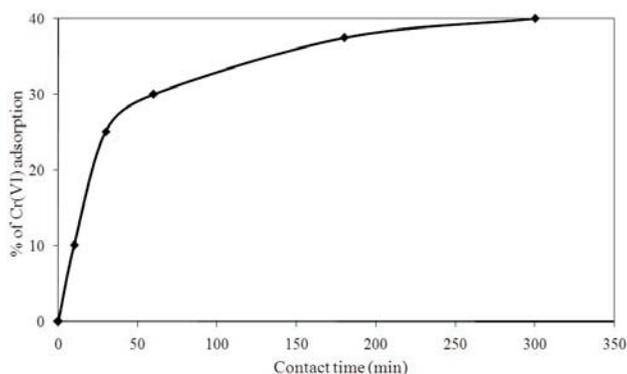


Fig. 9. Effect of contact time on the adsorption of Cr(VI) by Zeolite NaY

Effect of initial Cr(VI) concentration

Fig.10. represents the effect of initial Cr(VI) concentration on the removal of Cr(VI). Maximum adsorption was

achieved in case of the lowest concentration of chromium solution used for investigation. This is because, in this case the available surface area of the adsorbent (zeolite NaY) is fairly large enough and thus a better adsorption of Cr(VI) is facilitated. This indicates that in case of lower initial concentration of Cr(VI), the fractional adsorption becomes independent of initial concentrations. On the other hand, with the increase of initial concentration of Cr(VI), the adsorption efficiency decreases. Because, in case of higher concentration, the number of sodium cations of zeolite NaY which are neutralized by exchanging with chromium ions in the pore of zeolite framework are not enough as compared to the chromium molecules.

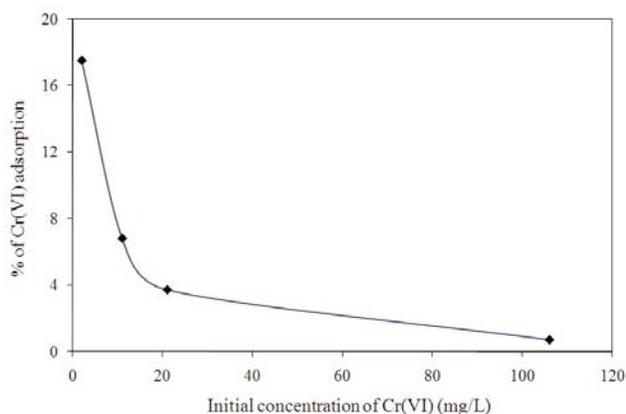


Fig. 10. Effect of initial concentration on adsorption of Cr(VI) by Zeolite

Effect of pH

The adsorption efficiency of the synthesized zeolite NaY was investigated as a function of pH of chromium solution. The observed result is summarized in Fig. 11 which clearly

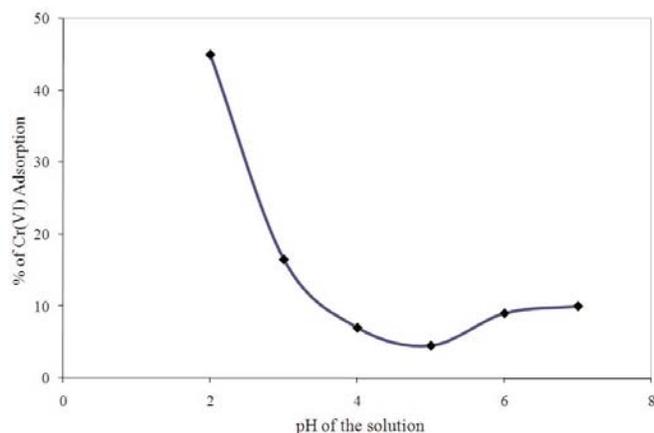


Fig. 11. Effect of pH on the adsorption of Cr(VI) by Zeolite

shows that the acidic medium is more favourable for the adsorption. The highest adsorption was achieved at pH 2.0 and the adsorption efficiency decreased gradually with the increase of pH.

Conclusion

Amorphous RHA was produced by controlled burning of rice husk and this amorphous RHA was used to synthesize zeolite NaY following the seed gel and feedstock gel methods. The adsorption efficiency of the prepared zeolite NaY was investigated by treating the synthetic waste water containing chromium. The adsorption results revealed that after careful manipulation of the morphology, particularly the size of the zeolite as well as forming composite with other materials and methodology, zeolite NaY could be used as a promising cost-effective adsorbent for the treatment of waste water containing chromium. However, development of zeolite NaY from RHA will be beneficial in many ways, such as:

- i. A cost effective and easy approach will be facilitated to remove Cr(VI) from tannery wastewater.
- ii. Utilization of RHA will be a promising material recycling technology for future waste management.
- iii. Pure silica produced from RHA could be used for the production of value-added materials (e.g. electronic devices, solar cells etc.) as well as in material science and environmental remediation.

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