
MINERAL
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Removal of Heavy Metals from Wastewater Solution Using a Mechanically Activated Novel Zeolitic Material

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Abstract—The removal of heavy metals from the wastewater solution using a novel zeolitic material was conceived and experimentally probed. The natural zeolite was ground in a planetary ball mill to increase negative surface charge and amorphization of the material as well as a conventional ball mill. The ground materials were used for the removal of heavy metals from the wastewater solution. The maximum removals were found to be 78% for Pb, 67% for Ni and 54% for Cd by using the conventional milled natural zeolitic material at pH 11. However, 93% of Pb, 72% of Ni and 57% of Cd were removed at pH 9 with the novel zeolitic material milled by a planetary ball mill. It was revealed that the novel zeolitic material produced by a planetary ball mill increased the absorption capacity of the heavy metals and reduced the alkali requirement for pH adjustment. The removal order of heavy metals with the novel zeolitic material is determined as follows: Pb> Ni>Cd.

Keywords: Hekimhan/Malatya, mechanical activation, heavy metals, natural zeolite, adsorption, wastewater.

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INTRODUCTION

The scientific developments and the high-tech industrial applications in the world have caused the disruption of nature, which is the source of life. The excessive release of heavy metals into the environment due to industrialization and urbanization is a major problem worldwide. On the one hand, these developments in the field of industrialization have increased the quality of life of the people, and on the other hand, these resources have led to air, soil and water pollution to threaten living beings [1–5]. Metals are often present in soluble waters in inorganic, soluble, adsorbed, insoluble, oxidized, precipitated, reduced or free metal forms. The most common metals in industrial wastewater are; chromium, copper, cadmium, nickel, lead, zinc and mercury. Pollution from heavy metals is a major problem both in the water and in the soil, which has caused worldwide concern in terms of wastewater produced by the industries such as mineral processing, petrochemical and metal recovery facilities [6, 7]. The heavy metal removal capability of natural substances, especially zeolites and the other clay minerals are of great importance. Besides, the economic heavy metal removal methods have an increasing interest.

Since heavy metals such as lead, nickel and cadmium, which cause environmental pollution, are present in wastewater, they must be treated before they are released to the environment. Alkaline proportions of heavy metals tend to undergo biological accumulation. Besides, they are highly toxic. Treatment of industrial wastewater containing high concentrations of heavy metals contains adsorption, sorption, coagulation, chemical precipitation, neutralization, ion exchange, reverse

osmosis, evaporation, flotation, pressure flotation, and membrane purification methods [8–14]. On the other hand, it is more suitable to utilize natural cation exchangers like natural zeolitic materials in wastewaters where heavy metal removals are not cost-effective and cannot be simply eliminated owing to their chemical properties.

The term mechanical activation is defined as a process that increases the reactivity of a solid whose chemical properties remain unchanged [15]. The primary effect of mechanical activation on the mineral is comminution. During mechanical activation, while the particle size of the mineral is reduced by grinding, defects occur in the crystal structure depending on the mechanical energy density [16, 17]. Therefore, fresh, clean surfaces and ultimately semi-stable (metastable) species that have not been subjected to any effect before being formed [18]. Ball-milling of the materials causes the changes in their morphology, particle size and amorphization [19-21]. Mechanical activation enhances the chemical activity of oxides. Thus, the recovery efficiency in mineral processing techniques such as leaching is increased [22]. In addition, the breaking of “external” Si-O-Si and Si-O-Al bonds of the zeolitic frameworks leads to the amorphization of zeolites [23].

There are approximately 60 different types of natural zeolite, such as clinoptilolite, mordenite, and chabazite in unique physical and chemical characteristics. In particular, zeolite deposits are mostly composed of volcanic tuffs or crystals in the holes of alkali rocks and low-grade metamorphic deposits [24]. Hekimhan/Malatya zeolites mainly consist of clinoptilolite- (Ca), heulandite and calcite minerals. Sources of zeolite deposits are tuffs, volcanic rocks, and sea tuffs accumulated in marine beds [25]. Zeolites, which are one of the alumina silicate minerals, have generally microporous structures. Zeolites have many usage areas in the industry due to their versatile and unique properties such as catalyst, ion exchange, adsorption, and separation.

In the present work, the removal of heavy metals from synthetic wastewater solution by using a mechanically activated novel zeolitic material was investigated. The conventionally milled zeolites were also tested in the adsorption experiments. The purpose of the mechanical activation is to make the structure of the zeolite amorphous; more porous and larger surface area. The effects of pH, stirring time and temperature on the removal of heavy metals from the wastewater solution were examined. In addition, the removal order of the heavy metals was determined.

1. MATERIALS AND METHODS

Natural zeolitic samples were taken from Hasançelebi region, Hekimhan district of Malatya province in Turkey. The XRD (X-Ray Diffraction) pattern of the sample is given in Fig. 1. The XRD patterns were obtained using Bruker D8 Discover XRD Device equipped with the current PDF 2 mineral database. DIFFRAC.SUITE EVA software was used for the XRD pattern analyses and the measurements of the amorphization degree. It was determined that the main structure of the natural zeolitic material consists of montmorillonite, calcite, gottardiite, heulandite, and clinoptilolite-Ca minerals. Minipal-4 Panalytical XRF device was used for revealing the chemical contents (see below). The main chemical components of the sample were SiO₂, CaCO₃ and Al₂O₃.

Elements	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MnO	TiO ₂	Na ₂ O	CuO	BaO	SrO	SO ₃
Contents, %	52.00	11.60	23.20	7.89	0.14	0.75	0.80	0.05	0.10	0.41	0.40

Three-dimensional topographic images of the samples were obtained by using SEM (Scanning Electron Microscope) device (LEO-EVO 40) at İBTAM-İnönü University Scientific and Technological Research Center. The SEM images gave information about the surface morphology and composition of the samples. The SEM analysis revealed that the sample is a layered in shape, which is an indicator of the natural zeolitic framework (Fig. 2).

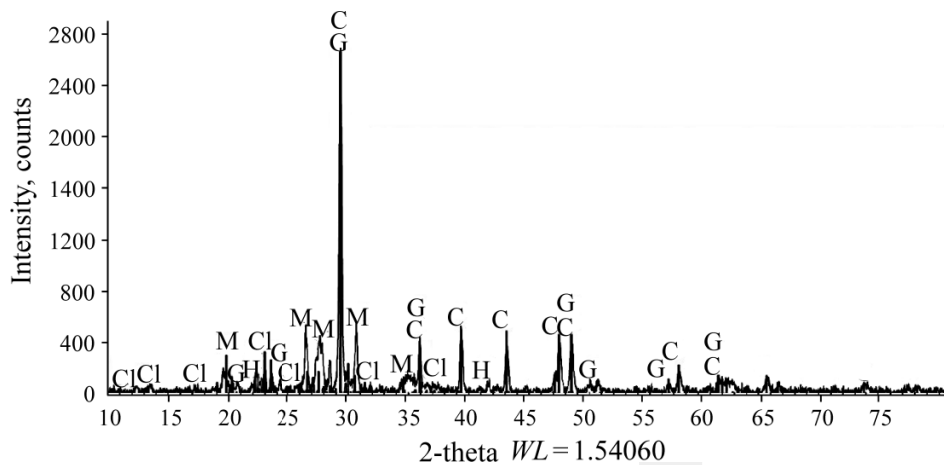


Fig. 1. XRD pattern of the sample: M—montmorillonite (40%); C—calcite (32.8%); G—gottardiite (15.5%); H—heulandite (6.1%); Cl—clinoptilolite (5.6%).

The supplied samples were ground by a conventional ball mill (Denver brand) at a speed of 70 rpm for 30 min in a dry environment. The drum has a height of 20 cm, a diameter of 19.5 cm and 5970 cm³ of volume. The drum was charged with stainless steel balls of four different sizes (20-25-30-40 mm) as grinding media weighting 8 kg. The milling medium was adjusted to 60% of the internal volume of the drum. The particle size of the ground sample was determined as less than 150 µm. The novel zeolite samples were produced by grinding with a planetary ball mill (Retsch PM 100 Planetary Mill model) for the mechanically activation using samples with sizes less than 150 µm (Fig. 3). A 125 ml stainless steel drum was filled with 100 and 208 stainless steel balls with a diameter of 7 mm (1.38 g) and 5 mm (0.26 g), respectively.

The mill was operated at various speeds. These speeds were 180, 270, 360, 450, 540 and 600 rpm. The materials were milled at milling times ranging from 1-15-30-45-60-120-180-240-300-360-420-480-540-600 min. Grinding with the planetary ball mill was carried out by utilizing 5 g of the samples. The samples were dried in an oven at 80 °C at least 30 min before grinding to remove moisture. To prevent overheating of the planetary ball mill, the device was stopped and cooled every 15 min.

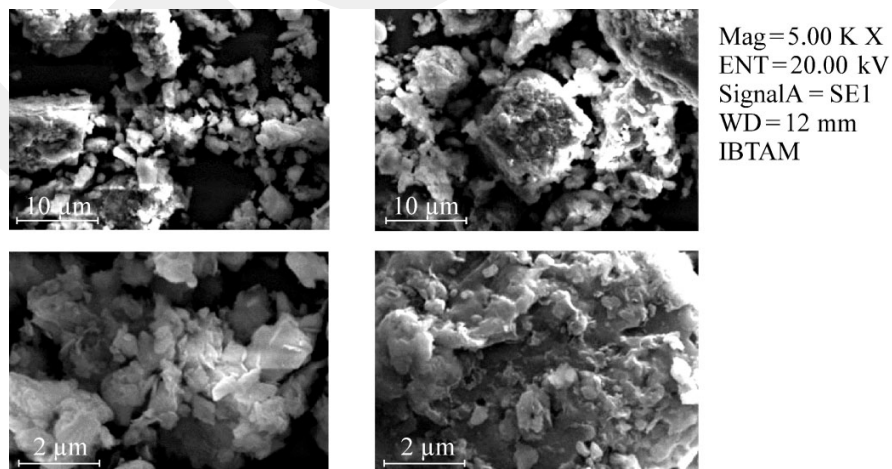


Fig. 2. SEM micrographs of the sample.

In the adsorption experiments, the materials decreased in size less than 150 μm by conventional ball mill as well as the mechanically activated novel zeolite. The operation was performed by the planetary ball mill for 180 minutes at 450 rpm and 120 minutes for 540 rpm.

The degree of crystallinity (DOC) method, which is a Rietveld-based technique, was used for the amorphous phase determination via DIFFRAC.SUITE EVA software. The technique relies on the estimation of the entire intensity or area contributed to the overall pattern by each component in the analysis [26-27]. The DOC and amorphous phase quantities ($W_{\text{amorphous}}$) was calculated according to the following equations:

$$\text{DOC} = \frac{\text{Crystalline area}}{\text{Crystalline area} + \text{Amorphous area}} \cdot 100,$$

$$W_{\text{amorphous}} = 100 - \text{DOC}.$$

Synthetic wastewater solutions containing heavy metals were prepared using analytical grade stock chemicals under laboratory conditions. 1000 mg/l of stock solutions were prepared by Sigma-Aldrich branded PbCl_2 , NiCl_2 and CdCl_2 salts. A 10 ml of each solution was taken and put into a 100 ml flask. 1M of HCl and 1M of NaOH were used for the pH adjustments in the experiments. The adsorption values were found with the difference of concentrations in solutions before and after adsorption using the formula:

$$\text{Adsorptions (\%)} (\text{Pb, Ni and Cd}) = \frac{C_1V_1 - C_2V_2}{C_1V_1} \cdot 100.$$

Here, C_1 is the initial concentration of stock solution, mg/l; V_1 is the initial volume of stock solution, l; C_2 is the final concentration of stock solution, mg/l; V_2 is the final volume of stock solution, l. All the tests were duplicated to confirm the reproducibility of the experimental results.

The characterization of samples by XRD, SEM, XRF, zeta potential, and BET specific surface analysis methods were carried out. Particle size analyses were conducted by Malvern Mastersizer 3000. BET surface analyses were measured by N_2 adsorption in the Tristar 3000 BET analyzer. Zeta potentials of the ground materials were calculated by Malvern Nano ZS Zetasizer.

The main factors affecting adsorption such as pH, mixing time, temperature and stirring speed were investigated by using conventionally ground and planetary ball milled zeolite samples less than 150 μm in size. AAS (Atomic Absorption Spectrophotometer) was used to determine the adsorption amounts. OFAT analysis (One Factor at a Time) was used to determine the optimum parameters. In this statistical analysis method, firstly the levels of one factor are changed and the other factors are kept constant. The most appropriate value is determined after the interpretation of the results. Then, the appropriate value is kept constant and the other parameters, which are kept constant at the earlier stages, are tested at varying levels and the optimum values of all parameters are determined within the tested values.

2. RESULTS AND DISCUSSIONS

XRD analysis. When the patterns are examined, it is seen that as the grinding speeds increase, the crystal structure of the material deteriorates in a shorter time. Although there was a decrease in peak intensities due to the effect of grinding especially at 180 and 270 rpm, the gottardiite, clinoptilolite, heulandite and calcite peaks did not disappear despite the grinding operations performed for 10 h (Figs. 3a and 3b). In the experiments carried out at 360 rpm, the peaks of the zeolite minerals were mostly abolished after 420 min (Fig. 3c). The samples with the same characterization were obtained at 5 h in the experiment carried out at 450 rpm (Fig. 4d). Most of the amorphization was achieved after only 2 h of milling test at 540 rpm (Fig. 3e).

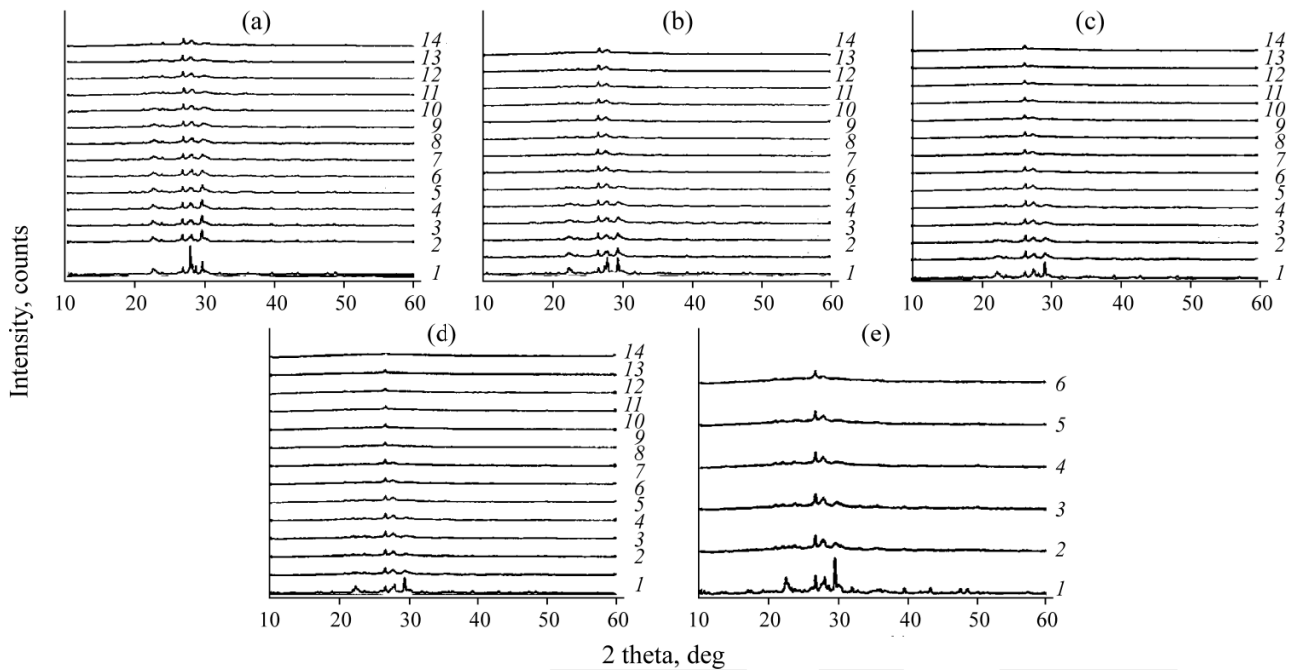


Fig. 3. XRD patterns of zeolites milled at different times in planetary ball mill at (a) 180 rpm, (b) 270 rpm, (c) 360 rpm, (d) 450 rpm and (e) 540 rpm; 1—1 min; 2—15; 3—30; 4—45; 5—60; 6—120; 7—180; 8—240; 9—300; 10—360; 11—420; 12—480; 13—540; 14—600 min.

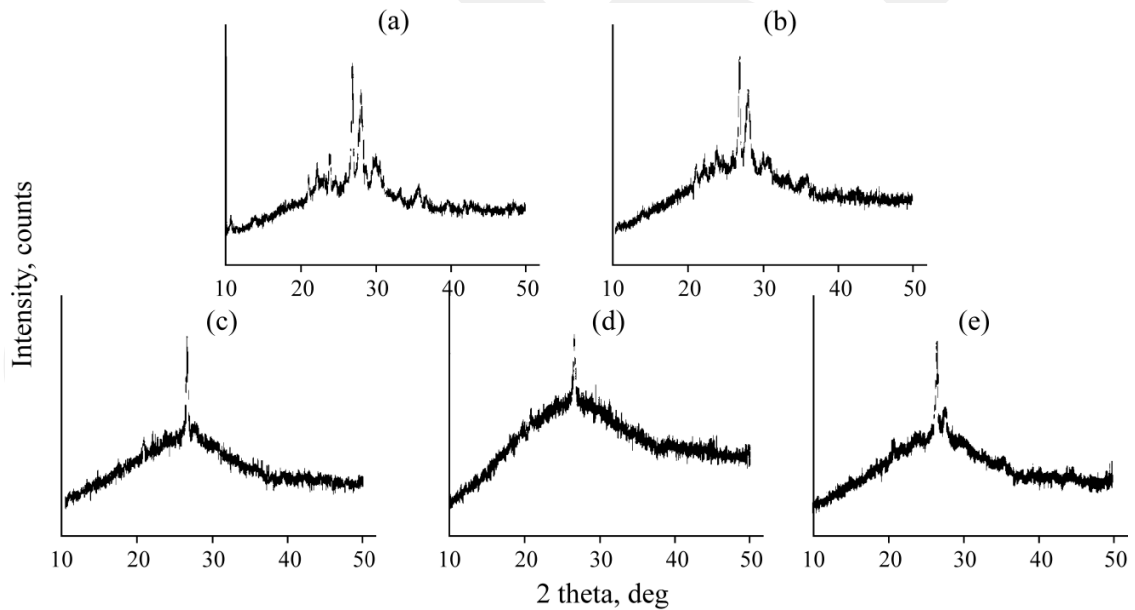


Fig. 4. View of halo peaks for ground zeolites: (a) 180 rpm, 600 min; (b) 270 rpm, 600 min; (c) 360 rpm, 600 min; (d) 450 rpm, 600 min; (e) 540 rpm, 120 min.

Amorphous materials do not have long continuity compare to the crystalline materials and they do not show long-range order. Atoms are unsystematically scattered in space. Amorphous materials have order only a few atomic or molecular dimensions (very short range). To better illustrate the halo peaks, which are indicative of amorphization, Fig. 4 was created. In particular, grinding peaks at 360, 450 and 540 rpm showed that narrower crystal peaks were largely lost.

The best fingerprint of the halo peak was obtained by grinding at 450 rpm considering the camber and the broadening of the peak at $2\theta=26^\circ$ (Fig. 4d). This shows that the amorphization efficiency is also strongly dependent on time, although amorphization takes place at a shorter time by higher rotational speeds.

Amorphous content percentages of the ground samples are seen in Fig. 5. The crystallinity of the material, which is ground in the conventional ball mill and also used as feed material in the planetary ball mill, was determined as 68.1% corresponding to 31.9% of the amorphous phase.

The amorphous phase in the product obtained from the experiments carried out at 540 rpm increased to 80.5% after 2 h, while this value was determined as 74.2% in the product obtained from the experiment carried out at 450 rpm for 2 h. The amorphization degree of the products did not increase significantly after 2 h. Therefore, the materials milled for 180 min at 450 rpm (sample PM1—with 78.6% amorphization) and 120 min at 540 rpm (sample PM2—with 80.5% amorphization) were used for the following tests. Besides, economic reasons were taken into consideration for the choice of the products obtained at the low-grinding time.

SEM analysis. Three-dimensional topographic images of natural zeolite samples milled at planetary ball mill were obtained by SEM (Fig. 6).

It was observed that the angular and layered structures, which confirm the zeolitic material structure, were replaced by tuber and rounded particles after excessive grinding which is similar to the findings of a previous study [28]. The average particle size was from about 60 nm to 30 nm for 450 rpm and less than 30 nm for 540 rpm. The size distributions indicated that the surface areas of the milled samples increased.

Particle size distributions and BET specific surface areas. The particle size distributions of PM1 and PM2 materials were close to each other. For PM1 and PM2 materials, d_{100} values were found as 58.8 and 66.8 μm , respectively. Besides, d_{50} values were 18.8 μm for PM1 and 20.1 μm for PM2 material (Fig. 7).

Unlike micrographs observed from scanning electron microscopy, higher size values were obtained in laser diffraction particle size analyses. Guzzo et al. (2015) observed that there was an agglomeration between mineral particles after grinding at a certain time in a planetary ball mill [29]. As a result, the size of the agglomerated particles is measured rather than the individual ones. To overcome this common problem for ultrafine particles, some researchers stated that the difference in measured and true particle sizes can be distinguished from each other by BET specific surface area analyses [30–32]. The multi-point BET specific surface analysis values, which were measured as 27.53 m^2/g for the original zeolitic sample conventionally milled below 150 μm , were determined as 175.04 m^2/g and 164.76 m^2/g for PM1 and PM2 materials milled by planetary ball mill, respectively.

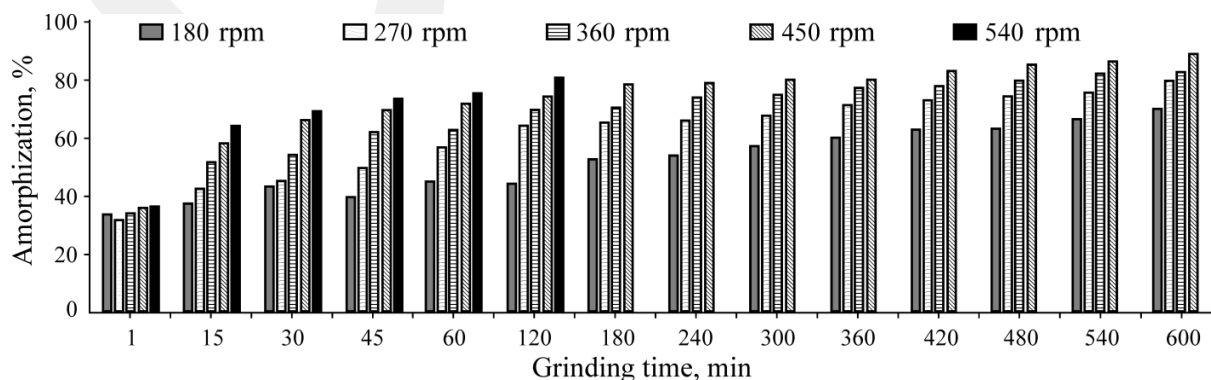


Fig. 5. Amorphization degrees of the ground samples as a function of grinding time.

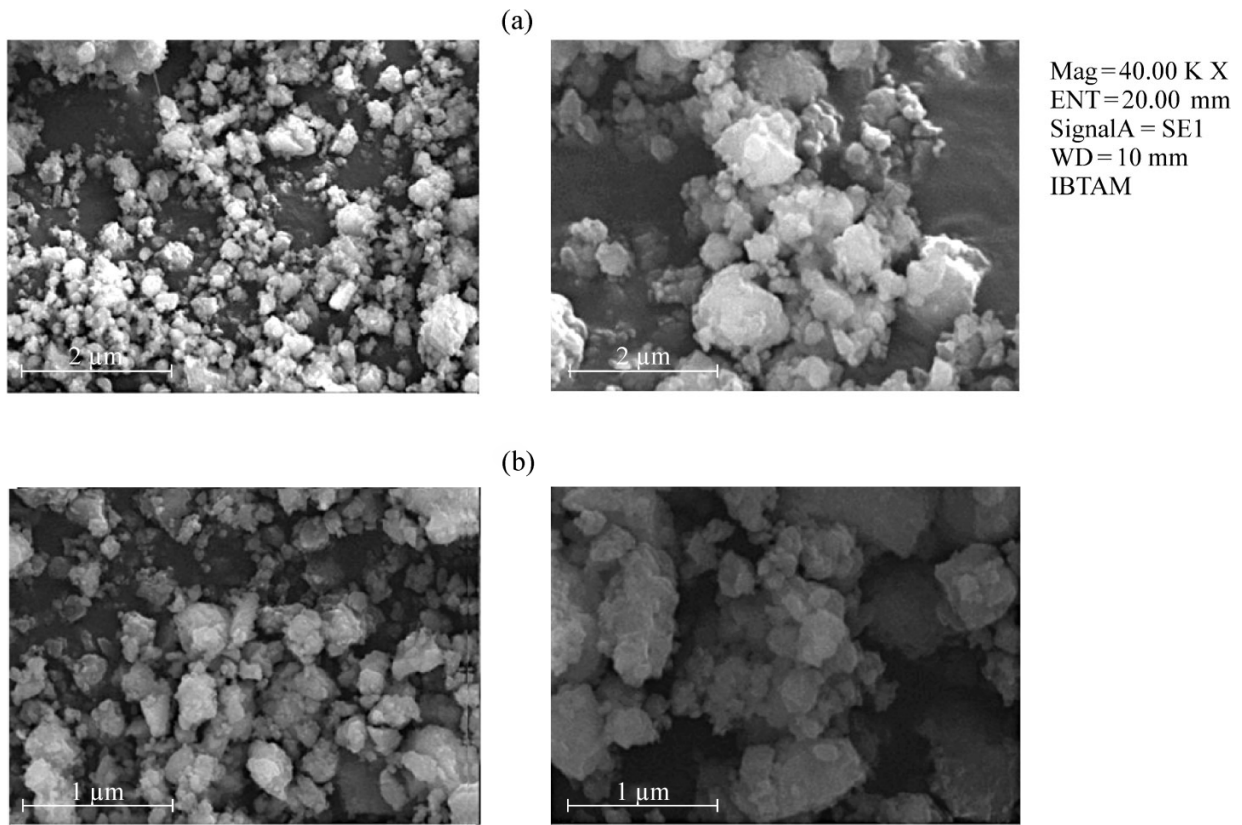


Fig. 6. SEM images of samples milled (a) at 450 rpm for 180 min and (b) at 540 rpm for 120 min.

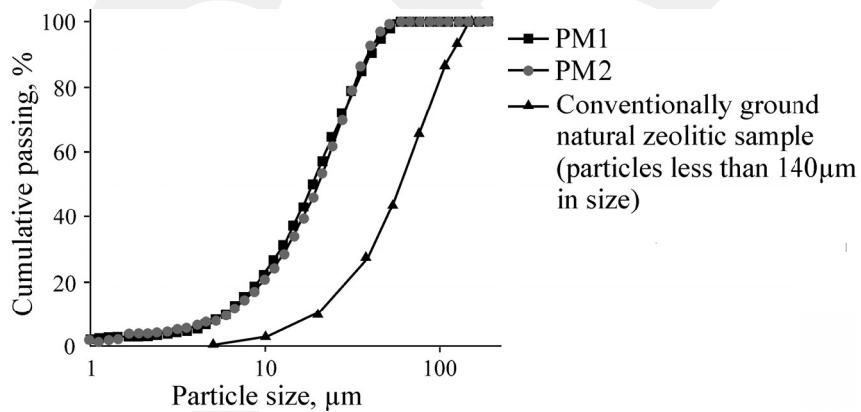


Fig. 7. Particle size distributions of the samples (logarithmic scale).

Zeta potentials. The amorphization of materials as a result of the breaking of chemical bonds caused changes in surface charges. The natural zeolitic material, which was conventionally ground, had -11.8 mV and -21.6 mV zeta potential at pH 7 and pH 11, respectively. Observed zeta potential values of the planetary ball-milled materials at various pH values are given below.

Zeta potential values of the ground samples at different pH, mV

Sample	pH 7	pH 9
PM1	-23.2	-29.2
PM2	-21.5	-27.6

It was concluded that $=\text{Si}=\text{O}$ bonds were exposed to breakages in the early stages of grinding and more kinetic energy (grinding time) required to break $=\text{Al}-\text{O}$ bonds giving higher negative surface charge. Breakages of the alumina molecules led to a higher negative surface charge. The fact that the materials milled in the planetary mill have a higher negative electric charge at lower pH values is also an indication that zero point charge values of the materials decrease because of overgrinding. These findings are in good agreement with those of previous studies [33–34].

Parameters affecting heavy metal adsorption properties of natural zeolitic materials ground by a conventional ball mill. Heavy metal concentrations (in a 100 ml beaker, 10 ppm Pb, Ni, and Cd) were kept constant by using 1M of HCl and 1M of NaOH in pH adjustment to determine the optimum pH. The pH values were adjusted to 3-5-7-9-11-13 and the experiments were carried out by adding 0.5 g of adsorbent material in all experiments and stirring at 500 rpm for 30 min with a magnetic stirrer so that all solids were suspended. The temperature was 25°C. After filtering and drying, the liquid phases obtained were centrifuged and the concentrations of heavy metals (Pb, Ni, Cd) in the solutions were determined by AAS.

Adsorption of Pb^{+2} , Ni^{+2} and Cd^{+2} ions increased as the pH increased. This is because the adsorbent surfaces become more negatively charged with increasing pH. Pb, Ni and Cd heavy metals were more easily able to interact with negatively charged zeolitic materials. The highest adsorption values of three heavy metals were reached at pH 11 for natural zeolitic samples. The maximum adsorption yields of 78% for Pb, 67% for Ni and 54% for Cd were achieved (Fig. 8a).

After determining the optimum pH, the stirring times were adjusted to 5, 15, 30, 45 and 60 min, keeping the optimum pH and heavy metal concentrations constant to determine the appropriate mixing times. The magnetic stirrer was stirred at 25°C, 500 rpm and 30 min. After filtering and drying, the liquid phases obtained were centrifuged and the concentrations of heavy metals were determined.

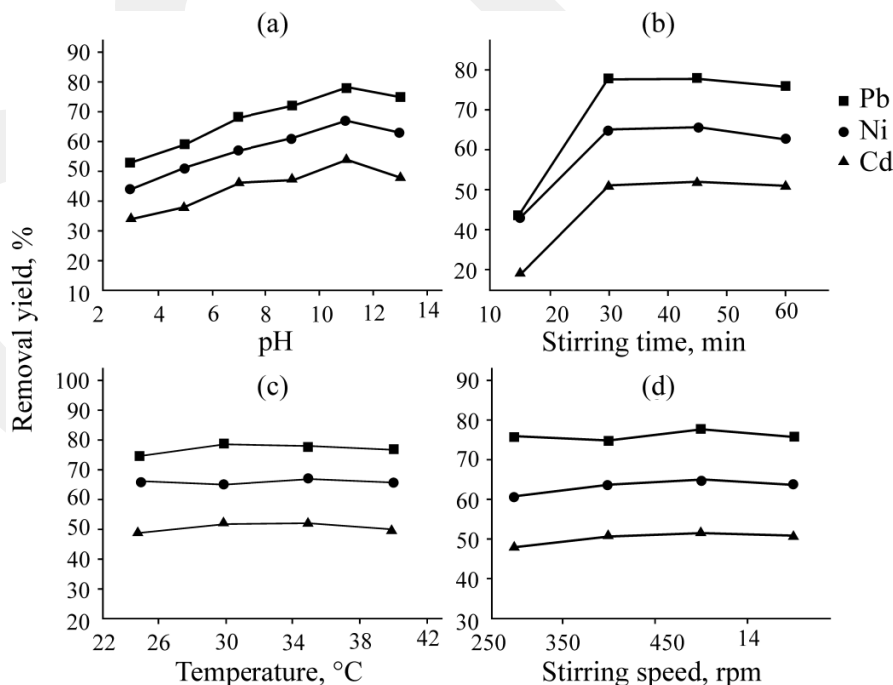


Fig. 8. Effects of (a) pH, (b) stirring time, (c) temperature and (d) stirring speed on heavy metal removal yields.

When the effect of stirring time was examined, it was seen that the adsorption percentage of Pb^{+2} , Ni^{+2} and Cd^{+2} ions increased as the mixing time increased. The maximum adsorption time of the natural zeolite was determined to be 30 min. After 30 min, no significant change in adsorption yield was observed (Fig. 9b). After 30 min stirring time, it was found that maximum adsorption efficiencies of 78% for Pb, 66% for Ni, and 52% for Cd were achieved when three heavy metals were compared. The temperatures were adjusted to 25°C, 30°C, 35°C and 40°C at optimum pH and stirring time, keeping the heavy metal concentrations constant to determine the appropriate temperature effect.

The effects of temperature factors on adsorption are very important. It is desirable to remove heavy metals from wastewater at room temperature. This is important because of both the cost and the difficult heating conditions. The investigation of the adsorption reaction depending on the temperature gives us information about the enthalpy change of the adsorption event. From the results of the experiment, it was observed that the adsorption capacity of the sample did not change much with increasing temperature for Pb^{+2} , Ni^{+2} and Cd^{+2} ions (Fig. 8). The maximum adsorption yields of 78% for Pb, 67% for Ni and 50% for Cd were achieved at 30°C.

By keeping the optimum parameters determined in the previous steps constant, stirring speeds were set at 300-400-500-600 rpm and 0.5 g of adsorbent was added in all experiments. All the solids were suspended with a magnetic stirrer.

As the mixing speed increases, there is no significant change in the adsorption efficiency of Pb^{+2} , Ni^{+2} and Cd^{+2} ions. There was no need to compare the adsorption effect of stirring speed on the planetary ball mill for further tests.

Parameters affecting heavy metal adsorption properties of natural zeolitic materials ground by a planetary ball mill. Materials milled for 180 min at 450 rpm (PM1) and 120 min at 540 rpm (PM2) were subjected to adsorption tests, separately. The same procedures applied to the natural zeolitic materials used by grinding in the conventional ball mill were applied to the samples milled by the planetary ball mill.

Using PM1 natural zeolites, it was observed that adsorption of heavy metal ions changed at different pH. The surface area and pore structure of the natural zeolite were observed to be increased by SEM analysis. The increase in pH made the heavy metals more easily interact with Pb^{+2} , Ni^{+2} and Cd^{+2} ions and adsorbent.

The natural zeolitic materials reached the highest yield at pH 11 without milling in the planetary mill, while the maximum yield at pH 9 was reached in the planetary ball mill with PM1 zeolites (Fig. 9a). From an economic point of view, less sodium hydroxide (NaOH) will be used. When comparing heavy metal removals at pH 9, it was seen that maximum adsorption yields of 93% for Pb, 72% for Ni and 57% for Cd were achieved.

Adsorption of heavy metal ions using PM2 natural zeolite absorbents was investigated at varying pH ranges and is given in Fig. 9a. When the figure is examined, it is seen that the values are changeable. While the adsorption capacity of lead and nickel ions increased more, the adsorption capacity of cadmium ions increased slightly.

It was observed that the adsorption yields reached maximum values at lower pH values as in 450 rpm. The only difference was that the maximum value for Cd ion at 450 rpm was reached at pH 7, while the maximum values at Pb and Ni were reached at pH 9. It is seen that removal can be done even in neutral (pH 7) environment for cadmium removal. When comparing heavy metal removals at pH 9, it is seen that maximum adsorption yields of 90% for Pb, 65% for Ni and 41% for Cd are achieved. Better removal efficiencies have been achieved with PM1 materials.

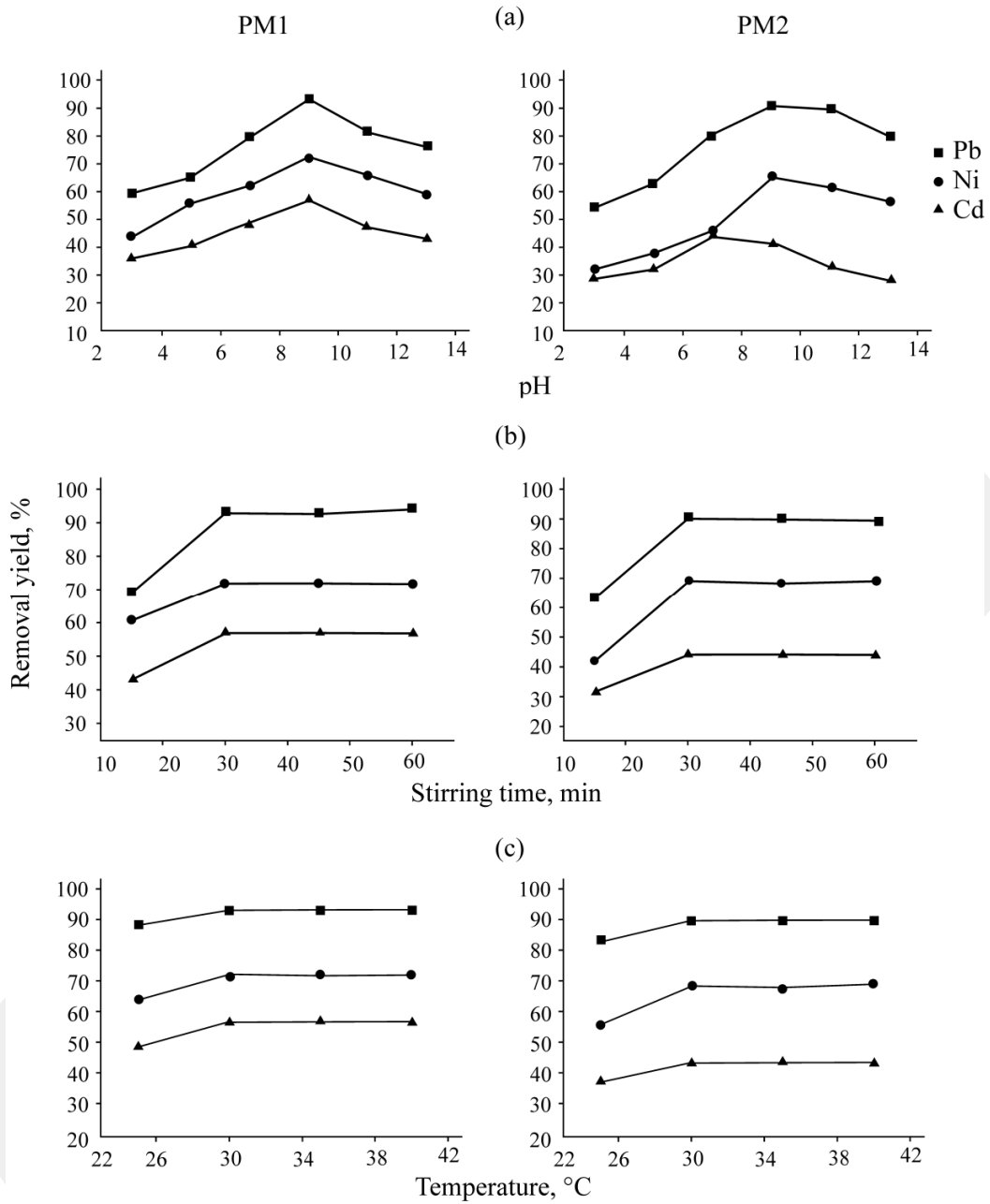


Fig. 9. Effect of (a) pH, (b) stirring time and (c) temperature on adsorption for PM1 and PM2 materials.

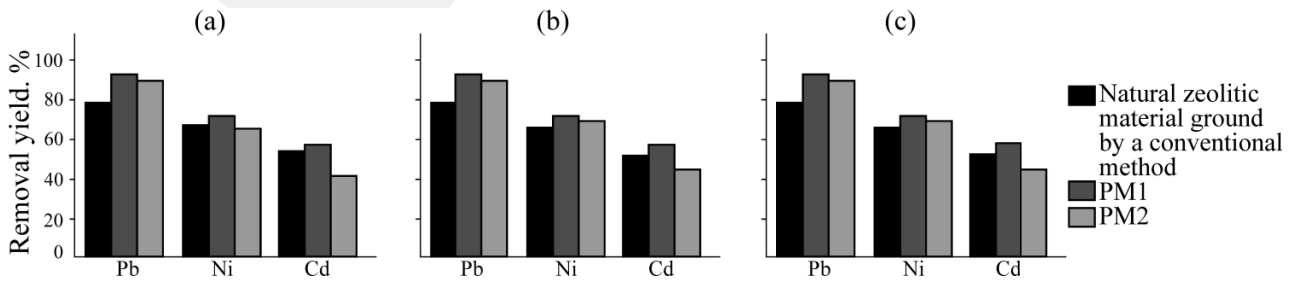


Fig. 10. Comparison of adsorbents for heavy metal removal values at optimum conditions: (a) pH, (b) stirring time, (c) pulp temperature.

It was observed that the adsorption yields of heavy metal ions increased as the stirring time increased for PM1 materials. The adsorption reached maximum values in 30 min for PM1 (Fig. 9b). There was no significant change in adsorption yields after 30 min. Comparing the stirring times and heavy metal removals for classical and planetary mills, it is seen that higher removal efficiency is achieved in the planetary mill for 15 min.

Due to the enlarged pore and surface areas of the milled natural zeolite in the planetary ball mill, maximum values could be reached at lower stirring times in the adsorption tests. The maximum adsorption yields of 93% for Pb, 72% for Ni and 57% for Cd were achieved at 30 min stirring time. The similar results were obtained by using PM2 materials. After 30 min of grinding, there was not much change in adsorption yields. The maximum adsorption yields of 90% for Pb, 69% for Ni and 44% for Cd were achieved at 30 min stirring time. There was no significant adsorption difference between PM1 and PM2 absorbents in terms of stirring times.

Experimental results showed that the adsorption capacity of Pb^{+2} , Ni^{+2} and Cd^{+2} ions did not change significantly with the increase in temperature by using PM1 materials like natural zeolitic materials milled by conventional ball mill. The most important difference is the increase in adsorption efficiency at lower temperatures. At 30° C, the maximum adsorption yields of 93% for Pb, 72% for Ni, and 57% for Cd were achieved (Fig. 9c). Maximum adsorption yields of 90% for Pb, 69% for Ni and 44% for Cd were achieved at 30° C using PM2 samples (Fig. 9c).

Comparison of adsorbents by optimum adsorption values. In this research, heavy metal removal was investigated by using three samples. The first sample was reduced to a size less than 150 μm in conventional ball mill and the other samples (PM1 and PM2) were reduced to smaller dimensions in the planetary ball mill. Optimum heavy metal removal conditions for adsorption tests were determined as 30 min stirring time, 30 °C pulp temperature and 500 rpm stirring speed for all absorbents used. Optimum pH values were determined as pH 11 for the sample milled in the conventional ball mill and pH 9 for the samples milled in the planetary ball mill. Figure 10 was created, based on the heavy metal removal values of the absorbents at optimum pH, mixing time and pulp temperatures.

As can be seen in Fig. 10a, PM1 absorbent material provided the best values for heavy metal removals. Better results were obtained with PM2 material at optimum pH values compared to the original material conventionally milled below 150 μm in terms of Pb and Ni removal. In all optimum conditions, PM2 absorbent provided the worst removal values in cadmium removal (Figs. 10b and 10c).

CONCLUSIONS

In this study, the removal of heavy metals from synthetic heavy metal loaded solutions was investigated by the adsorption method. Three types of natural zeolitic materials, which were reduced to the size below 150 μm in conventional ball mill and milled to smaller dimensions in the planetary ball mill, were used as adsorbents. The XRD analysis indicated that planetary ball mill decomposed the crystal structure of the materials and made them amorphous after various time intervals. Amorphization percentages increased with increased grinding times and stirring speeds. Besides, the halo peaks became clearer. Overgrinding with planetary ball mill led to the higher negative surface charge by breaking the alumina molecules and made the ground samples more attractive for metal cations. The SEM micrographs demonstrated that the grinding process enlarged the surface areas and increased the pore structures of the samples. After the adsorption tests using ground products as adsorbent, the optimal adsorption parameters were determined. The superior adsorption capacity of the planetary ball-milled samples was revealed.

Optimum heavy metal removal conditions for adsorption tests were determined as 30 min of stirring time, 30° C of pulp temperature, and 500 rpm of stirring speed for all absorbents used. Optimum pH values were determined as pH 11 for the sample milled by the conventional ball mill and pH 9 for the samples milled by the planetary ball mill. It was concluded that the use of milled materials in the planetary ball mill as an absorbent in wastewater treatment processes will reduce the alkali requirement for pH adjustment. PM1 absorbent material, which was obtained by grinding in planetary ball mill at 450 rpm and 180 min, provided the best values for heavy metal removal. The heavy metal removal yields with natural zeolitic materials were determined as Pb > Ni > Cd from increasing to decreasing.

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