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Characterization of Alginate/Perlite Particles

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Abstract: In this study alginate/perlite composite particles obtained by ionic gelation method were characterized and their usability on the removal of Pb (II) and Ni (II) ions from aqueous solutions was tested. The effects of pH, contact time, initial metal ion level and perlite concentration on the adsorption capacity of particles were investigated in a batch system. Desorption of tested heavy metal ions from particles and reusability of particles were also investigated. Optical microscopy analysis showed that diameters of wet and dried particles were between 2.5-2.8 mm and 1.8-1.9 mm, respectively. Incorporation of perlite decreased the swelling degree of the particles. SEM and SEM-EDX analysis indicated that perlite appeared as thin plates and mainly composed of silica. SEM-EDX also indicated that alginate/perlite particles were composed of C, O, Na, Al, Si, and K. XRD analysis indicated that perlite had amorphous structure and distributed in the alginate matrix. According to TGA analysis, perlite improved the thermal properties of particles. The optimum pH value varied between 6 and 7 for the removal of Pb (II) and Ni (II). The adsorption efficiency of particles reached maximum level while the perlite/alginate (wt. /wt.) ratio was 2.

Aljinat/Perlit Parçacıkların Karakterizasyonu

Anahtar Kelimeler
Aljinat,
Perlit,
Kurşun,
Nikel,
Adsorpsiyon

Özet: Bu çalışmada iyonik jelasyon yöntemi kullanılarak elde edilen aljinat/perlit kompozit parçacıkların karaterizasyonu ve sulu çözeltiden Pb (II) ve Ni (II) iyonlarının uzaklaştırılmasında kullanılabilirliği test edilmiştir. Parçacıkların adsorpsiyon kapasitesine çözeltinin pH'nın, çalkalama süresinin, başlangıç metal iyon miktarının ve perlit konsantrasyonunun etkisi kesiklik sistemde araştırılmıştır. Test edilen ağır metal iyonlarının parçacıklardan desorpsiyonu ve yeniden kullanılabilirliği de araştırılmıştır. Optik mikroskop analizi ıslak ve kuru parçacıkların çaplarını sırasıyla 2.5-2.8 mm ve 1.8-1.9 mm olduğunu göstermiştir. Perlit eklenmesi parçacıkların şişme değerlerini azaltmıştır. SEM ve SEM-EDX analizi perlitin plaka şeklinde olduğunu ve ağırlıklı olarak silikadan oluştuğunu göstermiştir. SEM-EDX analizi ayrıca aljinat/perlit parçacıkların C, O, Na, Al, Si, ve K içerdiğini belirtmiştir. XRD analizi perlitin amorf karakterde olduğunu ve aljinat içerisinde dağıldığını göstermiştir. TGA analizi perlitin parçacıkların termal özelliklerini geliştirdiğini ortaya koymuştur. Parçacıklar tarafından Pb (II) ve Ni (II) giderimi için optimum pH değeri 6 ila 7 arasında değişmektedir. Ağırlıkça perlit/aljinat oranı 2 olduğunda parçacıkların adsorpsiyon verimi maksimuma ulaşmıştır.

1. Introduction

Heavy metal ions can accumulate in living tissues and this may lead to several diseases and disorders due to their toxic nature. Thus, water pollution by these ions is an important topic for many years. [1,2]. Several techniques including ion-exchange, reverse osmosis, co-precipitation and membrane filtration have been proposed to remove metal ions from water [1,2]. However, these methods are incapable of removing heavy metal ions mainly at trace level concentrations. In addition, they are costly and can have a role in the formation of toxic sludge or other waste products [3]. Therefore, there is a need to develop effective, inexpensive and safe technologies that can be utilized in water purification [4].

Adsorption is considered as an effective method for the removal of heavy metal ions from aqueous solution. In recent years, many types of bacteria, plants and biopolymers have been used as low cost natural adsorbents to remove heavy metal ions.[5-8]. Among various bio sorbents, alginate is an interesting natural polymer in the removal of heavy metal ions

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*Corresponding author: hasanture@odu.edu.tr due to its low price and efficient adsorption capacity. [9,10]. The particles or microspheres obtained from alginate have been tested for removing heavy metal ions from aqueous solutions [11].

Although alginate particles have high adsorption capability, their weak mechanical integrity, chemical instability and thermal properties limit their applications in industrial processes [12]. These drawbacks can be overcome by chemical modifications using chemical cross-linkers such as glutaraldehyde and epichlorohydrine [11,13]. On the other hand, these chemicals are not commonly preferred due to their hazardous effects. There has been great interest in the preparation of polymer composites to enhance their durability, chemical stability and increase the adsorption capacities of bio based polymer particles [14-16]. Several studies have tested the use of various fillers to obtain composite particles [17,18]. Among the fillers used, particular attention can be given to perlite because of its high porosity, large surface area, abundance and low cost [19,20]. It has been reported that perlite is an ideal adsorbent to remove dyes and metal ions [21]. This is, to our knowledge, the first study where sodium alginate/perlite composite particles have been prepared as bio sorbents to remove metal ions from aqueous solutions.

In this work, alginate/perlite composite particles have been synthesized with ionic-gelation method, and then characterized with optical microscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD). Their thermal stabilities and swelling properties in water were also investigated. Pb (II) and Ni (II) ions, which are discharged from several industries, were selected to examine the adsorption capacity of particles. Batch adsorption experiment was carried out as functions of pH, initial metal ions levels, contact time and varying perlite level. Reusability of particles was studied as well.

2. Material and Method

2.1. Materials

The expanded perlite (P) was kindly supplied by Siteper, Ordu, Turkey. Sodium alginate (SA) was purchased from Sigma Aldrich, Germany. Calcium chloride ($CaCl_2$), $Pb(NO_3)_2$ (≥99.5% trace metal basis), $NiSO_4.6H_2O$ (≥99.5% trace metal basis), NaOH (95-100%) and HCl (35% content) were obtained from Tekkim, Turkey. The Pb (II) and Ni (II) solution (1000 mg/L) were prepared using deionized water and used as stock solution.

2.2. Preparation of alginate/perlite particles

For the preparation of alginate/perlite composite particles, sodium alginate was first dissolved in deionized water at a concentration of 1% (w/v) using a magnetic stirrer. Different mass ratio of perlite (perlite:alginate =1, 2, 3, 4, 5 wt./wt.) was then added to the solution and the mixture was stirred at 2000 rpm for 20 min. using a homogenizer (WVR VDI25, Germany). Obtained solution was then dropped using pipette tip (1 mL) into 100 ml $CaCl_2$ solution (20%, w/v). Particles were incubated at $CaCl_2$ bath for 24 hours and then rinsed with deionized water and finally dried at room temperature. Samples were denoted with respect to their perlite content, P1/SA is the particle with a weight ratio of Perlite:SA =1

2.3. Optical microscopy

Particles were examined with an optical microscope equipped with a digital camera (Nikon SMZ 800, Japan). Mean diameters were calculated using an image analysis software (Nikon NIS Elements 4.5, Japan).

2.4. Swelling study

The dried particles were weighted and then put into petri dishes containing 50 mL of deionized water, in order to observe the swelling capacity of particles. Particles were kept in water at room temperature for 0, 1, 3, 6, 24 and 48 hours and then removed from water and weighted again.

$$\text{Swelling capacity (S)} = \frac{(Ws - Wo)}{Wo} x\ 100 \quad (1)$$

in which, Wo is the weight of dry particles (after a 12 hours dry at room temperature) and Ws is the weight of particles exposed to deionized water (50 mL).

2.5. Thermogravimetric analysis (TGA)

The thermogravimetric analysis were performed in a Perkin Elmer Diomand TG/DTA by heating approximately 5 mg of the samples in 70 µl open alumina pans from 25 °C to 800 °C at a heating rate of 10 °C min^{-1} in N_2.

2.6. X-ray diffraction (XRD)

X-ray analysis was carried out with ƛ=1.54 Å. The scans were made in the reflection mode from 2 to 80°.

2.7. Scanning electron microscopy (SEM)

Particles were scanned with SEM (Phillips XL-30S FEG, Holland). Before insertion into SEM, particles were coated with gold (100 - 200 Å) thickness. Elemental analysis of the particles was evaluated with SEM equipped with Energy-Dispersive X-ray (EDAX).

2.8. Batch studies

Sorption experiment was performed to examine the adsorption of Pb (II) and Ni (II) from aqueous solution. All tests were conducted under agitation on mechanical shaker (WiseCube WIS-20, Korea) at 150 rpm by addition of 25.0 ±2.0 mg particles to 25 mL of metal ion solution at 30.0±2.0 °C. The initial pH of the solution was adjusted using 0.1 M HCl or NaOH solutions. After shaking, samples were filtered and then used for analyzing Pb (II) and Ni (II) level using Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) (Bruker 820-MS, USA). The adsorption of metal ions on particles was done at different time intervals (0–240 min), initial pH solution (2.0–9.0), initial Pb (II) and Ni (II) level (5.0–300 mg/L) and the perlite content in 25 mL aqueous solution.

The amount adsorbed per unit mass of adsorbent at equilibrium. qe (mg/g) was determined.

$$qe = \frac{(Co - Ce)}{m} x\, V \qquad (2)$$

where C_0 and C_e (mg/L) are the initial and equilibrium metal ion level (mg/L), respectively. “V” is the volume of the solution in liter and “m” is the mass of the particles (g).

2.9. Desorption studies

For desorption studies, 25.0 ±2.0 mg particles were contacted with Pb (II) and Ni (II) utilizing 25 mL (25 mg/L) metal ion solution under optimum conditions. The particles were then shaken with 25 ml of 0.1M HCl solutions for roughly 30 min. The final concentration of the metal ions in the medium was determined by ICP. The desorption ratio of Pb(II) and Ni (II) ions from particles was calculated from the amount of ions adsorbed on particles and the final level of metal ions in the desorption medium. To test the reusability of the samples this process was repeated for three times.

3. Results and Discussions

3.1. Optical microscopy

The diameters of alginate particles were given in Table 1. Diameters of wet and dried particles were found between 2.5-2.8 mm and 1.8-1.9 mm, respectively. Ely et al. [12] synthesized the sodium alginate microcapsules by ionic gelation method using pipette tip. They calculated the diameters of wet and dry alginate microcapsules containing sodium montmorillonite (montmorillonite/sodium alginate=1) as 2.92 mm and 0.99 mm, respectively. On the other hand, calculated diameters of neat wet and dry alginate microcapsules was found as 2.92 mm and 1 mm, respectively. In a study conducted by Lagoa and Rodrigues [22], mean diameters of alginate gel and dry particles were calculated as 3.0 mm and 1.2 mm, respectively. Particles were removed from $CaCl_2$ solution and excess water was removed by filter paper. Then, the geometries of the particles were observed with an optical microscopy. (Figure 1.).

Table 1. Diameters of wet and dry particles (mm)

Sample	wet particles	dry particles
SA	2.6±0.2	1.8±0.3
P1/SA	2.6±0.2	1.9±0.1
P2/SA	2.8±0.3	1.8±0.3
P3/SA	2.5±0.3	1.9±0.2
P4/SA	2.6±0.1	1.8±0.2
P5/SA	2.8±0.2	1.9±0.1

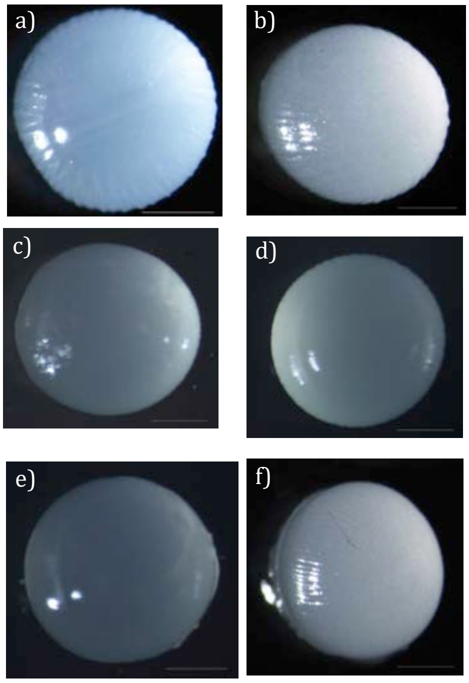


Figure 1. Optical microscopy of particles a) SA, b) P1/SA, c) P2/SA, d) P3/SA, e) P4/SA, f) P5/SA. The scale bar is 1 mm.

3.2. Swelling test of particles

Adding perlite dramatically changed swelling capacity of the samples. Figure 2. shows the swelling ratios of alginate and alginate/perlite composite particles. As seen in Figure 2, swelling degree of alginate and alginate/perlite composite particles increased in the first 10 hours and reached equilibrium after 24 hours. The results revealed that swelling capacity of particles decreased by adding perlite. This behavior can be attributed to the decreases in the ratio of hydrophilic groups on alginate and increases in the cross-linking density of particles through the interaction between perlite and alginate polymeric chains. [23]

In a study performed by Yan et al. [24], the composite microspheres composed of sodium alginate -chitosan -bentonite were synthesized by ionic gelation method and swelling behavior of these synthesized microspheres were investigated. Swelling of microspheres increased rapidly in about 12 hours. Adding chitosan and bentonite decreased swelling ratios by 44% and 40%, respectively. At the end of 50 hours, the swelling degree of samples were ordered as alginate>alginate+chitosan>alginate+bentonite> alginate+bentonite+chitosan.

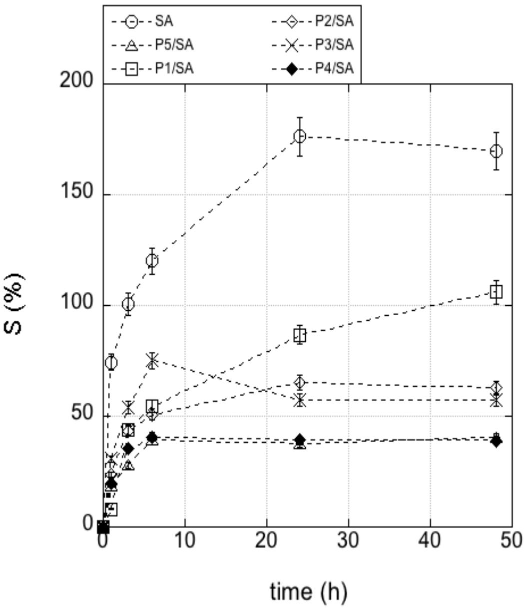
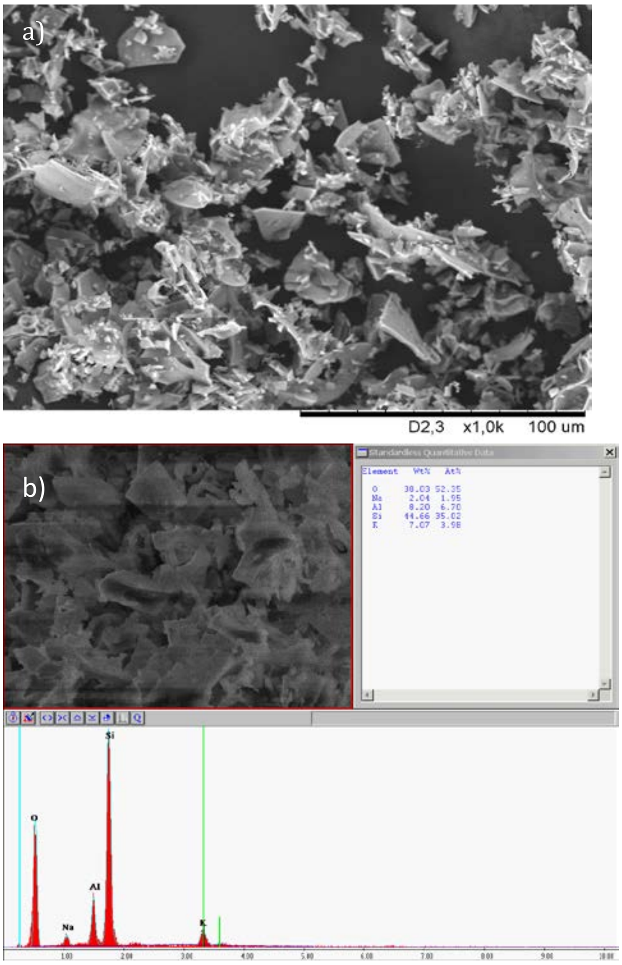


Figure 2. Swelling degree of alginate and alginate/perlite composite particles

3.3. SEM and SEM-EDX analysis

Figure 3. illustrates the SEM images of dry alginate and alginate-perlite containing particles. It can be seen from Figure 3a that pure alginate particles represent smooth surface with some scratches. The rough surface shown in Figure b-f demonstrated that perlite mineral was entrapped in the alginate polymer. The roughness of the surface of the particles may be an important criterion for the adsorption of heavy metal ions since it increases the surface area. SEM analysis also indicated that particles were not perfectly spherical in shape after drying at room temperature. According to the SEM analysis, the mineral perlite was observed in plate form (Figure 4a). SEM-EDX analysis showed that perlite composed of ; O (38.03%, wt./wt.), Na (2.04%, wt./wt.), Al (8.20%, wt./wt.), Si (44.66%, wt./wt.) and K (7.07%, wt./wt.) (Figure 4b).

Celik et al. [25], examined the elemental composition of the expanded perlite by energy disperse spectroscopy (EDS) and reported that the perlite mineral consisted of 38.91% oxygen, 2.37% sodium, 8% aluminum, 45.13% silicon and 5.58% potassium, which supports the results of this study. When the cross-section of alginate/perlite (P1/SA) particles was examined, it was seen that the perlite mineral in plate form was embedded in alginate polymer (Figure. 5a). SEM-EDX analysis showed that P1/SA particles composed of; C (41.93%, wt./wt.), O (43.64%, wt./wt.), Na (10.20%,wt./wt.), Al (0.74%, wt./wt.), Si (2.72%, wt./wt.) and K (0.77%, wt./wt.).(Figure. 5b)



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Element   Wt%   At%

  O      38.03 52.35
  Na      2.04  1.95
  Al      8.20  6.70
  Si     44.66 35.02
  K       7.07  3.98
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Figure 3. a) SEM of perlite b) Elemental analysis of perlite by SEM-EDX

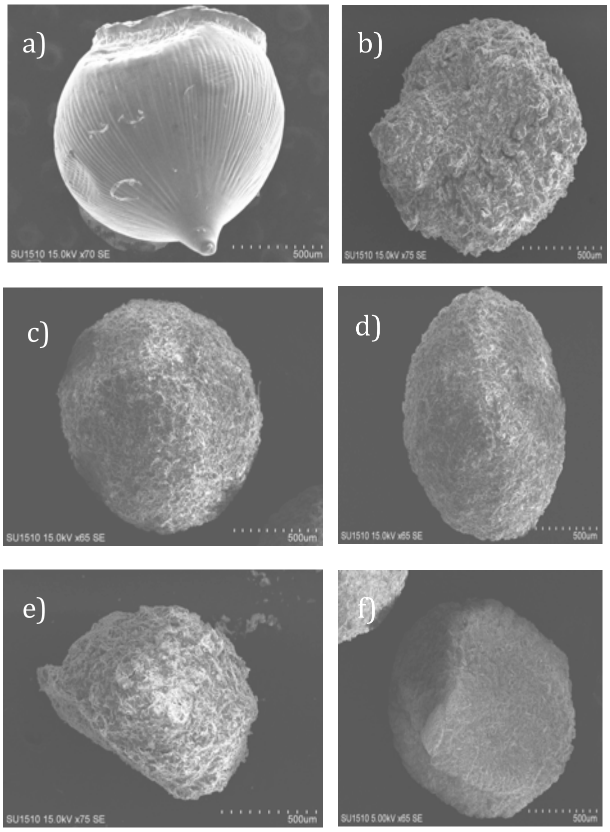
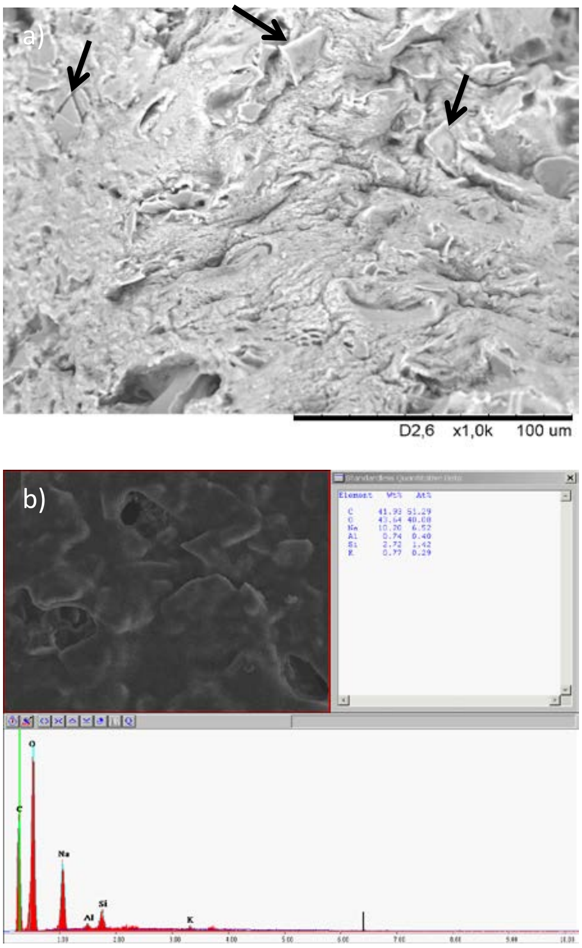


Figure 4. SEM of particles a) SA, b) P1/SA, c) P2/SA, d) P3/SA, e) P4/SA, f) P5/SA.



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Element   Wt%   At%

  C     41.93 51.29
  O     43.64 40.08
  Na    10.20  6.52
  Al     0.74  0.40
  Si     2.72  1.42
  K      0.77  0.29
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Figure 5. a) cross-section of P1/SA b) elemental analysis (P1/SA) particles. The arrows on picture indicate perlite.

Elemental compositions of particles were obtained by SEM-EDX analysis and the values were given in Table 2. As can be seen in Table 2, Si is the main components of perlite and as the perlite level increased the Si content in the particles increased. Thus, EDX analysis confirmed existence of perlite in the alginate particles. The results reveal that composite particles contain SiO_2 that derived from perlite. Rahim et al. [26] characterized the calcium alginate beads containing kaolinite, which has molecular structure similar to perlite. EDX analysis indicated that beads composed of 13.97% C, 43.69% O, 28.96% Ca, 6.46% Al and 6.91% Si and EDX spectra confirmed the existence of clay elements in the beads.

3.4. XRD analysis

XRD patterns of the particles containing perlite, alginate and alginate/perlite were shown in Figure 6. In Figure 6, it is seen that alginate particles have amorphous characteristic. Also perlite has amorphous characteristic and contains mostly silicon or crystal phases (quartz and anorthite (An)) bearing silicon-aluminum [27]. The XRD patterns of alginate particles containing different amounts of perlite are very similar, except slight differences in the intensities.

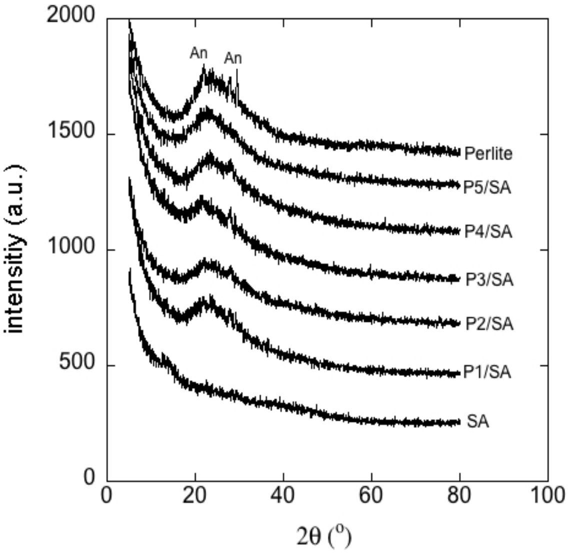

Figure 6. XRD patterns of particles containing perlite granular, alginate and alginate/perlite

3.5. TGA analysis

The TGA thermographs of perlite, alginate and alginate/perlite containing particles were shown in Figure 7. When thermal behaviors of alginate particles were examined; the weight lost below 200 °C was because of the removal of free/bounded water. The weight lost occurring between 200-500 °C was due to the depolymerization of alginate biopolymer. The weight lost above 500 °C was due to the degradation of Na_2CO_3 [12,28]. The incorporation of perlite into alginate particles led to changes at these temperatures. The temperature corresponding to the maximum rate of weight loss (T_m) for SA was 248.2 °C, while it was 300.2 °C for P1 and P2. The T_m for P3, P4 and P5 particles was approximately 250 °C, which are slightly higher than neat alginate particles. Adding of the perlite into alginate enhanced the thermal decomposition temperatures. The differences could be due to the fact that at low concentrations perlite is distributed more homogeneously in alginate matrix. The role of perlite can be attributed to its barrier effect, which hinders the diffusion of the volatile decomposition product. [29]. It should also be mentioned that the residual content at 800 °C increased with increasing levels of perlite.

3.6. Adsorption of Pb (II) and Ni (II) ions

3.6.1. Effect of pH

The adsorption of Pb (II) and Ni (II) ions was investigated in the pH range of 2-9. As the pH increased, the amount of Pb (II) adsorbed onto the particles increased and reached a maximum at pH=7 and then decreased. (Figure. 8) The amount of Pb (II) adsorbed onto the SA, P1/SA, P2/SA, P3/SA, P4/SA and P5/SA at pH=7 was 16.9, 17.8, 18.8, 16.3, 15.4 and 15.1 mg/g, respectively.

Table 2. Elemental composition of perlite, alginate and alginate containing perlite

Sample	O (wt.%)	Na (wt.%)	Al (wt.%)	C (wt.%)	K (wt.%)	Si (wt.%)
Perlite	38.03	2.04	8.2	-	7.07	44.66
SA	42.83	14.29	-	42.88	-	-
P1/SA	43.64	10.2	0.74	41.93	0.77	2.72
P2/SA	36.8	2.82	3.65	46.23	3.3	7.25
P3/SA	45.24	4.01	5.2	28.41	5.01	12.2
P4/SA	48.47	4.22	5.25	23.54	4.96	13.55
P5/SA	55.98	3.07	4.91	16.05	3.53	16.49

The effect of pH value on Ni (II) adsorption potential of synthesized particles was demonstrated in Figure. 9. At pH=6, at which heavy metal removal was maximum, the amount of Ni (II) adsorbed on the SA, P1/SA, P2/SA, P3/SA, P4/SA and P5/SA was 12.7, 18.3, 20.2, 19.3, 18.9 and 18.0 mg/g, respectively. Tirtom et al. [3] pointed out that the maximum pH value, at which Ni (II) ion was adsorbed by epichlorohydrine cross-linked with chitosan clay composite particles, was 6. In a study [30], it was stated that the most suitable pH value was 7 for the best Ni (II) adsorption efficiency by bentonite containing composite alginate particles.

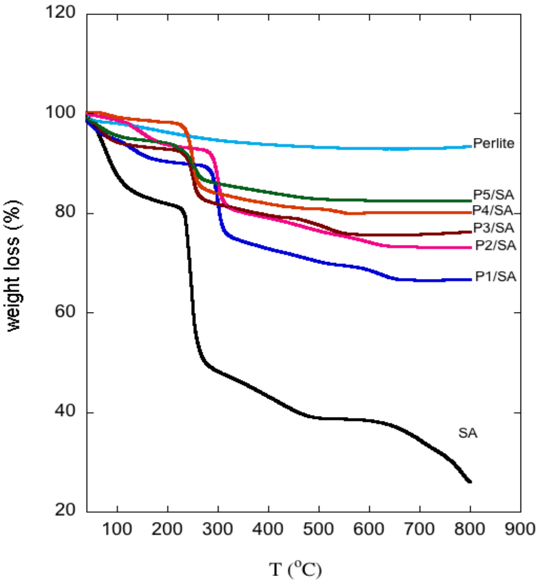

Figure 7. The TGA thermographs of perlite, alginate and alginate/perlite containing particles

The reasons for the variety of affinity between heavy metal ions and samples are; the distinct ionic dimensions of metals, distribution of functional carboxyl groups [4] in alginate molecule and difference in interactivity between metal ions and bio-sorbent [31]. The results revealed that Pb (II) and Ni (II) removal were low at lower pH. This is because at low pH, carboxyl groups of alginate are occupied by hydrogen ions, where Pb (II) and Ni (II) ions cannot easily bound to available binding sites [14]. In addition, at lower pH electrostatic repulsion could occur between positively charged surface sites of particles and metal ions, leading to low adsorption. As the pH increased, the adsorption capacity of particles increased until it reached the maximum value. This could be assigned to the presence of electrostatic attraction between negatively charged active sites and positively charged metal ions. [1]. At high pH values, the uptake capacity of particles decreased. This can be attributed to formation of insoluble Pb (II) and Ni (II) hydroxide. [14].

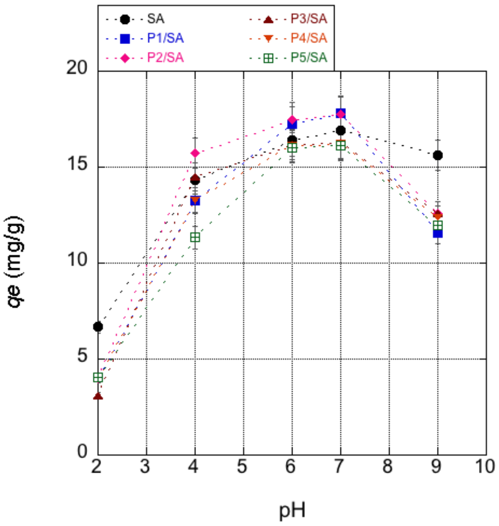

Figure 8. Effect of pH on the adsorption capacity of particles for Pb (II) (initial metal ion concentration=25 mg/l, V=25 ml, m=25±2 mg, T=30 ^{o}C, mixing time=3 h, mixing speed=150 rpm)

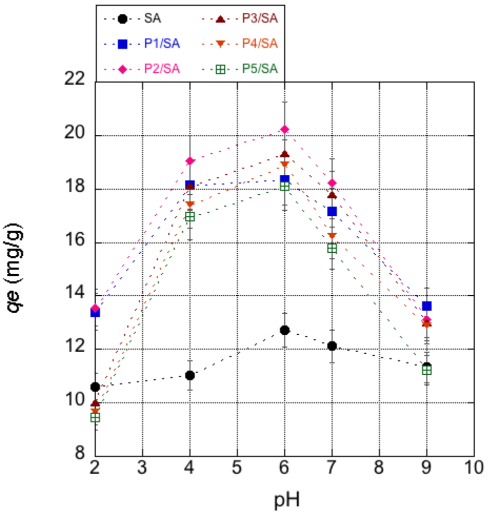

Figure 9. Effect of pH on the adsorption capacity of particles for Ni (II) (initial metal ion concentration=25 mg/l, V=25 ml, m=25±2 mg, T=30 ^{o}C, mixing time=3 h, mixing speed=150 rpm)

3.6.2. Effect of initial concentration of metal ions

The amount of Pb and Ni (II) adsorbed by alginate based particles in tested initial metal ion level were shown in Figure 10 and 11. As seen in Figure 10 and 11, when the initial concentration of metal ions increased, the amount of Pb (II) and Ni (II) ions adsorbed on particles also increased. At pH=4, in 300 mg/l initial metal ion concentration, the adsorption of Pb (II) ions by SA, P1/SA, P2/SA, P3/SA, P4/SA and P5/SA was found as 70.4, 75.5, 79.8, 78.9, 77.8 and 75.0 mg/g, respectively. Under the same tested condition, the amount of Ni (II) ions adsorbed on SA, P1/SA, P2/SA, P3/SA, P4/SA and P5/SA were 228.7, 227.9, 247.2, 249.8, 246.2 and 245.0 mg/g, respectively. Oladipo and Gazi [30] also obtained the amount of adsorbed Ni (II) ions as 285.5mg/L using composite bentonite/alginate particles in a 300 mg/L initial metal ion concentration. The results indicated that Ni (II) ions showed higher affinity than Pb (II) ions for the tested particles. This can be related to the differences in the ionic radius of lead (1.19 A°) and nickel ions (0.72 A°). When the ionic radius is large, quick saturation of adsorption site can occur due to steric overcrowding, thus, the surface available for Ni (II) is larger than that of Pb (II) [32]. Similar observation was reported by Li et al. [1], when they studied the removal of Cu (II), Pb (II), Cd (II) and Zn (II) ions by poly (vinyl alcohol)/chitosan beads. They reported that Cu (II) ions exhibited strong affinity for beads because Cu (II) ions has smaller ionic radius than other metal ions. It should also be mentioned that adsorption capacity of alginate particles was affected by addition of perlite. The results reveal that the amount of adsorbed metal ions not only depend on metal ion properties but also depend on some properties of adsorbents such as distribution of functional groups, surface area and pore diameter [32].

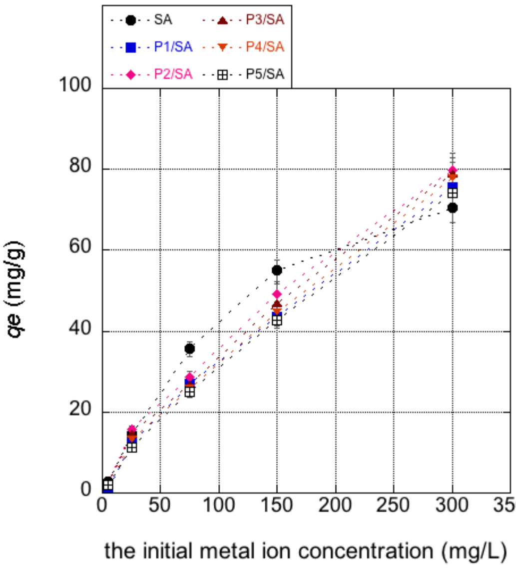

Figure 10. Effect of initial metal ion concentration on the adsorption capacity of particles for Pb (II) (pH=4, V=25 ml, m=25±2 mg, T=30 °C, mixing time=3 h, mixing speed=150 rpm)

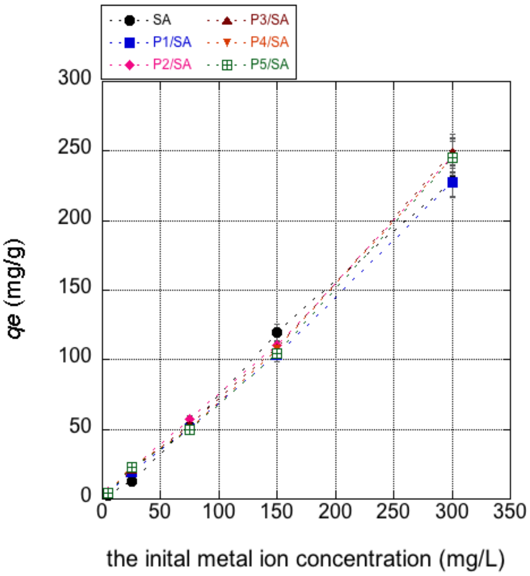

Figure 11. Effect of initial metal ion concentration on the adsorption capacity of particles for Ni (II) (pH=4, V=25 ml, m=25±2 mg, T=30 °C, mixing time=3 h, mixing speed=150 rpm)

3.6.3. Effect of contact time

The effect of this parameter was examined in 25 mg/L initial metal concentration at pH=4, T=30 °C with 25 ml metal ion solution and 25±2 mg adsorbent at 150 rpm. These parameter values were determined with conducted preliminary studies. In the beginning of the experiment, the mixing rate had been decided to 100 rpm but it was seen that this rate was not sufficient enough for an effective mixing and decided to be 150 rpm. The experiments were planned to be conducted at room temperature but when temperature in incubator was measured it was marked as 30 °C. Due to precipitation limit of lead (pH> 5) and nickel (pH> 6), the experiments were performed at pH=4. [2,32]. The tested adsorbent amount, contact time, initial metal ion level and solution volume were chosen similar to the values of other studies in the literature in order to compare the obtained results effectively [2]. The effect of contact time on the kinetics of Pb (II) adsorption by alginate particles was shown in Figure. 12. The amount of adsorbed Pb (II) ions rapidly increased in first 60 minutes. After 180 min, particles reached steady-state position. The rapid adsorption at the beginning can be explained by numerous number of available adsorption bounding regions on particles [30]. By the end of 240 minutes, the amount of adsorbed Pb (II) ions for SA, P1/SA, P2/SA, P3/SA, P4/SA and P5/SA was found as 13.0, 13.0, 15.7, 14.5, 13.3 and 11.3 mg/g, respectively. Figure 13. shows the effect of contact time on the kinetics of Ni (II) adsorption by alginate particles. An increment observed in Ni (II) adsorption by particles between 120-180 minutes and the adsorbed amount of Ni (II) reached equilibrium by the end of 180 minutes. At the end of 240 min. the amount of Ni (II) ions adsorbed by SA, P1/SA, P2/SA, P3/SA, P4/SA and P5/SA was found as

12.8, 18.3, 19.0, 18.1, 17.4 and 16.9 mg/g respectively.

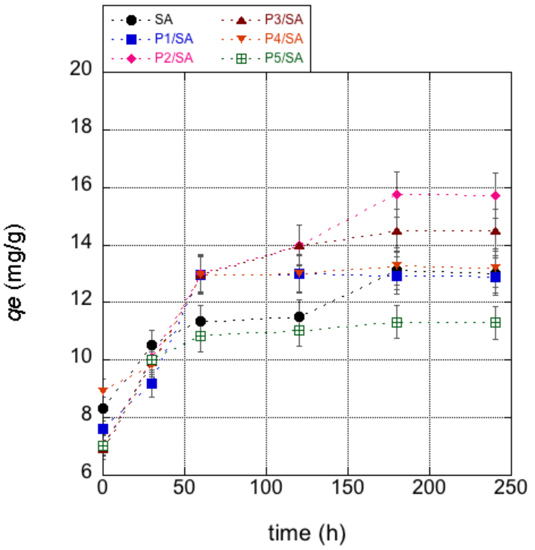

Figure 12. Effect of contact time on the adsorption capacity of particles for Pb (II) (pH=4, initial metal ion concentration=25 mg/l, V=25 ml, m=25±2 mg, T=30 °C, mixing speed=150 rpm)

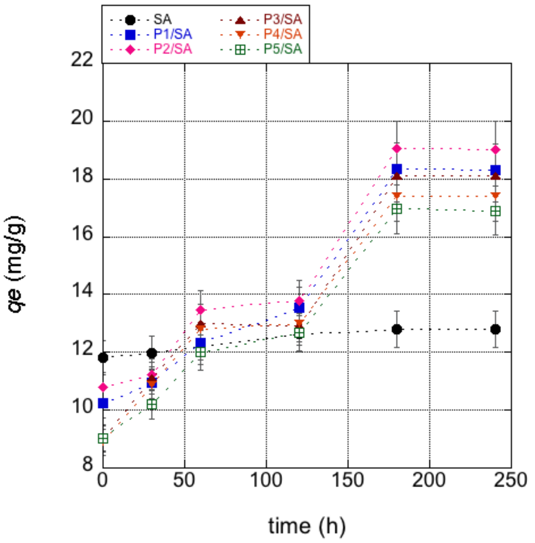

Figure 13. Effect of contact time on the adsorption capacity of particles for Ni (II) (pH=4, initial metal ion concentration=25 mg/l, V=25 ml, m=25±2 mg, T=30 °C, mixing speed=150 rpm)

3.6.4. Effect of various alginate-perlite ratios

Figure.14 demonstrates the effect of perlite ratio on the adsorption capacity of particles. Under test conditions, the adsorption efficiency of particles was maximum when the ratio perlite/alginate was 2. However, when perlite amount in alginate particles increased, there were decreases observed in adsorption efficiency of particles. Ely et al.[12] investigated the effects of sodium montmorillonite (Na-mont) ratio on cupper ion adsorption capacity of sodium alginate (SA) particles. It was stated that as sodium montmorillonite ratio in alginate particles increased, the adsorption capacity of particles decreased. The adsorption capacity of tested particles was found as; SA > Na-mont/SA (1/1) > Na-mont/SA (2/1) > Na-mont/SA (4/1) >Na-mont. In a similar study, effects of Na-mont amount on Pb (II) ion adsorption capacity of alginate particles was examined and it was reported that as Na-mont percentage (10%-90%) increased in particles, Pb (II) ion adsorption capacity of particles decreased from 246.4 mg/g to 63.4 mg/g [17]. Increment in efficiency of metal ion adsorption capacity of particles by adding low amount of perlite can be explained by metal ion adsorption capacity of perlite mineral [21,34,35]. On the other hand, adding higher amount of perlite decreased adsorption efficiency of particles. This could be due to the fact that perlite cover or fill the pores on alginate particles, thus eliminating the possible metal ion binding sites [36].

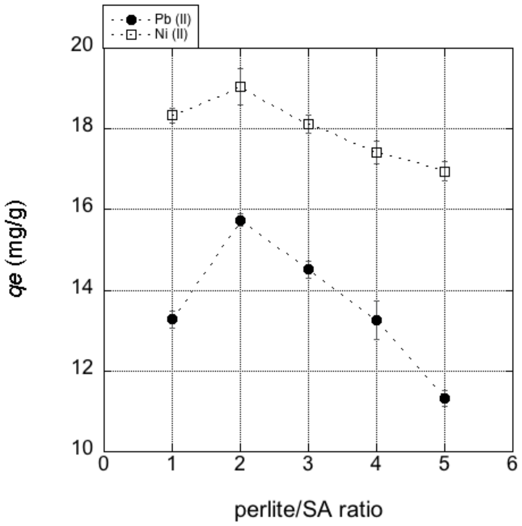

Figure 14. Effect of perlite concentration on adsorption capacity of particles for Pb (II) ve Ni (II) (pH=4, V=25 ml, m=25±2 mg, T=30°C, initial metal ion concentration=25 mg/l, mixing time=3 h, mixing speed=150 rpm)

3.7. Desorption and reuse

The desorption ratios of Pb (II) and Ni (II) ions from the particles were shown in Figure 15 and 16, respectively. Using 0.1 m HCL, approximately 30% and 40% of adsorbed Pb (II) and Ni (II) can be desorbed from particles, respectively. Pandey et al. [31] tested EDTA, NaOH and H_2SO_4 agents for desorption of Pb (II) ions from calcium alginate particles after three repetition of desorption cycle. They reported 0.1M EDTA was found to be the most suitable desorption agent and approximately 35% efficiency was observed within 60 minutes at pH =2. Tirtom et al. [3] used epichlorohydrin cross-linked chitosan/bentonite composite particles to remove Ni (II) ions from water and they stated that 0.01M EDTA was the most effective desorption agent with 86.50% efficiency. Li et al. [1] reported that for the desorption of Pb (II) from poly (vinyl alcohol)/chitosan beads, the best performance was obtained using 0.1 M HCl with desorption value of 96.7%. It could be concluded that desorption of heavy metal ions from particles is affected by the type of desorption agent used, contact time and pH. In order to test reusability and stability of the particles, adsorption-desorption processes were repeated three times using same particles. The adsorption ratios of Pb (II) and Ni (II) ions from the particles were shown in Figure 17 and 18, respectively. While no significant changes were adsorbed in the adsorption capacities of SA, P2/SA, P3/SA, P4/SA and P5/SA for the Pb (II) ions at the end of three adsoption-desoption cycle, approximately 5% decrease was observed in adsorption capacity of P1/SA. In contrast to this study, Pandey et al. [37] revealed that the adsorption capacity of calcium alginate particles decreased by 14% for Pb(II) ions after three consecutive cycles. When Ni (II) ions were taken into account, no significant change was observed in adsorption capacities of P1/SA, P2/SA, P3/SA, P4/SA and P5/SA. However, adsorption capacity of SA increased (~%2.7) at the end of three cycle. It could be concluded that adsorption capacity of the tested adsorbents may be affected by the formation of anionic complexes between the Cl- and Pb (II) and Ni (II) ions [4].

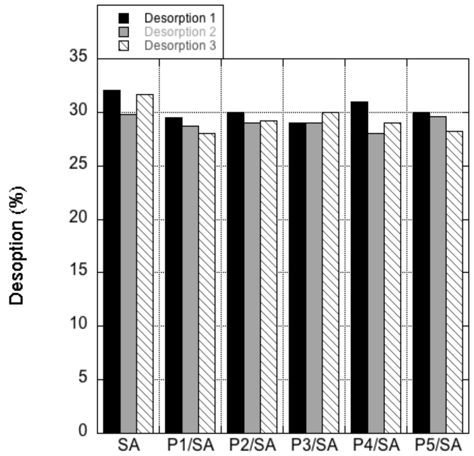

Figure 15. Desorption ratio of Pb (II) ions after 3 repeated cycle

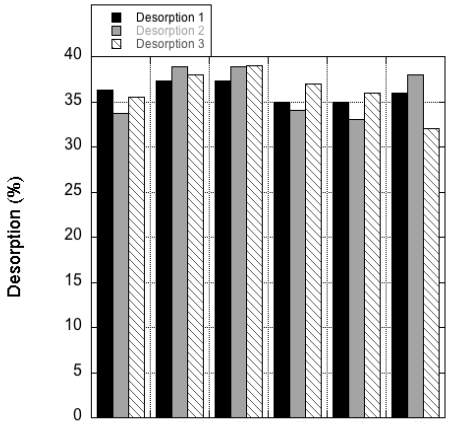

Figure 16. Desorption ratio of Ni (II) ions after 3 repeated cycle

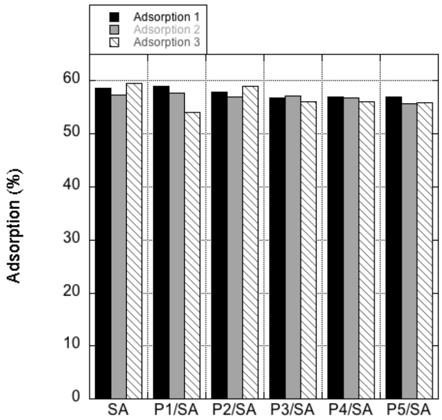

Figure 17. Adsorption ratio of Pb (II) ions after 3 repeated cycle

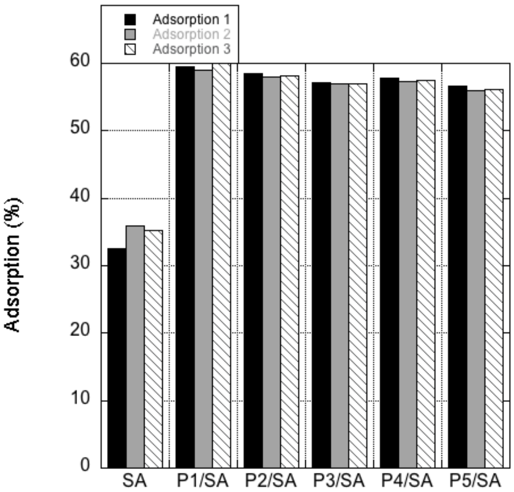

Figure 18. Adsorption ratio of Ni (II) ions after 3 repeated cycle

4. Conclusion

Alginate/perlite composite particles were successfully synthesized with ionic gelation method. Characterization of obtained particles was performed with optical microscopy, SEM, SEM-EDX, XRD and TGA analysis. Adsorption capacity of selected particles was tested against Pb (II) and Ni (II) ions in batch experiment. The findings imply that obtained particles can be desorbed and can be utilized again to remove Ni (II) and Pb (II) metal ions from water. In this study, some experiment such as different pH values (1, 2, 3, 4, 5, 6,) and higher metal ion levels (>300 ppm) could not be tested due to limited project budget. In order to demonstrate the effectiveness of the alginate particles and make a general assumption, higher initial metal ion concentration, pH level and different metal ions such as Hg, Cu, Zn and Cd should be considered.

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