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Surface modified bentonite mineral as a sorbent for Pb²⁺ and Zn²⁺ ions removal from aqueous solutions

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Abstract: Environmental pollution by lead (Pb²⁺) and zinc (Zn²⁺) ions has become an important issue due to its harmful effects on human health and environment. This work aims to evaluate the application of surface modified Egyptian bentonite mineral by acid activation using H₂SO₄ and thermal treatment as an adsorbent to remove lead (Pb²⁺) and zinc (Zn²⁺) ions from aqueous solution. X-ray diffraction (XRD), Fourier Transformed Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM) techniques were used to investigate the modified bentonite. The impact of organic and inorganic dispersants on rheological characteristics of bentonite suspensions was investigated. Adsorption of Pb²⁺ and Zn²⁺ ions using modified bentonite mineral was performed with different adsorbent doses and pH values. Removal efficiencies of lead and zinc are 99.67% and 99%, respectively with adsorbent dose of 25 g/l at pH of 6.2.

Keywords: Ca-montmorillonite, adsorption, heavy metals, surface modification, rheology

1. Introduction

Environmental contamination with toxic metals has become a global concern that threatens human health (Nguyen et al., 2013). The existence of heavy metals in drinking water sources and in edible agricultural crops can be toxic, e.g. they harm the nerves, liver, and bones and they plug functional groups of vital enzymes (Kumar et al., 2012). Heavy metals like Cr, Cu, Pb, Zn, Hg, and Cd are found in wastewater comes from the draining of effluents of processing industries e.g: metal plating, mining processes, fertilizer industries, tanneries, batteries, paper industries, pesticides, ceramic paints, and chemical manufacturing (Cheremisinoff, 1995). There are many typical processes for the elimination of toxic ions from water, which include chemical precipitation, coagulation, reverse osmosis, evaporation, ion-exchange, and adsorption (Fenglian and Wang, 2011). Most of utilized techniques have drawbacks as incomplete removing of metal, high costs, equipment requirements and establishing system generation of other contaminates (Nagwa and Mahmoud, 2016). Adsorption methods are more effective and powerful because of their lower costs and high removal performance of contaminants (Wang et al., 2020). Numerous kinds of adsorbents are developed to get highly adsorption capacity in an inexpensive way.

Many adsorbents have been applied from natural sources, industrial wastes, agricultural wastes and food waste (Meng et al., 2020; Wang et al., 2019; Yehia et al., 2008). Clays that are cost-efficient adsorbing material were applied for removing heavy metals (Selim et al., 2014). Bentonite is an adsorbent aluminum phyllosilicates and properly consisted of montmorillonite (smectite) with inorganic minerals (Selim et al., 2016; Sdiri et al., 2011). The major parameters that affect adsorption and distribute of heavy metals through clay and water are clay type, metal category, pH, adsorbent dose, and contact time (Agha et al, 2013). Clays have exceptional adsorbent capacity which would be increased by acid

activation and/or thermal treatment due to high specific area and the ability of holding water (Ehssan, 2013).

Acid activation of clays is normally done treating them with HCl or H₂SO₄ and the cost of production of these clays is low. If acid activation is accompanied by thermal activation, clays surface area increases to a large extent. Clay thermal activation is a physical behavior which requires calcination of clays at high temperatures. Thermally activated clays are extensively utilized in textile, oil and sugar industry to remove color and other contaminants. Based on their extraordinary rheological characteristics, bentonite suspensions are used extensively in various industrial applications, like pharmaceuticals, dyes, paper, cement, ceramics and nano-composites (Moghadamzadeh et al., 2013). Different polymers have been utilized in dispersing bentonite to control the rheology of dispersions that proper to the specification of the required applications, e.g. poly vinyl pyrrolidone, poly vinyl alcohol, polyethylene amine, and poly ethylene glycol. The inorganic impurities in effluents could be assembled as acids, bases and neutral salts, such as sodium chloride, sodium sulfates and calcium carbonates.

This paper aims to strengthen the adsorbing performance of bentonite mineral through improving its characteristics such as pore volume, surface area and permeability. Also, to investigate the chemical and physical changes resulted by the modification. Removing of Pb²⁺ and Zn²⁺ ions from aqueous solution will be investigated.

2. Materials and methods

2.1. Materials

Bentonite sample was supplied from south of El Hammam city, North Western Desert, Egypt. All chemicals in this work are of analytical grade. The Pb²⁺ and Zn²⁺ ions solutions were prepared using pure water.

2.2. Methods

2.2.1. Acid and thermal activation

Bentonite was acid activated using H₂SO₄ of different concentration. A 50 g of bentonite was mixed with 150 ml of H₂SO₄ solution then agitated at 30°C for one hour. The treated bentonite was separated and washed via pure water then dried at 100°C for 12 hours. The acid activated bentonite was heated in Muffle Furnace to be thermally activated. It was performed over temperature ranging from 200°C to 900°C during two hours. Subsequently, calcined sample was cooled in a desiccator.

2.2.2. Surface modification

Viscosity of suspended bentonite in a non-ionic polymer (Polyethylene Glycol) PEG solution was measured at 25°C. The viscometer (Model DV-3P) was used for viscosity measurements. Different inorganic (salt) of Na⁺, Ca²⁺, Al³⁺ at various concentrations were studied to evaluate the permeability of bentonite slurry. The flow behavior (rheology) of Ca-montmorillonite dispersions containing Na⁺, Ca²⁺, Al³⁺ ions were characterized by the plastic viscosity and yield value.

2.2.3. Characterization of bentonite mineral

A Philips PW 1730 powder X-ray diffractometer with Fe-filtered Co (K-alpha) run at 30 kV and 20mA was utilized to determine the qualitative and the semi-quantitative mineralogical constitution of original and modified bentonite. Surface area of bentonite was measured using the Quanta-chrome NOVA Automated Gas Sorption. The sample was degassed and dried in a vacuum at 100°C for 24 hours before analysis. Densities and porosity were measured using a Quanta-chrome Ultra-pycnometer with helium gas to access the open porosity in samples. The scanning electron microscope (SEM) JSM-6400 investigated the surface morphology. Nicolet Magna-750 FTIR was employed to investigate the function groups of bentonite with transmittance mode over 400-4000 cm⁻¹. The pressed KBr disc employed for this purpose. Zeta potential measurements have been achieved via laser zeta meter "Malvern Zeta-Sizer-2000". This model is connected to a computer unit which contains special software for zeta potential calculation (Selim et al., 2016).

2.2.4. Sorption properties

Methylene blue cation exchange capacity method was performed using guidelines described in ASTM Method F726-81, "Sorbent Performance of Adsorbents." It measures the maximum adsorption of oils and floating immiscible liquids (Selim et al., 2016).

2.2.5. Separation experiments

The removal efficiency was conducted for heavy metal ions from synthetic solutions contain 50 mg/l Pb^{2+} or Zn^{2+} at 25°C. A definite weight (g) of activated bentonite is added to a certain volume (ml) of metal ions solution at pH 6.2 in a round bottom flask and agitated at 200 rpm for 20 min. Then the bentonite was filtered. The supernatant was reserved for chemical analysis using Perkin-Elmer Atomic Absorption "AAAnalyst-200" (Selim et al., 2016).

The removal efficiency was calculated as follows: (El-Wakeel et al., 2017)

$$\text{Removal efficiency \%} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where, C_i and C_f are initial and final concentrations of a heavy metal ions (mg/L); V is solution volume (L) and M is mass of bentonite (g).

3. Results and discussion

3.1. Characterization of original bentonite

Fig. 1 shows the XRD pattern of clay which reveals that Egyptian bentonite clay was influenced by Ca-montmorillonite associated with traces of kaolinite and quartz. Chemical analysis indicated that bentonite is enriched in SiO_2 and Al_2O_3 , Table 1.

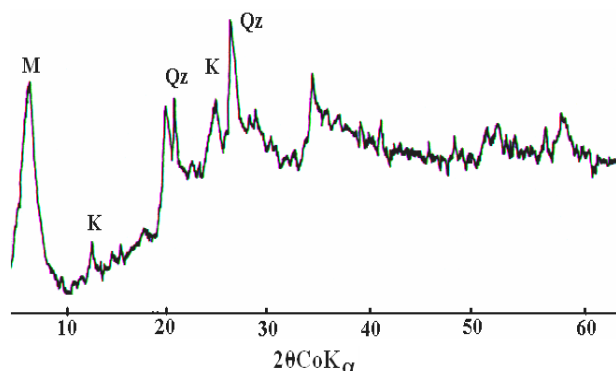


Fig. 1. XRD pattern of bentonite sample

Table 1. XRF analysis of bentonite sample

Analyte	SiO_2	Al_2O_3	K_2O	CaO	TiO_2	P_2O_5	MnO	Fe_2O_3	MgO	Na_2O	L.O.I.
%	55.12	16.14	1.05	1.17	1.18	Zero	Zero	8.25	2.86	1.41	12.35

Fig. 2 displays FTIR of bentonite clay sample which verified the existence of a wide peak at 1027 cm^{-1} which is corresponding to the stretched Si-O of phyllosilicate clay structure. This peak was partially resolved as a result of considerable clay film thickness. Peaks at 3627 and 3692 cm^{-1} are the results of stretched vibrations of structural OH groups, and the peak at 3692 cm^{-1} is characteristic of kaolinite while the 3627 cm^{-1} peak is frequently found in phyllosilicate samples. Peak at 690 cm^{-1} corresponds to OH group structured vibrations, while peak at 919 cm^{-1} corresponds to deformation of Al_2OH group. The shoulder peak at 880 cm^{-1} is belonged to $AlFeOH$ vibrations, thereby indicating the existence of iron in octahedral sheets of montmorillonite. The remaining bands were assigned to vibrations arising from water molecules as the peaks at 3426 cm^{-1} which corresponds to stretched vibrations (ν_3 and ν_1 modes), whereas the 1642 cm^{-1} peak corresponds to H-O-H bending in H_2O molecule (ν_2 mode) (Selim et al., 2016; Sdiri et al., 2011).

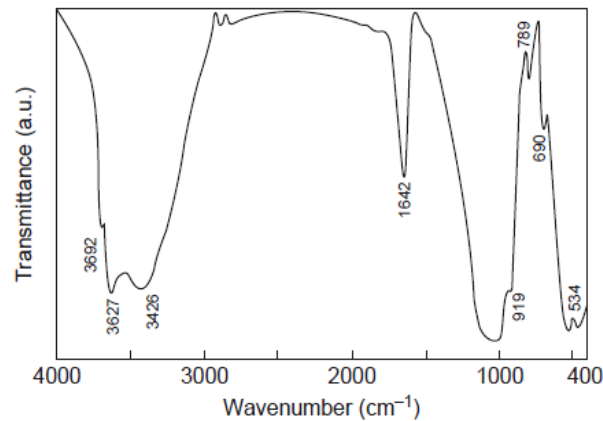


Fig. 2. FTIR of bentonite sample.

BET isotherm displayed that surface area of bentonite sample is about 83.79 m²/g and the porosity percentage is 28.60 %. These results are confirmed through the measurement of sorption properties which indicate that CEC is between 80-120 meq/100 g, water absorption is between 15-20 % and the oil absorption is between 30-45g/100g, Table 2. Fig. 3 shows the results of zeta potential measurements which indicate that bentonite has an iso-electric point at pH ~ 2.8. All of these results indicate that the bentonite samples need specific modification to act as a good adsorbent for heavy metals.

Table 2. Physical properties of bentonite sample

Property	Value
CEC (Cation Exchange Capacity), (meq/100g)	80-120
Water Absorption (weight %)	15-20
Oil Absorption (g/100 g)	30-45

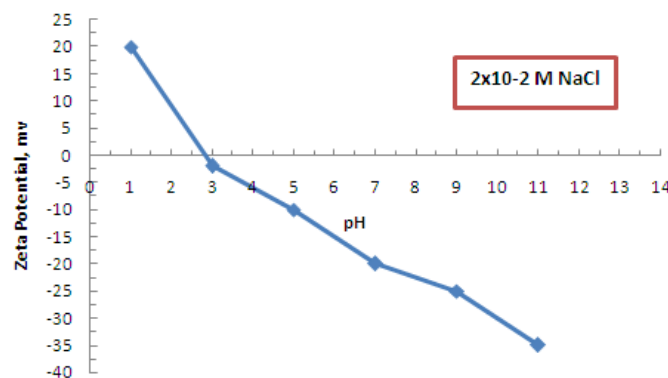


Fig. 3. Zeta potential of bentonite sample

Fig. 4 demonstrates the typical morphology for calcium montmorillonite sample. As observed, the mineral consists of complex collections of grains of few microns in size. The edges of these grains are sharp and rough. The grainy collections are not translucent to an electron beam. The tactoid morphology (face-to-face aggregation) of montmorillonite may be related to its moderate CEC value and relative large particle size. This morphology affects surface area and porosity of this mineral.

3.2. Acid and thermal bentonite activation

Acid activation modifies physical characteristics as upgrading surface area and average pores volume. The chemical properties, cation exchange capacity and surface acidity of clays could be also changed, thus, generating excellent characteristics required for an effective adsorbent. BET isotherm indicated that the surface area of bentonite after modification increased from 83.79 m²/g to 96.65 m²/g, the porosity measurements indicated that porosity percentage increased from 28.6 % to 71.51 %. The results

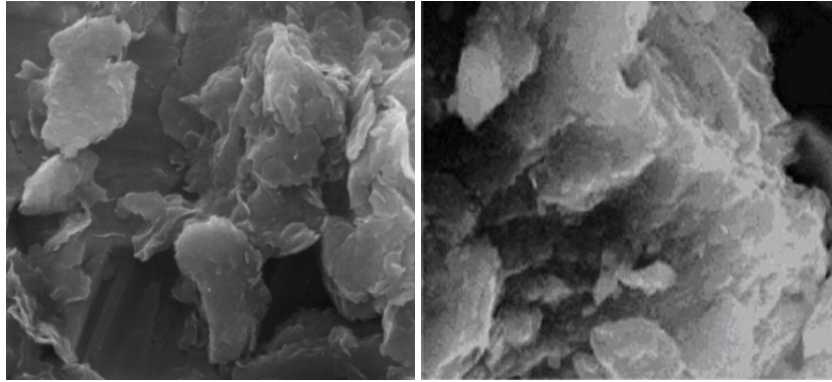


Fig. 4. Common morphological form of bentonite

revealed that modifying clay via H_2SO_4 was effective and also demonstrated that acid activation largely depends on acid strength and time. FTIR spectrum of acid activated bentonite reveals that during acid activation of bentonite, the protons penetrate into clay layers attacking the OH groups causing variation in adsorbent peaks attributed to the OH vibrations and octahedral cations. The strength of stretching bands noticed at 3617 cm^{-1} (Al-OH-Al along with the Al-Mg-OH stretching vibrations) decreases with increase in acid concentration. The increase in H_2SO_4 concentration resulted in a decrease of bands associated with the adsorbed water at 3405 cm^{-1} (H-O-H stretching) and 1635 cm^{-1} (H-O-H bending). The peak of Si-O-Si at 988 cm^{-1} has been remained unchanged, Fig. 5.

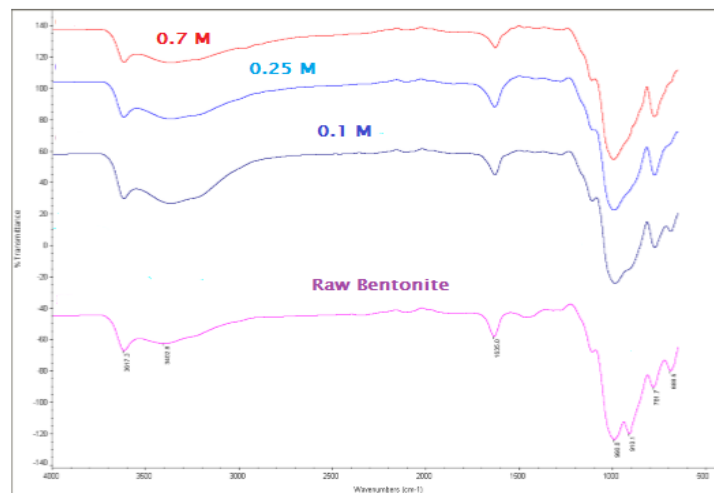


Fig. 5. FTIR spectra of acid activated bentonite

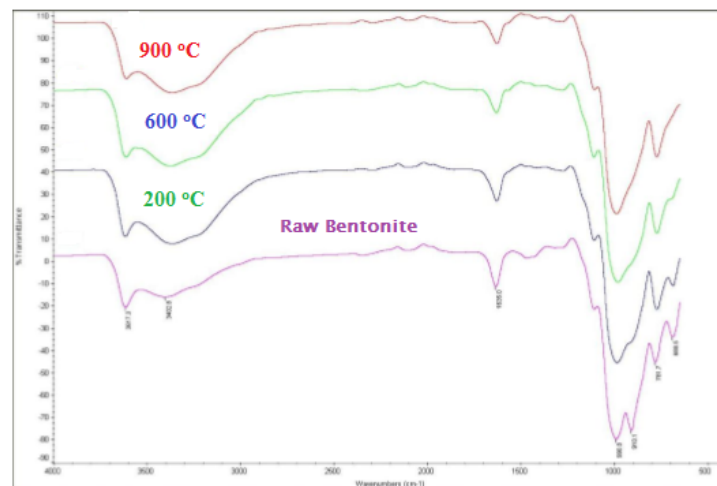


Fig. 6. FTIR spectrum of thermal activated bentonite

Fig. 6 shows the FTIR spectra of thermal activated bentonite which is acid activated at 0.1 M H_2SO_4 . Spectra reveal that on heating Ca-montmorillonite up to 900°C , deeper penetration of protons into the activated clay layers occurred. The increase in activation temperature resulted in a decrease in the intensity of peaks at 3617 cm^{-1} , 3405 cm^{-1} and 1635 cm^{-1} . The beak of Si-O-Si at 988 cm^{-1} remained unchanged. The peaks at 906 cm^{-1} disappeared with temperature increase. The increased peak strength at 781 cm^{-1} indicates the alteration of tetrahedral sheet. The intensity of peak at 688 cm^{-1} , (Al-OH-Si bending) decreased with increase in temperature. Also, it is obvious that rising temperature yielded degrading of structure.

As shown in Fig. 7, the leaching of cations on acid activation creates voids in the bentonite making the clay surface more porous at low acid concentration, clumps of uneven surface of low porosity. With increasing concentration of acid, the surface is getting highly porous with even distributing pores. Further acid concentration increase reduces porosity.

Fig. 8 shows the distinctive morphology characters of heated montmorillonite which is acid activated at 0.1 M H_2SO_4 . They are thin and short leaves, onion-shape, honeycombed, lath-shape and distributed thin flake. Small pore establishment occurred due to impurities removal and replacement of exchangeable cations by H^+ ions. These physico-chemical reactions modify bentonite morphology as the pores open up and the surface appears as more porous and homogenous. Acid activation followed by thermal activation (Fig. 8) provides more porous clay than that of acid activated only (Fig. 7) due to absence of any water which is presented in clay and was adsorbed during washing. Various clays possess several structures and compositions upon rising temperature and depend largely on size and heating method. Moreover, clay minerals are calcined prior using in order to remove any impurities or moisture attached to clay particles (Yeon and Bai, 2015).

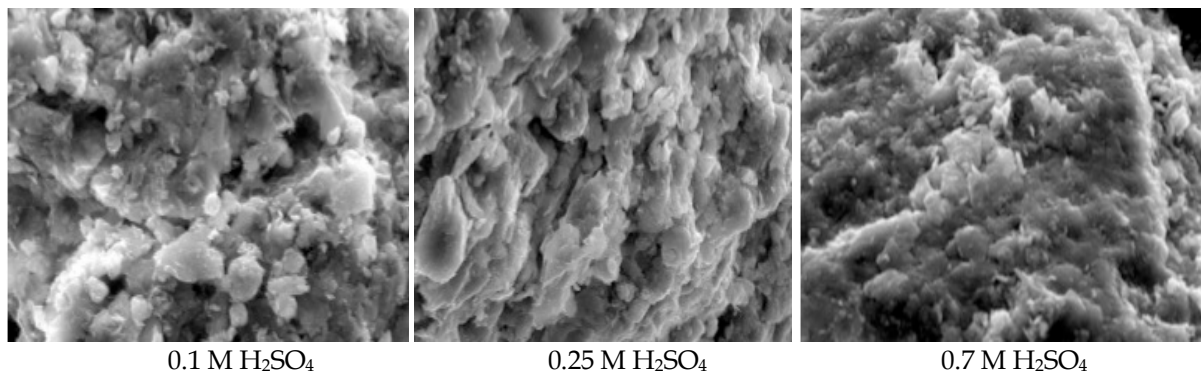


Fig. 7. SEM of acid activated bentonite

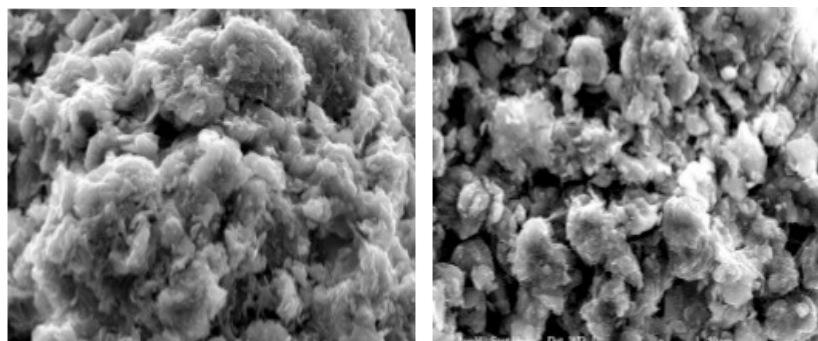


Fig. 8. SEM of thermal activated bentonite

3.3. Rheological properties of minerals' suspension

The rheological characteristics of a bentonite-water system are highly dependent on chemical additives. When water bentonite system includes electrolytes, polymers and surface active agents they shift its rheological characteristics due to interaction with its particles. Modification of bentonite with inorganic or organic materials altering it into a gel like structure which is suitable for use as a thickening agent in water supported paints (Yeon and Bai, 2015).

3.3.1. Effect of organic dispersants

Fig. 9 shows that the viscosity values increase especially after adding 1.25 mol/m³ or more of PEG. This reveals that Ca-montmorillonite sample has naturally a higher plastic viscosity because of its smaller size, a greater number of clay particles in dispersion and increased surface area of clay. At the beginning, when (η_{pl}) values were estimated it was thought that addition of polymer into the system would cause flocculation. It is possible that PEG creates H-bonds with O atoms on clay mineral surfaces; therefore, PEG molecules could be joined on different clay surface places.

PEG could hold on the clay surfaces and at exact time, some PEG molecules can attach to other clay surfaces and those already attached PEG molecules on surface of other clay minerals may form bridging flocculation. In this case, this new appearance in slurry could end up with flocculation. For this cause, the relative viscosities of slurries have been estimated to decide which alternative is correct. The relative viscosity ($\eta_{rel} = \eta_{pl} \text{ dispersions} / \eta_{pl} \text{ medium}$) is not changed so significantly as η_{pl} with polymer concentration. However, keeping relative viscosity values (η_{rel}) in constant together with rising polymer concentration showed that an increase in η_{pl} values, after adding of 1.25 mol/m³ additive, is not belonged to the system flocculation, but it is belonged to swell of PEG molecular weights in water. On increasing the concentration of PEG, there is a slight change occurred in the η_{rel} up to concentration of 1.25 mol/m³. This slight increase is more likely due to bridging flocculation formed between the clay particles. Further additions of PEG caused slight decrease in the η_{rel} (Ben Azouz et al., 2016).

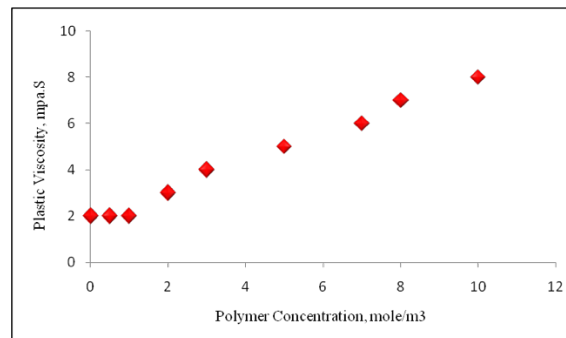


Fig. 9. Plastic viscosity based on polymer concentration

The decrease of viscosity may be resulted from deflocculation of clay particles. XRD data revealed that beyond this concentration, PEG preferentially entered into clay platelets instead attaching on the surface, Fig. 10. This caused swell of dispersing and raised η_{pl} of dispersion. Beyond 1.25 mol/m³ PEG concentration, η_{rel} continued to increase. This revealed that small molecular weight of PEG still attached to the surfaces of clay at high concentrations of polymer. However, polymer attachments created on surface of clay are not strong enough to progress yield value. XRD techniques were used to measure the d-spacing up to 20 mol/m³ concentration in order to better examine the swelling properties of bentonite-PEG suspensions. The PEG increases swelling properties due to its higher molecular weight and bentonite basal space is increased by 32% from its initial value.

Fig. 11 displays FTIR spectra of Ca- montmorillonite and PEG. Peaks correlated to structural stretched hydroxyl at 3627 cm⁻¹ were belonged to Ca-smectite. Hydrogen vibration, confirmed by a broad peak centered on 3465 cm⁻¹ was assigned to O-H stretching and an H-O-H deformation peak at 1641 cm⁻¹ also existed in FTIR spectrum of Ca smectite. The sharp peak belonged to Si-O stretching at 1043 cm⁻¹, and other sharp peaks attributed to Si-O bending at 523 and 466 cm⁻¹ were distinguished. While standard PEG showed peaks at 3482 cm⁻¹ (stretched O-H), 2888 cm⁻¹ (stretched alkyl CH), 1469, 1361, 1344, 1282, and 1242 cm⁻¹ (distorted alkyl CH), 1113 cm⁻¹ (stretched C-O-C), 1060 cm⁻¹ (stretched C-OH), the FTIR spectra of PEG adsorbed on Ca- montmorillonite showed additional peaks including: 3436 cm⁻¹ (stretched O-H), 2888 cm⁻¹ (stretched alkyl CH), 1472, 1361, 1346, 1281, and 1244 cm⁻¹ (distorted CH), 1116 cm⁻¹ (stretched C-O-C) and 1062 cm⁻¹ (stretched C-OH).

3.3.2. Effect of inorganic dispersants

The pertinent types of reactions between bentonite clay and the inorganic permeate are ion exchange interactions, change in ionic strength in solution, dissolution of clay minerals, flocculation and precipi-

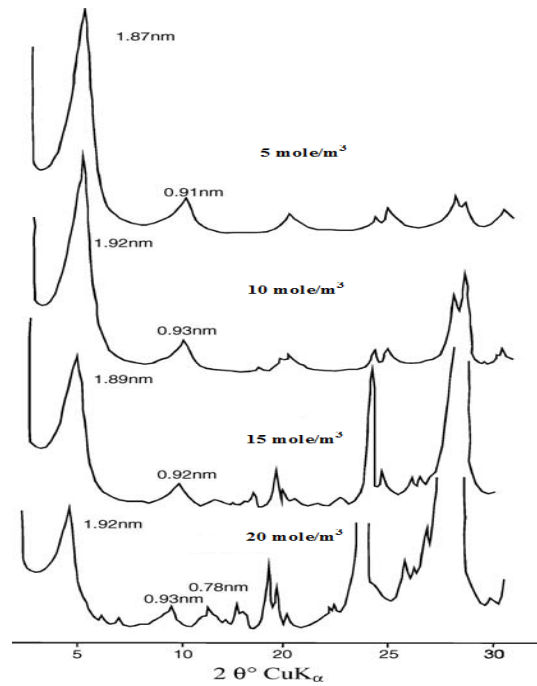


Fig. 10. XRD of Ca- montmorillonite treated sample

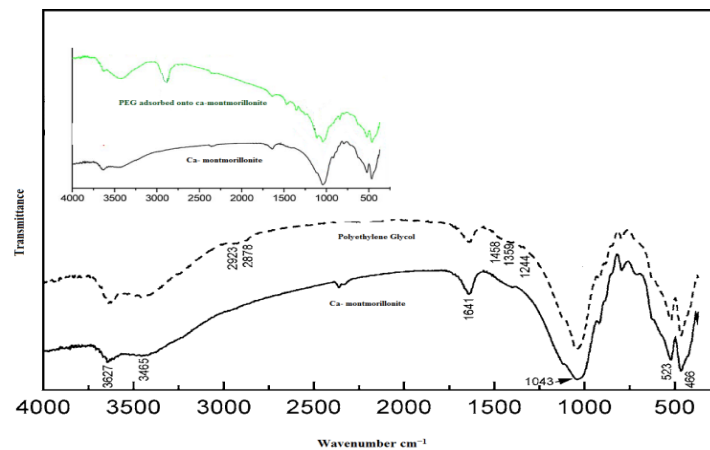


Fig. 11. FTIR of Ca- montmorillonite and PEG

tation process. The reactions depend upon kind of ionic categories in aqueous solution and their existing state, which includes size, charge (type and density), and the correlated environment (pH and dipole moment). Bentonite permeability generally increases in response to permeation with the aqueous salts; however, there are obvious differences in permeability demonstrate that it is distinctive to each chemical. The clay tends to approach a more flocculated structure because of decrease in the double layer thickness. Hence, progressively more flocculated and more permeable structure would be expected with increasing aqueous salt concentration. Permeability generally enhanced with increasing salt concentration. Also, it could be adjacent to the colloidal surface of clay particle. This means, lower is the hydrated ion, lower is the double layer and larger is flocculated clay structure.

Table 3 lists permeability of bentonite suspensions permeated with different inorganic (salt) contaminants at different concentrations. The flow behavior (rheology) of dispersed Ca-montmorillonite containing various in organic contaminants was characterized by plastic viscosity. The plastic viscosity based on concentration of salt changed similarly for all dispersions: an initial decrease to a minimum, then a steep increase, Fig. 12. Increasing valence of inorganic cations strongly reduced the critical salt concentration.

The adsorption process would be continued together with swelling and dispersion when clay minerals are added into water. Colloidal clay particles dispersed in a continuous medium are in cons-

Table 3. Permeability of bentonite slurries with different inorganic contaminants

Bentonite slurry permeability (cm/s) change by contaminants				
Contaminants	Amount of contaminant added, % by wt.			
	0%	0.5%	2%	3%
Sodium chloride	0.4×10^{-7}	-	0.5×10^{-7}	0.9×10^{-7}
Calcium chloride	0.4×10^{-7}	1.6×10^{-7}	2.0×10^{-7}	2.0×10^{-7}
Magnesium chloride	0.4×10^{-7}	1.4×10^{-7}	1.7×10^{-7}	1.7×10^{-7}
Potassium chloride	0.4×10^{-7}	0.5×10^{-7}	0.7×10^{-7}	1.6×10^{-7}
Ammonium chloride	0.4×10^{-7}	0.6×10^{-7}	1.1×10^{-7}	3.0×10^{-7}
Calcium carbonate	0.4×10^{-7}	-	-	0.4×10^{-7}
Magnesium carbonate	0.4×10^{-7}	-	0.5×10^{-7}	0.5×10^{-7}
Calcium sulfate	0.4×10^{-7}	1.1×10^{-7}	1.1×10^{-7}	0.9×10^{-7}
Sodium sulfate	0.4×10^{-7}	-	0.4×10^{-7}	0.4×10^{-7}
Sodium nitrate	0.4×10^{-7}	-	0.5×10^{-7}	0.6×10^{-7}
Ferrous sulfate	0.4×10^{-7}	0.6×10^{-7}	1.0×10^{-7}	1.4×10^{-7}

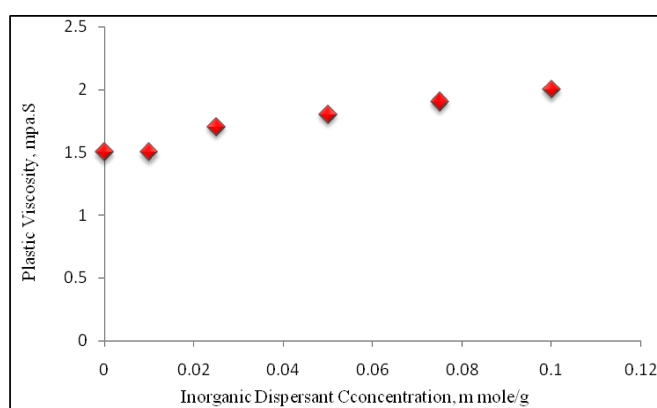


Fig. 12. Plastic viscosity as a function of inorganic dispersant concentration

tant Brownian movement. The combination of interaction energies determines whether particles remain separate, so that dispersion is stable in colloidal sense in which coagulation or flocculation occurs. Particles generally interact with repulsion or attraction electrical double-layer, Vander-Waals attraction and steric effects. The natural sample (Ca-bentonite) has a minimal plastic viscosity. Convertible cations, which determine orientation of many physical properties of bentonitic clays, such as particle size, surface charge, surface area and particle number per unit volume, also have a powerful effect on the dispersion mechanisms. The enhancement of viscosity to Ca-bentonite dispersions after addition of sodium ion is a direct concomitant of the opposite effect of Na^+ and Ca^{++} ions. When chemical additives (electrolytes, polymers, surface active agents, etc.) added to a water-clay system, they would interact with clay, Fig. 12 (Ben Azouz et al., 2016; Kelessidis, 2017).

3.4. Removal of some heavy metal ions

Based on previous results, surface modifications of bentonite were achieved via acid activation using 0.1 M H_2SO_4 followed by thermal activation at 900°C. Adsorption of Zinc and Lead ions using acid-thermal modified bentonite minerals was tested under different adsorbent doses 5, 10, 15, 20 and 25 g/l, Different initial ions concentration and pH range of 4.2 - 7.3.

3.4.1. Effect of pH

pH affects significantly on metal ions removal via influencing ions speciation and integrity of bentonite. Moreover, H^+ ions are stated as competitive in ions exchange (Hui et al., 2005; Dimirkou, 2007). It influences the degree of ions precipitation and type of complexes created among ligands and ions. Also, solution chemistry of heavy metal ions is controlled by pH (Esposito et al., 2002). pH

influences adsorption extent due to changing distribution of bentonite surface charge. This led to variation in adsorption extent. Various species, dominated in solution at different pHs, differ in their charge and ability to be adsorbed on modified bentonite. pH of solution affects greatly on affinity of adsorbent's functional groups. Results demonstrated that pH would be more than 6 and below 7 and ideally at pH 6.2, Fig. 13. At lower pH, the functional groups are protonated and the positively charged surfaces dominate. Deprotonation occurs at higher pH and thus they acted as moieties of negative charge, attracting heavy ions (Acheampong et al., 2010). Nevertheless, in alkaline solutions, metals solubility is decreased providing precipitation that complicates sorption process (Hui et al., 2005). Removal abilities of different metal ions were in this order: $Zn^{2+} > Pb^{2+}$, which may be due to ionic size where zinc has small ionic radius (0.74 Å) with comparing to lead ions (1.19 Å) (Covelo et al., 2004).

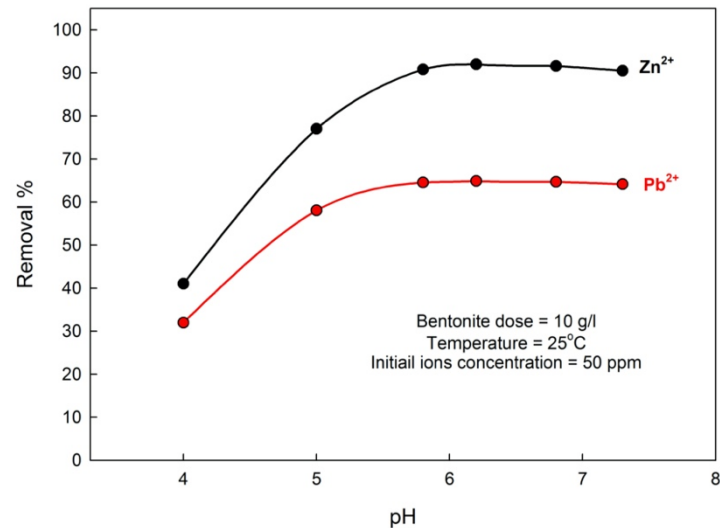


Fig. 13. Effect of pH on the removal efficiency of Zn^{2+} and Pb^{2+} ions

3.4.2. Effect of initial metal ions concentration

Initial ions concentration in aqueous solutions significantly affects process of adsorption. It is shown that process efficiency is increased with increasing concentration, Fig. 14. Increasing initial Zn^{2+} and Pb^{2+} concentration increased capacity of adsorption while decreased removing efficiency (Oren and Kaya, 2006; Wu et al., 2008). High initial concentration caused more accessibility of ions so, more ions are adsorbed at specific bentonite mass. Also, the driving forces, to control mass transfer resistance for migration of metal ions from solution bulk to modified bentonite surface, is increased. However, modified bentonite is subjected to a huge number of metal cations which subsequently fill its sites until saturation is occurred. Furthermore, surface precipitation is highly dependent on initial concentration of Zn^{2+} and Pb^{2+} ions. At low ions concentrations, the modified bentonite surface coverage becomes low and surface complexes formation is a proper mechanism. Increasing Zn^{2+} and Pb^{2+} concentration prefers the concentration of compounds and aggregates on bentonite surface. Further increase in metal ions concentration caused saturation of adsorption sites and surface precipitation is the main uptake mechanism [Arief et al., 2008; Doula and Dimirkou, 2008].

3.4.3. Effect of bentonite dose

Influence of adsorbent on removing Zn^{2+} and Pb^{2+} ions displayed that removal efficiency is increased with increasing bentonite dose, Fig. 15. The mineral mass in solution affects adsorption process, as it monitors accessibility of active sites. Numerous studies reported that higher mineral concentrations resulted in increased metal removal (Coruh and Ergun, 2009; Mishra and Patel, 2009) and reduced amount of ions adsorbed on adsorbent surface (Oren and Kaya, 2006). Decrease in adsorption capacity could be explained as a result of unsaturated adsorption sites as well as particle aggregation resulted in decreasing total surface area while increasing diffusion path length. Increasing solid concentration increased adsorbent surface area, which resulted in increasing binding sites number at constant volume. Therefore, the total metal removal is increased (Camacho et al., 2011).

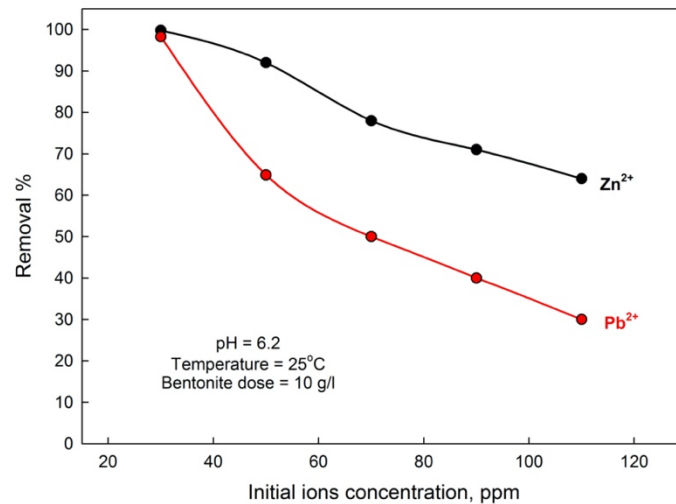


Fig. 14. Effect of initial concentration of Zn²⁺ and Pb²⁺ ions on the removal efficiency

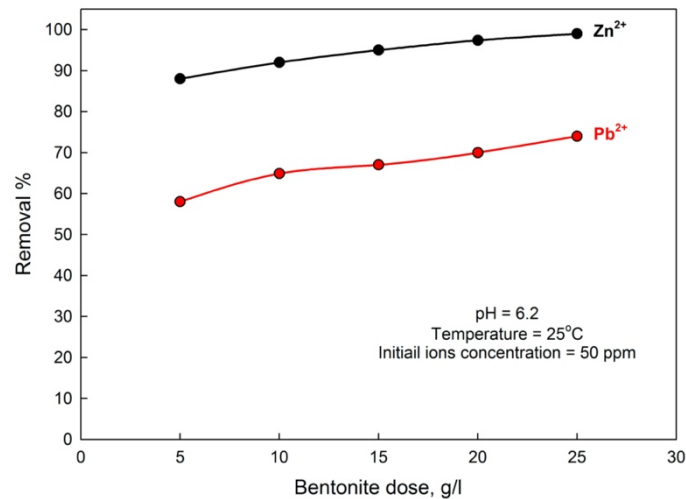


Fig. 15. Effect of bentonite dose on the removal efficiency of Zn²⁺ and Pb²⁺ ions

4. Conclusions

The Egyptian bentonite clay was influenced by Ca-montmorillonite associated with kaolinite and quartz. The FTIR confirmed the existence of phyllosilicate clay structure. Zeta potential showed that bentonite has an iso-electric point at pH ~ 2.8. The morphology showed that it consists of complex collections of grains of few microns in size.

Acid activation increased both surface area and average pores volume. Surface area of bentonite after modification increased from 83.79 to 96.65 m²/g. The porosity is increased from 28.6% to 71.51%. FTIR indicated that the protons penetrate into clay layers attacking the OH groups. Thermal activation up to 900°C caused deeper penetration of protons into activated clay layers. Acid activation followed by thermal activation provides more porous clay than that of acid activated only.

The rheology of bentonite-water system is highly dependent on chemical additives which are important parameter for its application as a thickening agent in paints. The modification using organic dispersants (PEG) at concentration of 1.25 mol/m³ improved colloidal and rheological characteristics of bentonite slurries. The rheology of bentonite dispersions was characterized by plastic viscosity and yield value. Increasing valence of inorganic cations strongly reduced critical salt concentration.

Modified bentonite by acid activation using 0.1 M H₂SO₄ followed by thermal treatment at 900°C was applied as an adsorbent for removing Zn and Pb ions from aqueous solutions. Results showed a maximum removal at pH 6.2. Removal order was Zn²⁺ > Pb²⁺ based on their ionic size. Efficiency is increased with increasing both initial ions concentration and bentonite dose. The maximum Zn²⁺ and Pb²⁺ removal, at adsorbent dose 25g/l and pH 6.2, was 99% and 99.67% respectively.

References

- ACHEAMPONG, M.A., MEULEPAS, R.J.W., LENS, P.N.L., 2010. *Removal of heavy metals and cyanide from gold mine wastewater*, J. Chem. Technol. Biotechnol., 85, 590–613.
- AGHA, M.A., FERRELL, R.E., HART, G.F., EL GHAR, M.S.A., ABDEL-MOTELIB, A., 2013. *Mineralogy of Egyptian Bentonitic Clays II: Geologic Origin*. Clays Clay Miner. 61, 551–565.
- ARIEF, V.O., TRILESTARI, K., SUNARSO, J., INDRASWATI, N., ISMADJI, S., 2008. *Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: characterization, biosorption parameters and mechanism studies*, Clean Soil Air Water, 36, 937-962.
- BEN AZOUZ, K., BEKKOUR, K., DUPUIS, D., 2016. *Influence of the temperature on the rheological properties of bentonite suspensions in aqueous polymer solutions*. Applied Clay Science. 123, 92–98.
- CAMACHOA, L. M., PARRAB, R. R., DENGGA, S., 2011. *Arsenic removal from ground water by MnO₂-modified natural clinoptilolite zeolite: Effects of pH and initial feed concentration*, J. Hazardous Materials, 189, 286-293.
- CHEREMISINOFF, P.N., 1995. *Handbook of Water and Wastewater Treatment Technology*, Marcel Dekker Inc., New York.
- CORUH, S., ERGUN, O.N., 2009. *Ni²⁺ removal from aqueous solutions using conditioned clinoptilolites: kinetic and isotherm studies*, Environ. Prog. Sustain. Energy, 28, 162-172.
- COVELO, E.F., ANDRADE-COUCÉ, M.L., VEGA, F.A., 2004. *Simultaneous adsorption of Cd, Cr, Cu, Ni, Pb and Zn by different soils*, Journal of Food Agriculture and Environment 2(3).
- DIMIRKOU, A., 2007. *Uptake of Zn²⁺ ions by a fully iron exchanged clinoptilolite. Case study of heavily contaminated drinking water samples*, Water Res., 41, 2763–2773.
- DOULA, M.K., DIMIRKOU, A., 2008. *Use of an iron-overexchanged clinoptilolite for the removal of Cu²⁺ ions from heavily contaminated drinking water samples*, J. Hazard. Mater., 151, 738-745.
- EHSSAN, N., 2013. *Thermodynamics and Kinetic Study of Using Modified Clay as an Adsorbent for the Removal of Zn ions from waste water*. Journal of American Science. 9,141-149.
- EL-WAKEEL, Sh.T., EL-TAWIL, R.S., ABUZEID, H.A.M., ABDEL-GHANY, A.E., HASHEM, A.M., 2017. *Synthesis and structural properties of MnO₂ as adsorbent for the removal of lead (Pb²⁺) from aqueous solution*. Journal of the Taiwan Institute of Chemical Engineers. 72, 95–103.
- ESPOSITO, A., PAGNANELLI, F., VEGIO, F., 2002. *pH-related equilibria models for biosorption in single metal systems*, Chem. Eng. Sci., 57, 307–313.
- FENGLIAN, F., WANG, Q., 2011. *Removal of heavy metal ions from wastewaters: A review*. Journal of Environmental Management. 92, 407-418.
- HUI, K.S., CHAO, C.Y.H., KOT, S.C. Kot, 2005. *Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash*, J. Hazard.Mater., 127, 89-101.
- KELESSIDIS, V.C., 2017. *Yield Stress of Bentonite Dispersions*. Rheol: open access. 1, 1-12.
- KUMAR, P.S., RAMALINGAM, S., SATHYASELVABALA, V., KIRUPHA, S.D., MURUGESAN, A., SIVANESAN, S., 2012. *Removal of cadmium (II) from aqueous solution by agricultural waste cashew nut shell*. Korean J. Chem. Eng. 29, 756-768.
- MENG, B., GUO, Q., MEN, X., REN, S., JIN, W., SHEN, B., 2020. *Modified bentonite by polyhedral oligomeric silsesquioxane and quaternary ammonium salt and adsorption characteristics for dye*. Journal of Saudi Chemical Society. 24, 334-344.
- MISHRA, P.C., PATEL, R.K., 2009. *Removal of lead and zinc ions from water by low cost adsorbents*, J. Hazard. Mater., 168, 319-325.
- MOGHADAMZADEH H.R., NAIMI, M., RAHIMZADEH, H., ARDJIMAND M., NANSA, V.M., GHANADI, A.M., 2013. *Experimental Study of Adsorption Properties of Acid and Thermal Treated Bentonite from Tehran (Iran)*. Intern. J. of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering. 7, 426-429.
- NAGWA B., MAHMOUD S., 2016. *Adsorption Behavior of Cd²⁺ and Zn²⁺ onto Natural, Egyptian Bentonite Clay*. Minéral. 6, 1-15.
- NGUYEN, T., NGO, H., GUO, W., ZHANG, J., LIANG, S., YUE, Q., LI, Q., NGUYEN, T., 2013. *Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater*. Bioresour. Technol. 148, 574–585.
- OREN, A.H., KAYA, A., 2006. *Factors affecting adsorption characteristics of Zn²⁺ on two natural zeolites*, J. Hazard. Mater., 131, 59-65.

- SDIRI, A., HIGASHI, T., HATTA, T., JAMOSSI, F., TASE, N., 2011. *Evaluating the adsorptive capacity of montmorillonitic and calcareous clays on the removal of several heavy metals in aqueous systems*. Chem. Eng. J. 172, 37-46.
- SELIM, K.A., EL-TAWEEL, R.S., ABDEL-KHALEK, N.A., 2016. *Heavy Metals Removal Using Surface Modified Glauconite Mineral*. International Journal of Mineral Processing and Extractive Metallurgy. 1, 46-55.
- SELIM, K.A., YOUSSEF, M.A., ABDEL RAHIEM, F.H., HASSAN, M.S., 2014. *Dye Removal Using Some Surface Modified Silicate Minerals*. International Journal of Mining Science and Technology. 24, 183-189.
- WANG, F., XU, W., XU, Z., LIU, H., 2020. *CTMAB-Modified Bentonite-Based PRB in Remediating Cr(VI) Contaminated Groundwater*. Water Air Soil Pollut. 231, 20. <https://doi.org/10.1007/s11270-019-4386-4>.
- WANG, M., WANG, Z., ZHOU, X., LI, S., 2019. *Efficient Removal of Heavy Metal Ions in Wastewater by Using a Novel Alginate-EDTA Hybrid Aerogel*. Appl. Sci. 9, 547. doi:10.3390/app9030547.
- WU, D., SUI, Y., HE, S., WANG, X., LI, C., KONG, H., 2008. *Removal of trivalent chromium from aqueous solution by zeolite synthesized from coal fly ash*, J. Hazard. Mater., 155, 415-423.
- YEHIA, A., ABD EL-RAHIEM, F.H., EL-TAWEEL, R.S., 2008. *Removal of heavy metals from aqueous solutions by unburned carbon separated from blast furnace flue dust*. Mineral Processing and Extractive Metallurgy (Trans. Inst. Min Metall. C). 117, 4.
- YEON, C.K., BAI, K., 2015. *Effects of bentonite concentration and solution pH on the rheological*. Applied Clay Science. 108, 182-190.