

Preparation, Characterization, and Heavy Metals Adsorption Behavior of Unmodified Zr-MCM41 and ZrFe-MCM41

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Abstract

The potential of removing Ni and Pb cations from industrial electroplating wastewaters by using mesoporous materials of MCM-41 structure doped with different ratios of Zr and Fe, namely Zr-MCM41, ZrFe-MCM41(61), and ZrFe-MCM41(31) was evaluated. The prepared adsorbent materials were characterized by powder X-ray diffraction, nitrogen gas sorption, FTIR, TGA, and SEM. The adsorbents were employed to remove Pb and Ni ions from aqueous solutions at room temperature. The effect of several process variables such as metal concentration (50 to 1,000 ppm), stirring time (0.5 to 5 h), and solution pH (1.5 to 12) was studied in the batch mode. Flame atomic absorption spectrometry was used to determine the concentration of cations in the eluted solution. Results obtained indicate that under optimum conditions, pH in the vicinity of 6 – 8, Zr-MCM41 had the maximum adsorption capacity for both cations, i.e., Ni: 25.92 and Pb: 73.63 mg/g. On the other hand, ZrFe-MCM41(61) containing a higher molar ratio of iron showed lower adsorption capacity for the cations, i.e., Ni: 12.57 and Pb: 39.01 mg/g.

Keywords: Zr-MCM-41, ZrFe-MCM41, mesoporous silica, nickel, lead.

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1. Introduction

Contamination of water by toxic heavy metals through the discharge of industrial wastewater is a worldwide environmental problem. Rapid industrialization has seriously contributed to the release of toxic heavy metals to water streams. Mining, electroplating, metal processing, textile, and battery manufacturing industries are the main sources of heavy metal ion contamination. Metals such as lead, cadmium, copper, arsenic, nickel, chromium, zinc,

and mercury have been recognized as hazardous heavy metals.

Heavy metal toxicity can result in damage or reduced mental and central nervous function, lower energy levels and damage to blood composition, lungs, kidneys, liver and other vital organs. Presence of metals in water streams and marine water causes a significant health threat to the aquatic community [1-8]. Since heavy metals have toxic effects on the environment and human life, the removal of heavy metal ions from polluted waters is currently one of the more important environmental challenges. Different processes are used in industry to remove these metals from

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aqueous media (e.g., ion exchange, adsorption, reverse osmosis, chemical precipitation, sedimentation, filtration, electro dialysis, etc.). Chemical precipitation is one of the most widely used processes [9]. Successful removal of metal ions from aqueous solutions using nonspecific and specific solid adsorbents has been fully demonstrated [10-14]. Nonspecific adsorbents, such as activated carbon, silica, clays, zeolites, and ion-exchange resins, suffer from inherent problems, such as low removal capacity, low selectivity, long equilibrium time, or mechanical and thermal instability [10-12].

Nowadays, mesoporous silica has received considerable attention because of their unique large surface area, and well-defined pore size and shape [14]. Surfactant molecules are used to form supramolecular assemblies in solution. Metal alkoxides precursors can undergo hydrolytic polymerization around these assemblies. Subsequent surfactant removal results in a solid material having ordered porosity. The pores of the hexagonal ordered adsorbent, MCM41, discovered by Mobil Oil Research scientists, can be engineered with diameters from 15 to 100 Å. These large pore sizes make these materials very attractive for applications such as catalytic supports, sensors, and sorbents.

Applications of mesoporous silica as a heavy metal ion adsorbent have been studied recently [15-19]. In this study, the MCM41 that contains zirconium and iron with different molar ratios was synthesized, characterized, and used as an adsorbent. As is mentioned in most of the literature, for environmental applications, functionalized nanoporous materials are necessary. This is particularly emphasized in the preparation of adsorbents for heavy metals. The functionalization of mesoporous silica has been mostly investigated by using a mercaptopropyl group [15-18, 20]. For instance, a mesoporous silica (MCM41) was functionalized with mercaptopropyl groups and its mercury loading was 2.5 mmol/g [21]. The functionalization of mesoporous silica with an aminopropyl group has also been studied [20-22]. In this work, however, it was attempted to prepare appropriate adsorbents for the removal of Ni and Pb cations from the aqueous solution without any functionalization. It is notable that the application of adsorbents without any functionalization is more feasible and economic. Efficiency in the removal of toxic metals with the adsorption process in the batch mode was investigated under different conditions, including contact time, initial pH of the solution, and initial metal ions concentration. The adsorption capacity of the synthesized adsorbents was evaluated against a number of isotherm models.

2. Experimental

2.1. Materials

The synthesis of ZrFe-MCM41 and Zr-MCM41 materials was carried out by the hydrothermal method using sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$), zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), iron ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), cetyltrimethylammoniumbromide ($\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+\text{Br}$), and sulfuric acid. Standard stock solutions of Ni and Pb were also prepared by dissolving, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ in distilled water. All chemicals were purchased from Merck.

2.2. Synthesis of ZrFe-MCM41 and Zr-MCM41

2.2.1. Synthesis of ZrFe-MCM41

The ZrFe-MCM41 was synthesized using the hydrothermal method. For the synthesis of the ZrFe-MCM41, 2.12 g of sodium metasilicate (44 – 47% SiO_2) dissolved in 50 g of deionised water was mixed with 0.54 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and 0.4 g of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (dissolved in 10 g of deionized water) solution. This mixture was stirred for 30 min using a mechanical stirrer at a speed of about 250 rpm and in order to reduce the pH to 10.8, 1N of sulphuric acid was added with continuous stirring for another 30 min at a speed of about 250 rpm until the gel formation. After that, 9.1 g of cetyltrimethylammonium bromide was added drop by drop through the dual syringe pump so that the gel was changed into suspension. After further stirring for 1h, the resulting synthesis gel of composition 1 SiO_2 :0.015 ZrO_2 :0.015 Fe:0.25 CTMABr:100 H_2O was transferred into a Teflon-lined steel autoclave and heated to 90 °C for 24 h. After cooling to room temperature, the material was recovered by filtration, washed with deionised water and ethanol, and finally calcined in flowing air at 540 °C for 6 h. Two different ZrFe-MCM41 adsorbents (Si/Zr + Fe = 31 and 61) were also synthesized in a similar manner wherein only the ratios of sodium metasilicate, zirconium chloride, and iron were adjusted.

2.2.2. Synthesis of Zr-MCM41

The Zr-MCM41 (Si/Zr = 61) was also synthesized in a similar manner wherein only the ratios of sodium metasilicate and zirconyl chloride were adjusted without iron source and the input in gel molar compositions.

2.3. Characterization

XRD was performed using a Philips X'pert powder diffractometer system with Cu-K α ($\lambda = 1.541 \text{ \AA}$) radiation from 1° (2θ) to 10.0° (2θ). The adsorption isotherm of N_2 at 77 K was determined using a Micromeritic ASAP 2010 instrument. Specific surface area was determined by applying the BET equation to the isotherm. Mesopore size distribution was calculated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda formula [23]. SEM image was taken by JEM-1200 EX with 100 kV acceleration voltages.

2.4. Pb and Ni adsorption on mesoporous silica

Batch processes were employed to study the adsorption of Pb and Ni from aqueous solutions onto the mesoporous silica at 25 °C. Adsorption experiments were repeated three times. In all experiments, standard and blank solutions were prepared and treated in the same way as samples. The uptake of Pb and Ni by the silica was calculated from the difference between the initial amount and that remaining in the eluate.

3. Results and Discussion

3.1. XRD analysis

Figure 1 shows the X-ray powder diffraction patterns of calcined Zr-MCM41 and ZrFe-MCM41 samples having different ratios of Si/Zr + Fe, respectively. The X-ray diffractograms of ZrFe-MCM41 and Zr-MCM41 after calcinations in air at 540 °C for 6 h, contain a sharp d_{100} reflection line in the range $2\theta = 1.79$ to 2.93° and 1.97 to 2.69° , respectively. Physicochemical properties of these mesoporous materials are summarized in Table 1. For example, the pore-to-pore distance of ZrFe-MCM41 could be determined by the XRD patterns. The XRD patterns of calcined ZrFe-MCM41(61) with characteristic peaks of hexagonal symmetry and with d_{100} of 32.8° are shown in Figure 1. The repeating distance (a_0) between pore centers was 3.79° . The hexagonal unit cell parameter (a_0) was calculated using the formula $a_0 = 2d_{100}/\sqrt{3}$ from d_{100} , which was obtained from the peak in the XRD pattern by Bragg's equation ($2d \sin\theta = \lambda$, where $\lambda = 1.541 \text{ \AA}$ for the CuK α line). The value of a_0 was equal to the internal pore diameter plus one pore wall thickness. These peak reflections were indexed based on the hexagonal unit cell as described by Beck et al. [14]. At a large angle of 10 to 60° (Figure 1), no obvious diffraction peaks corresponding to crystalline iron or zirconium oxides could be observed for the calcined sample. Possibly, iron species were introduced into the framework of ordered mesoporous silica or the particle size of iron oxides in the sample was too small to be detected by X-ray diffraction [24].

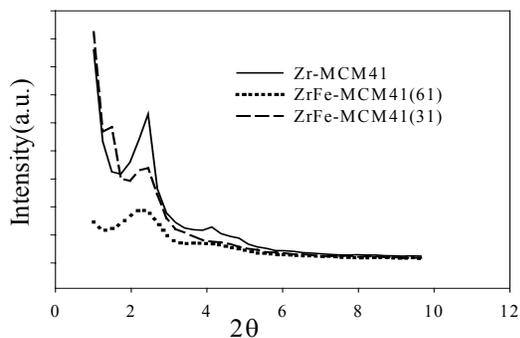


Figure 1. X-ray diffraction patterns of calcined Zr-MCM41 and ZrFe-MCM41 samples.

Table 1. Physicochemical characterization of Zr-MCM41, ZrFe-MCM41(61), and ZrFe-MCM41(31).

| adsorbent | d-spacing (Å) | Unit cell parameter a_0 (Å) | Surface area (m^2/g) | Pore size D (Å) | Pore volume (cm^3/g) |
|----------------|---------------|-------------------------------|----------------------------------------|-----------------|----------------------------------------|
| Zr-MCM41 | 85.698 | 85.92 | 778.63 | 48.4 | 0.942 |
| ZrFe-MCM41(61) | 35.74 | 35.83 | 770.2 | 41.2 | 0.85 |
| ZrFe-MCM41(31) | 41.54 | 41.54 | 768.5 | 39.7 | 0.8 |

3.2. SEM analysis

The SEM image (Figure 2) of this sample suggests that the sample is composed of sphere particles and there is no other structure phase [25].

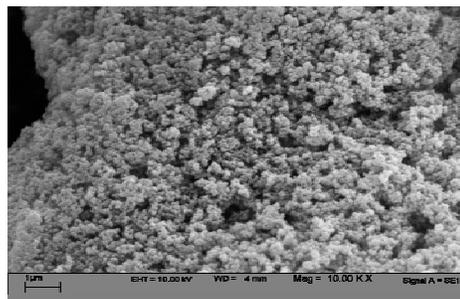


Figure 2. SEM image of ZrFe-MCM41(61).

3.3. Metal ion adsorption

3.3.1. Effect of the initial metal concentration

For investigating the effect of the initial metal concentration a 0.05 g sample of Zr-MCM41, ZrFe-MCM41(61), and ZrFe-MCM41(31) was suspended in 25 ml of Ni or Pb solution with a concentration in the range 50 to 1,000 ppm at pH 7. The mixture was stirred mechanically (300 rpm) for 1.5 h at 25 °C to attain equilibrium. After equilibration, the mixture was filtered through Whatman No. 50 filter paper and the concentration of heavy metal ions remaining in the solution was determined by flame atomic adsorption. Figures 3 and 4 show the percentage of ion removal for a range of Ni and Pb ion concentrations. Ion removal percentage increased when the initial ion concentration decreased. At low ion concentrations, the ratio of surface active site to the total metal ions in the solution was high and hence all metal ions may interact with the adsorbent and be removed from the solution. However, amount of metal adsorbed per unit weight of adsorbent, q , was higher at high concentrations as shown in Figures 5 and 6 [26].

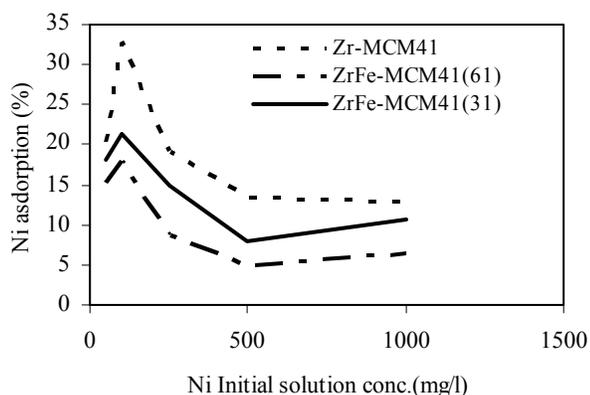


Figure 3. Effect of initial solution concentration on adsorption of Ni onto different mesoporous silicate.

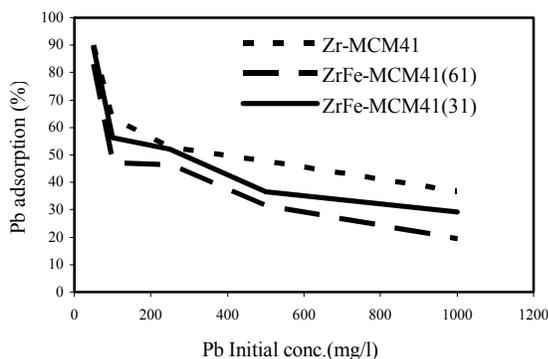


Figure 4. Effect of initial solution concentration on adsorption of Pb onto different mesoporous silicate.

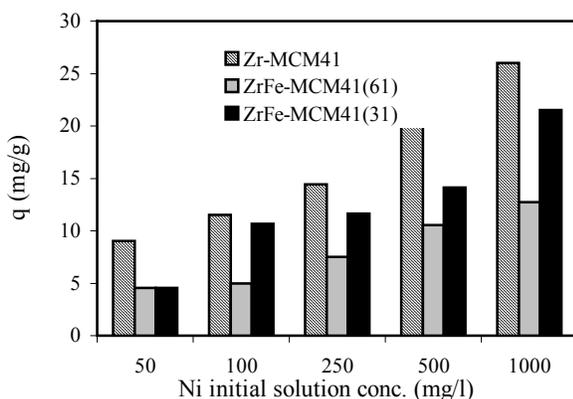


Figure 5. Effect of initial solution concentration on q (mg/g) of Ni onto different mesoporous silicate.

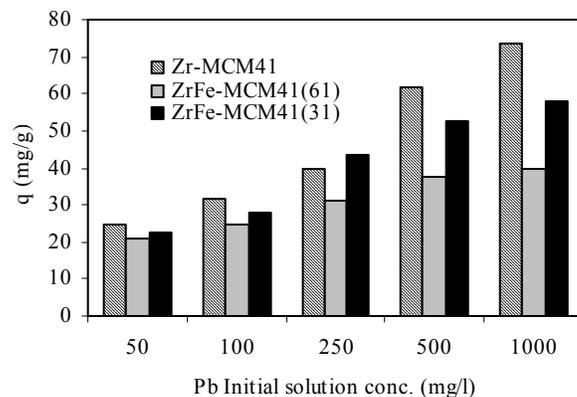


Figure 6. Effect of initial solution concentration on q (mg/g) of Pb onto different mesoporous silicate.

3.3.2. Effect of the stirring time

A 0.05 g sample of Zr-MCM41 and ZrFe-MCM41 was suspended in 25 mL of Ni or Pb solution with a concentration of 100 ppm and the mixture was stirred mechanically (300 rpm) at 25 °C for time periods ranging from 30 min to 5 h. After this time, the mixture was filtered through Whatman No. 50 filter paper and the concentration of heavy metal ions remaining in the solution was determined by flame atomic adsorption. One important characteristic of the prepared material was the velocity to which the solid phase adsorbed Ni and Pb from the aqueous solution and attained equilibrium conditions. Plots of % adsorption versus stirring time (Figure 7) indicated that the adsorption of Ni and Pb quickly increased with time, and shaking for 0.5 h was sufficient to saturate approximately 33.5 and 65% of the Ni and Pb, respectively. The binding rate gradually decreased and became almost constant after an optimum period of 1.5 h. The reasonably fast kinetics of the matrix-metal ion interaction reflects the good accessibility of the chelating sites of the modified matrix and high binding constants of Ni and Pb with the Zr-MCM41 on the silica surface. In addition, these high uptake rates represent significant advances to those reported earlier for other adsorbents [27, 28].

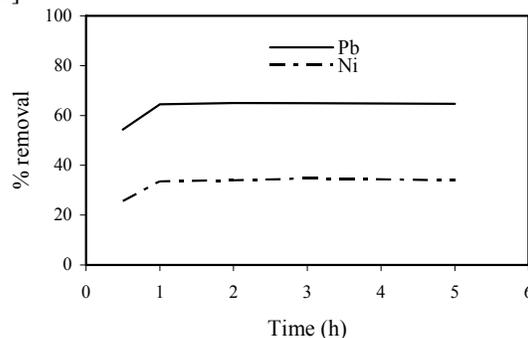


Figure 7. Effect of stirring time on the adsorption of Ni and Pb from aqueous solution onto the Zr-MCM41.

3.3.3. Effect of pH

A 0.05 g sample of either Zr-MCM41 or ZrFe-MCM41 was suspended in 25 mL of Ni or Pb solution with a concentration of 100 ppm at different pH (1.5, 5, 7, 9, or 12), and the mixture was stirred mechanically (300 rpm) for 1.5 h at 25 °C to attain equilibrium. After equilibration, the mixture was filtered through Whatman No. 50 filter paper and the concentration of heavy metal ions remaining in the solution was determined by flame atomic adsorption. The pH of the aqueous solution is an important controlling parameter in the adsorption and ion exchange processes and metal removal typically increases with increasing pH values. Chemically, the solution pH influences metal speciation. For instance, heavy metal ions may form complexes with inorganic ligands such as OH⁻. The extent of the complex formation varies with pH, the ionic composition, and the particular metal concerned [29]. Figure 8 shows percentage of metal ion adsorbed onto the Zr-MCM41 as a function of pH. Ni and Pb adsorption showed maximum removal in the pH range of 6 to 8. At a pH range of 1 to 4 the adsorption was very low and rapidly increased at a pH range of 6 to 8. This phenomenon can be explained by the surface charge of the adsorbent and the H⁺ ions present in the solution. At low pH, the cations competed for the active site with H⁺ ions in the solution and therefore adsorption was lower [30]. Therefore, at high pH values, the surface of the adsorbent had a higher negative charge, resulting in higher attraction of cations. At very high pH values, the metal complex formed and resulted in precipitation; therefore, the separation may not have been due to adsorption [31]. All types of adsorbents showed similar results.

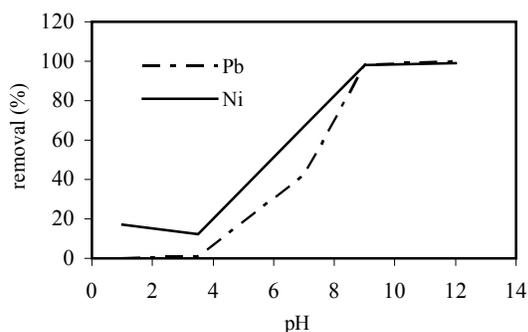


Figure 8. Effect of pH on adsorption of Ni and Pb onto Zr-MCM41.

3.3.4. Adsorption isotherms

Several equilibrium models have been developed to describe adsorption isotherm relationships [26]. The Langmuir model, originally developed for adsorption of

gases onto solids, is based on the assumption that adsorption occurs on localized sites with no interaction between adsorbate molecules, and maximum adsorption occurs when the surface is covered by a monolayer of adsorbate. For solid-liquid systems the linear form of the isotherm can be expressed by equation (1):

$$\frac{1}{q_e} = \frac{1}{bq_0C_e} + \frac{1}{q_0} \quad (1)$$

The Freundlich isotherm model is the empirical model for adsorption and is expressed as:

$$q_e = kC_e^{1/n} \quad (2)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium, q_0 is the amount of solute adsorbed per unit weight of adsorbent corresponding to complete coverage of available sites, C_e is the residual liquid phase concentration at equilibrium, b is the adsorption coefficient, and k and n are the constants related to adsorption capacity and adsorption intensity.

Adsorption isotherms for Ni and Pb (q_e versus C_e) onto the adsorbents are shown in Figures 9 through 11. The experimental data were fitted to both Langmuir and Freundlich isotherms. Pb showed a higher adsorption capacity and affinity compared to Ni. The results discussed so far indicate a higher adsorption of Pb compared to Ni for the experimental conditions under observation. This may be explained by hydration enthalpy, which is the energy that permits the detachment of H₂O molecules from cations and then reflects the easiness for the ion to interact with the functional groups on adsorbent particles. It is notable that the more a cation is hydrated, the stronger its hydration enthalpy and the less it interacts with the adsorbent [32].

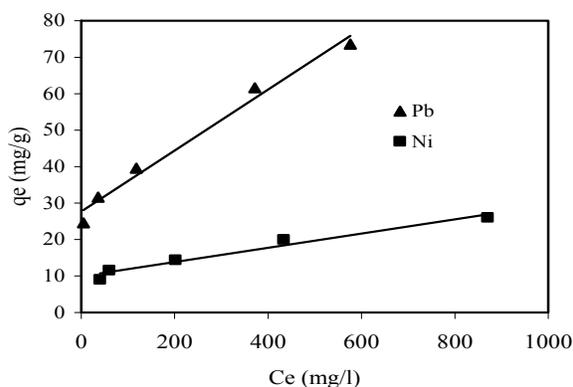


Figure 9. Adsorption isotherms for Ni and Pb on to Zr-MCM41 at 22 °C [eq. (2)].

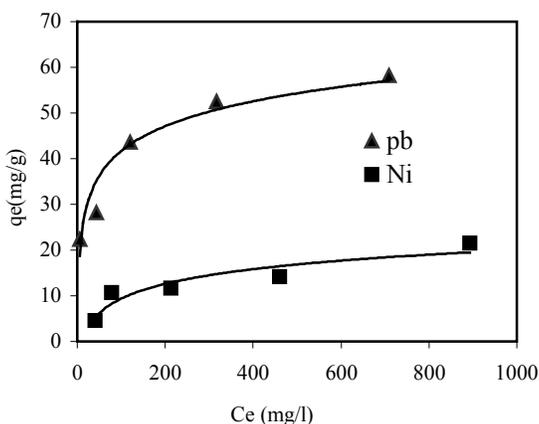


Figure 10. Adsorption isotherms for Ni and Pb onto ZrFe-MCM41(61) at 22 °C [eq. (2)].

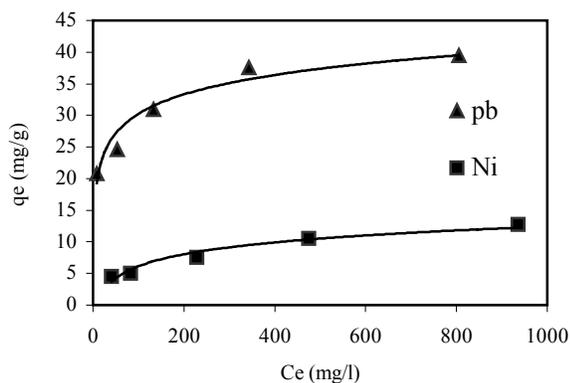


Figure 11. Adsorption isotherms for Ni and Pb onto ZrFe-MCM41(31) at 22 °C [eq. (2)].

4. Conclusions

Mesoporous silicate containing Zr and Fe with different molar ratios were synthesized and have been studied as adsorbents for removal of Ni and Pb ions from aqueous solutions.

The sorption isotherms of Ni and Pb ions onto the three adsorbents are well described by the Langmuir and Freundlich models. The maximum sorption capacity, in decreasing order for Ni and Pb respectively, is as follows: Zr-MCM41: (25.92 – 73.63 mg/g), ZrFe-MCM41(61): (12.75 – 39.01), and ZrFe-MCM41(31): (21.53 – 58.2). Zr-MCM41 is a better adsorbent for removal of Ni and Pb from wastewater than both ZrFe-MCM41; but for Pb showed higher adsorption capacity to Ni. Removal of metal ions was highest around a solution pH of 6 to 8. Adsorption rate and adsorption capacity depended on the adsorbent physicochemical properties, solution

concentration, and pH. Zr-MCM41 with more surface area (Table 1) showed better results for both cations. In this study, synthesized mesoporous silica without any functionalization was used as an adsorbent, and the results introduce these adsorbents as promising and economical.

5. References

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