CATION UPTAKE PROPERTIES OF CALCIUM ALUMINOSILICATE

M. S. Saghian, R. Naghizadeh* and H. Sarpoolaky

* *rnaghizadeh@iust.ac.ir*

School of Metallurgy & Materials Engineering, Iran University of Science and Technology,Tehran, Iran.

Abstract: *In this study, the effect of different parameters such as time and temperature of calcination and milling on the formation of calcium aluminosilicates was investigated. Raw materials used in this study were calcium carbonate and kaolin in high purity. Powder X-ray diffraction patterns were obtained from all samples after heat treatment at various temperatures and times. To study the microstructure scanning electron microscope was used. Milling the samples contributed to the amorphous structure due to inducing defects in the structure. Moreover, increasing the milling time reduced crystallization temperature of anorthite. Uptake experiments were performed using solutions containing different concentrations of nickel. Samples were exposed to the solution for 24 h with stirring then the samples were filtered and the concentrations of the cations in the separated solutions were analyzed. FTIR analysis was conducted on the adsorbents before and after nickel uptake. Nevertheless, they hardly helped understand sorption mechanisms. Therefore, adsorption isotherms were studied instead. Three adsorption isotherms of Langmuir, Freundlich and DKR were used to model sorption data. Results suggested monolayer sorption occurs on the surface of the adsorbent and sorption energy calculated by DKR model was 22.36 kJ/mol which can be described as a strong chemical adsorption mechanism.*

Keywords: *Calcium aluminosilicates; Planetary ball mill; Adsorption isotherm*

1. INTRODUCTION

Water pollution is a serious environmental concern of the 21st century. Wastewater discharged from industries that process ores and concentrates of non-ferrous metals is usually polluted with heavy metal ions such as Cd^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, etc. [1,2]. Various methods exist for the removal of heavy metal ions from wastewater such as chemical precipitation, precipitation/coagulation, membrane technology, electrolytic reduction, ion exchange and adsorption are reported frequently among them [2-5]. Materials used for adsorption process are usually abundant in the nature and do not impose high costs on industries [6]. Reports come from several recent studies confirming efficient sorption of heavy metal ions by kaolinites, montmorillonites, bentonite and zeolites has already been reported [1]. The alkali and alkaline earth ions present in zeolities framework structure can be exchanged in aqueous solutions. That is why they are used as water softeners [7,8]. However, zeolites are more prone to adsorb Ca^{2+} than heavy metal ions. This limits their applicability in industrial situations because Ca^{2+} ions are normally present in all environments [9].

A new type of compound showing good uptake of heavy metal ions are alkaline and alkaline earth aluminosilicates such as $KAlSiO_4$, $BaAl_2Si_2O_8$, $CaAl_2Si_2O_8$ and $Ca_2Al_2SiO_7$. To produce these compounds the solid-state reaction of kaolinite ($Al_2Si_2O_5(OH)_4$) with alkali and alkaline earth carbonates is generally used [9,10]. Uptake of various cations by $KAlSiO_4$ prepared from kaolinite and K_2CO_3 reaction at 550 °C for 24 hours, has shown that this compound has a very strong affinity for $Ni2+$ compared to zeolite A, a material known to have the highest cation exchange capacity of all the zeolites [11]. Alkaline earth aluminosilicates specially amorphous and layered compounds recently candidate for cation uptake from wastewater [9].Two main crystalline phases of calcium aluminosilicate are anorthite ($CaO.Al_2O_3.2SiO_2$) with theoretical chemical composition CaO=20.2 wt.%, Al_2O_3= 36.6wt.%, SiO_2=43.2wt.% and gehlenite ($2CaO-Al_2O_3-siO_2$) with theoretical chemical composition (CaO=40.9wt.%, Al_2O_3=37.2wt.%, SiO_2=21.9wt.%). Okada et al. examined the uptake of various cations by $CaAl_2Si_2O_8$ prepared from firing a ground mixture of Georgia kaolin and $CaCO_3$ in a 1:1 molar ratio for 24 hours at 900 °C and found a

M. S. Saghian ,R. Naghizadeh and H. Sarpoolaky

high selectivity for transition metal ions in this compound [4,9]. $CaAl_2Si_2O_8$ occur both as amorphore and crystalline forms. The crystalline forms of these compound occur in layered and framework structure. Layer structure consist of SiO_4 and AlO_4 tetrahedral layers with Ca^{+2} ions in the interlayers [11]. In this study the optimum conditions of process for obtaining of amorphous a $CaAl_2Si_2O_8$ were investigated.

The equilibrium relationships between adsorbent and adsorbate are usually described as the ratio of the adsorbed quantity to that remaining in the solution at a fixed temperature at equilibrium [1]. The uptake ability is described as the substitution of alkali ions which are released from the framework structure with heavy metal ions in the solution [4]. In this study the sorption isotherms of Ni^{2+} was simulated using mathematical model equations of Langmuir and Freundlich. However, these models do not give any idea about sorption mechanism. Thus, Dubinin–Kaganer–Radushkevich (DKR) [1,12] isotherm was also applied to assess sorption mechanism.

2. EXPERIMENTAL PROCEDURES

2. 1. Synthesis and Characterization of the Absorbent

Kaolin (Merck No: 104440) and $CaCO_3$ (Merck No: 102066) were used as starting materials. Kaolin chemical and mineral compositions are listed in Table 1. The major mineral is kaolinite, but minor minerals of muscovite and quartz are also available. A mixture of kaolin and $CaCO_3$ was chosen with chemical composition of sample in anorthite area of SiO_2-Al_2O_3-CaO ternary diagram which contains 44.5 wt.% SiO2, 32.08 wt.% Al_2O_3, 20.32 wt.% CaO and 3.05% other oxides.

Two type samples (unground and ground) were obtained from mixing of kaolin and calcite. In unground method powders were blended using a mortar and pestle. In ground method wet milling of starting powders was conducted in polyethylene jar with alumina balls (Ø= 10mm) using planetary ball mill (Vrej). Ball to powder weight ratio was 11 and milling was performed at 200 rpm for 1 and 12 hours, respectively. The ground slurry was dried at 110 °C in electric oven. Unground and ground samples were fired at various temperatures (800 - 900 °C) at a heating rate of 10 °C/min for 8 and 24 hours. Phase characterizations of synthesized powders were performed by XRD (PHILIPS-PW1800) using CuKα radiation and microstructural characterization was conducted by SEM (TESCAN Vega II).

2. 2. Sample and Solution Preparation

According to ASTM D5919 and ASTM D3860 standards which belongs to determination of adsorption capacity of activated carbon, powders have been reduced in particle size so that 90% or greater passes through a U.S. 325-mesh sieve.

A stock solution containing nickel is prepared by injecting 1000 mg Ni, ($NiCl_2$ in H_2O, Titrisol Merck No: 109989) into deionized water in a one liter volumetric flask and was used to prepare the adsorbate solutions by appropriate dilution.

2. 3. Batch Adsorption Studies

Uptake experiments were conducted by adding 0.1000 g adsorbent into 50 ml of solutions containing Ni^{2+} ions of desired concentrations which were stirred by magnetic stirring apparatus for 24 hours (100 rpm) at 20°C temperature. The pH values of solutions were measured after the test completed. The adsorbents were separated

Table 1. Chemical composition (wt. %) of Merck kaolin.

Kaolin	Mass Content %							
	SiO_2	Al_2O_3	K_2O	Fe_2O_3	MgO	Na_2O	TiO_2	L.O.I
Merck	49.49	35.66	2.39	0.63	0.31	0.05	0.03	11.44

from the solutions by filter paper (Whatman grade 6) and washed with de-ionized water. The concentrations of the various cations in the separated solutions were analyzed using atomic absorption spectrometer (Avanta Sigma).

According to D4646 ASTM standard sorption of solute onto the filter was evaluated by the use of blank solutions in all uptake experiments. Separated powders were dried at 100 °C for 24 hours. FTIR technique was applied to assess the spectra of the separated powders using a Brucker instrument. All the reported results are the average of two measurements.

3. RESULTS AND DISCUSSION

3. 1. Synthesis of Calcium Aluminosilicates

Fig. 1 shows XRD patterns of unmilled samples after calcination at 850 °C and 900 °C for 8 and 24 h at each temperature. It is seen that samples calcinated at 850 °C for 8 and 24 h have an amorphous structure. Gehlenite ($Ca_2Al_2SiO_7$) is the main crystalline phase formed in calcinated sample at 900 °C whether for 8 or 24 h. Slight amounts of anorthite ($CaAl_2Si_2O_8$) was also observed in samples after calcination at 900 °C for 24 h. $CaAl_2Si_2O_8$, in addition of amorphous state, is known to comprise two different structures; a metastable layered structure and a stable framework one (anorthite). Based on the

literature [6,11], amorphous samples and layered types of $AeAl_2Si_2O_8$ (Ae=Ca, Sr and Ba) show higher cation uptake. This is mainly due to a higher defect concentration in amorphous structure and location of Ae ions in the interlayered of the layered structure which facilitates ion release and contributes to the reaction between the adsorbed cation and the adsorbent [3,11]. Okada et al. [11], mixed Georgia kaolin with calcite in the stoichiometric composition of $CaAl_2Si_2O_8$ and calcinated the milled and unmilled mixtures at different temperature 500 - 1000 °C. In their results in unmilled samples weren't established amorphous phase and this phase obtained after milling for 12 h and firing at 800 °C with 24h soaking time.

For surveying of the grinding on the phase formation at CaO-Al_2O_3-SiO_2 system, planetry mill was also used in the present work. Fig. 2 shows that calcination of the samples for 8 and 24 h after a process of planetary milling for 12 h led to formation of amorphous samples. However, samples calcinated at 900 °C for 8 and 24 h were not amorphous and contained anorthite crystals as a main phase. In other words, milling the studied samples for 12 h led to the formation of anorthite after calcinations at 900 °C for 1 h, while in unmilled samples only gehlenite crystallized. We have prepared amorphous $CaAl_2Si_2O_8$ by solid state reaction kaolinite with

Fig. 1. XRD patterns of unmilled samples after calcinations at 850 °C for a) 8 h and b) 24 h and at 900 °C for c) 8 h and d) 24 h.(G: gehlenite, A: anorthite)
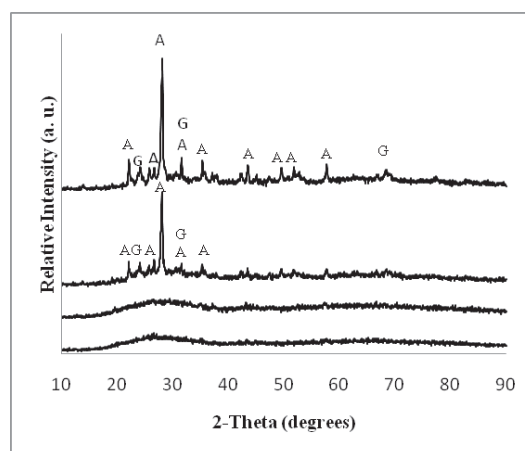

Fig. 2. XRD patterns of milled samples after calcinations at 850 ℃ for a) 8 h and b) 24 h and at 900 ℃ for c) 8 h and d) 24 h. (G: gehlenite, A: anorthite)

$CaCO_3$ for unmilled and milled samples at 850 and 800 °C respectively. But crystallization of this amorphous phase at 900 °C yield gehlenite phase in unmilled sample and anorthite phase in milled sample. During firing, dehydroxylation of kaolinite and calcination of $CaCO_3$ occur at around 600 and 800 °C respectively [16]. From reaction of amorphous metakaolinite and CaO, amorphous $CaAl_2Si_2O_3$ established. The structure of this phase in some crystallographic direction is similar to gehlenite and anorthite phases. In milled sample, due to homogenity of mixture, smaller particle size of raw materials and surface activation of particles, diffusion of Ca^{2+}, Al^{3+}, Si^{4+} are facilitated and formation of amorphous $CaAl_2Si_2O_8$ occur at lower temperature (800 versus 850 °C) in comparison with unmilled sample. Also establishment of intermediate gellenite phase is eliminated or occur as minor phase.

3. 2. Adsorption Evaluation

3. 2. 1. Selecting an Initial Sample

Table 2 lists the results of adsorption experiment on 8 samples that prepared by different synthesis condition as mentioned in this table. Four samples (No. 1, 2, 5. 6) have amorphous structure, in two samples (No. 3, 4) contain principally gehlenite and in other two samples (No. 7, 8) anorthite as a main phase to be present. Uptake experiments were performed using solution containing the chloride of nickel. The initial pH values immediately samples into solution were about 5.71-6.19 and after 24h tests were as mentioned in table 2. Since amounts of nickel adsorbed by the filter could affect the results, sorption of solute on the filter was evaluated by using blank solutions (without adsorbent) and the average amount of absorbed nickel by the filter was estimated to be 2.66 mg/l. this amount was subtracted from obtained results to eliminate the filter adsorption effect.

Two general ways of uptake of Ni^{2+} in solutions are supposed. One way need not to absorbent materials (precipitation method) and other way need to absorbent materials such as $CaAl_2Si_2O_8$ (cation exchange and absorption). In first way to eliminate heavy metals such as nickel in a solution is to increase the pH which results in precipitation of nickel hydroxides. For precipitation of nickel hydroxides pH of higher than 8 is reported to be suitable [6]. Since the final pH of samples with numbers of 1-4 are

Table 2. residual nickel ion concentration and pH of the samples after 24 h contact between the adsorbent and nickel chloride solution.

Sample	Calcination temperature (°C)	Calcination time (h)	Millimng time (h)	Main phase	Final pH	Initial concentration of nickel in the solution (mg/l)	Residual nickel concentration (mg/l)
1	850	8	0	amorphous	9.85	40	3.76
2	850	24	0	amorphous	9.30	40	5.20
3	900	8	0	gehlenite	8.23	40	3.82
4	900	24	0	gehlenite	8.47	40	4.07
5	800	8	12	amorphous	7.13	40	7.83
6	800	24	12	amorphous	6.92	40	5.70
7	900	8	12	anorthite	6.96	40	15.04
8	900	24	12	anorthite	6.74	40	24.20

Fig. 3. FTIR spectra of sample 6 a) before and b) after absorption.

calcinations temperature (900) have anorthite stable phase (Nos. 7,8) and haven't suitable for Ni^{2+} uptake. The Ni^{2+} uptakes were 80.4% and 85.7% in the amorphous samples 5 and 6 respectively. Nickel uptake was higher in samples 2, 3, 4 and 6 compared to other samples. Sample 6 was selected to investigate precisely nickel uptake mechanism by FTIR spectra. Iqbal et al. [12] studied Cd^{2+} and Pb^{2+} uptake on mango peel waste and observed a shift in some of the FTIR peaks after ion uptake. Fig. 3 shows the difference in the FTIR pattern before and after nickel uptake especially over the $460 – 500$ cm^{-1} region. However, to understand the uptake mechanism more investigation is needed. Okada et al. [6] noted that in 10-2M Ni^{2+} concentration solution probably low crystallinity Ni-bearing phases such as nickel hydroxide, layered double hydroxide (Ni-Al-OH), nickel phyllosilicate formed by precipitation in amorphous $CaAl_2Si_2O_8$ sample but in 10-3M Ni^{2+} surface chemical composition from $CaAl_2Si_2O_8$ altered to $(Ca, Ni)Al_2Si_2O_8$. This change can be motive the alteration of FTIR pattern after Ni^{2+} uptake (Fig. 3).

3. 2. 2. Quantitative Evaluation of Adsorption

Various models including Freundlich, Langmuir and Dubinin-Kaganner-Radushkevich (DKR) are applied for the assessment of uptake experiment results. In all of these models, an estimation of the nickel uptake in different initial nickel concentration is necessary to measure Q (the amount of adsorbed ion per unit mass) in the equilibrium state.

above 8, uptake by these samples occur by a precipitation mechanism and for other samples (Nos. 5-8) attributed to cation exchange of Ca^{2+} by Ni^{2+} and/or absorption of Na^{+2} cations because final pH of their solutions. Therefore for absorption mechanism study we need to samples that milled for 12h and calcined at 800°C for 8 or 24 hours calcination times (samples 5,6) with amorphous structure. Milled samples with above

Table 3. Cation uptake results at different initial nickel ion concentration.

Sample	Initial nickel ion concentration (mg/l)	Nickel ion concentration at equilibrium (mg/l)	Equilibrium Q (mg/g)
1	30	2.28	13.86
2	40	5.28	17.36
3	50	12.01	18.99
4	60	18.27	20.86
5	70	29.36	20.32

Therefore, five 50 ml solutions with different nickel concentration of 30, 40, 50, 60 and 70 mg/l were prepared, respectively. 0.1 g of sample 6 was added to each solution and was mixed at 100 rpm rate for 24 h. Table 3 lists the uptake results.

The empirical form of the Freundlich isotherm equation is applicable to monolayer adsorption (chemisorption) and multilayer adsorption (van der Waals adsorption) and is given by Eq. 1 or 2 [1]:

$$Q = K_f \times C^{1/n} \tag{1}$$

$$\ln Q = \ln K_f + 1/n \ln C \tag{2}$$

Where Q (mg/g) is the absorbed amount of metal ions at equilibrium, C (mg/L) is the equilibrium concentration of the metal ion in the solution and n and K are the Freundlich constants.

Another adsorption isotherm which is applicable to the studied samples in this work is Langmuir isotherm which assumes that the removal of metal ion occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The maximum adsorption capacity Q_0 (mg/g) and enthalpy of sorption b (l/mg) values of the samples are found from straight line plots of C_e/Q_e versus C_e using the following equation [1,7], where C_e is the equilibrium concentration of metal in solution (mg/l), Q_e is the amount absorbed at equilibrium onto sample.

$$C_e/Q_e = 1/(Q_0 b) + C_e/Q_0 \tag{3}$$

Langmuir and Freundlich isotherms were applied to the data to determine the adsorption type. In chemical adsorption, one layer of the ions forms on the surface of the adsorbent while in physical adsorption multilayer adsorption of the adsorbate occurs on the surface[13].

Figs. 4, 5 demonstrate Freundlich and

Fig. 4. Freundlich plot for adsorption of Ni at 20 °C.

Fig. 5. Langmuir plot for adsorption of Ni at 20 ℃.

Table 4. A comparison between Langmuir parameters of the present study with that of other researches.

Adsorbent	Langmuir isotherm parameters		
	Q_0 (mg/g)	b(l/mg)	R^2
fly ash [3]	0.59	-	-
Granular activated carbon [3]	1.70	-	-
Clinoptilolite [3]	2.37	-	-
Ca–bentonite [3]	6.53	-	-
Clay treated with HCl [3]	11.27	-	-
Natural clay [3]	12.36	-	-
Clay treated with NaCl [3]	14.84	-	-
Red mud [3]	15.43	-	-
Na–bentonite [3]	24	-	-
Present work	21.37	0.85	0.9984
Amorphous $CaAl_2Si_2O_8$ [6]	29	-	-
hydroxyapatite [13]	40	-	0.986

Langmuir isotherms drawn on the bases of the data in table 2. Regression coefficients of the two straight lines were compared to decide between the two adsorption isotherms. Regression coefficients of 0.909 and 0.9984 were obtained for Freundlich and Langmuir isotherms, respectively. Thus, Langmuir isotherm was selected for adsorption description. Based on this model, the uptake of Ni^{2+} ions on the surface of sample 6 was of monolayer type. Thus the occurrence of chemical reaction and ion exchange is quite possible.

Table 4 lists different parameters of Langmuir isotherm of this study in comparison with those obtained by other researchers. Nickel is studied as the contaminating metal in all of the researches provided in Table 3 as otherwise different metal ions could affect the results. For instance the maximum adsorbed amount Q_0 of the contaminating metal of Ni was found to be 40 mg/g for nano hydroxyapatite that prepared from high cost chemical method. [14]. The uptake of Ni^{2+} by amorphous low cost $CaAl_2Si_2O_8$

synthesize in this work are very good in comparison with other similar materials.

Freundlich and Langmuir models do not predict adsorption mechanism directly, nor do they determine reversibility of a reaction. These models do not even distinguish between chemical or physical sorptions. In order to distinguish between physical and chemical adsorption the data was subjected to the DKR isotherm model which is expressed as: [14,15]

$$\ln Q_e = \ln X_m - \beta \varepsilon^2 \tag{4}$$

Where Q_e is the number of metal ions absorbed per unit weight of absorbent, X_m is the maximum adsorption capacity in mol/g or mg/g, β (mol^2/J^2) is the activity coefficient related to mean sorption energy and **ε** is Polanyi potential which is calculated through the following equation:

$$\varepsilon = RT \ln(1 + 1/C_e) \tag{5}$$

Where R is the gas constant, T is absolute

Fig. 6. DKR isotherm for sorption of Ni at 20 ℃.

temperature in Kelvin and C_e (mol/l) is the equilibrium concentration. β and $\ln X_m$ are the slope and intercept in the diagram of $\ln Q_e$ as a function of ε^2, respectively. The advantage of this model with respect to the two above mentioned ones is that it helps understand the sorption mechanism as a function of sorption energy. This energy can be calculated through the following relation [14,15]:

$$E = 1/\sqrt{-2\beta} \qquad (6)$$

Sorption energy of 8 kJ/mol and below is assigned to physical sorption. On the energy range of 8-16 kJ/mol, ion exchange occurs and sorption energy higher than 16 kJ/mol is attributed to chemical sorption [15].

Regarding the above mentioned relations, $\ln Q_e$ was drawn as a function of ε^2 (Fig. 6). β and $\ln X_m$ was measured as the slope and intercept of the diagram, respectively and sorption energy was estimated to be 22.36 kJ/mol. Thus, sorption mechanism in amorphous sample is possibly chemical. Ion exchange in the adsorbent is a beneficial aspect in case we need the contaminating ion to be separated.

The maximum amount of adsorbed metal calculated through the DKR model is 35.60 mg/g which is higher than that of measured by Langmuir model (21.37 mg/g). However, this is more common in the literature to report maximum adsorbed amount of Langmuir model.

Fig. 6 indicates that regression coefficient (R^2) in the DKR model was equal to 0.9293 which is higher than that of Freundlich model and is lower than that of Langmuir model. Therefore, Langmuir and DKR isotherms provide more reliable information about the adsorption process in this study.

4. CONCLUSION

Alkaline aluminosilicates were prepared using kaolinite and calcite as starting materials. Milling the samples by a planetary mill prior to calcination resulted in the reduction of crystallization temperature. Moreover, milling contributed to the formation of an amorphous structure which is favorable from adsorption point of view.

FTIR analysis hardly helped understand sorption mechanisms. Therefore, adsorption isotherms were studied instead. Studying different models including Langmuir, Freundlich and DKR revealed that the adsorption mechanism of nickel ions on the adsorbent after 24 h is as of chemical and irreversible reactions. A comparison of the present study with other researches in the assessment of the sorption capacity showed that Langmuir model is suitable for this evaluation. This model measured the adsorption capacity as 21.37 mg/g which is higher than that of some zeolites such as clinoptiloite[3]. DKR model estimated the adsorption energy of nickel on the adsorbent to be 22.36 kJ/mol which undergoes stronger reactions than mere ion exchange; i. e. chemical reaction.

REFERENCES

1. Jha, V. K., Kameshima, Y., Nakajima, A., Okada, K.; MacKenzie,"Uptake properties of Ni^{2+} by $nCaO•Al_2O_3•2SiO_2$ (n = 1–4) prepared from solid-state reaction of kaolinite and calcite", K. J. D. J. Hazardous Mater. 2005, B123, 281-287.

2. Hosseini, A. A., Sadigzadeh, A., Mohammadi, S., Soltani, R., "Fabrication and characterization of high performance ceramic membrane having nanometer pores", (2011), 8(3), 17-22.

3. O'Connell, D. W., Birkinshaw, C., and O'Dwyer, T. F.,"Heavy Metal Adsorbents prepared from the modification of Cellulose : A Review", Bioresour. Technol., (2008), 99, 6709–6724.

4. Okada, K., Arai, H., Kameshima, Y., Yasumori A., and MacKenzie, K. J. D., "Uptake of various cations by amorphous $BaAl_2Si_2O_8$ prepared by solid-state reaction of kaolin with $BaCO_3$" Mater. Lett., (2003), 57, 3554–3559.

5. Kazemimoghadam, M., Mohammad, T., "Preparation of nano pore mordenite membranes ", IJMSE, (2011), 8(1), 19-24.

6. Al-Anber, Z. A., Al-Anber, M. A. S., Mex, "Thermodynamics and kinetic studies of iron (III) adsorption by olive cake in a batch system", J. Chem. Soc., (2008), 52(2), 108-115.

7. Kingery, W. D., Brown, H. K., Uhlmann, D. R., "Introduction to Ceramics", Wiley publication, 1975.

8. Soleimani, M. A., Naghizadeh, R., Mirhabibi, A. R., Golestanifard, F., " Effect of calcination temperature of the kaolin and molar Na_2O/SiO_2 activator ratio on physical and microstructural properties of metakaolin based geopolymers". IJMSE, (2012), 9(4), 43-45.

9. Okada, K., Watanabe, N., Jha, V. K., Kameshima, Y., Yasumoria, A., and MacKenzie, K. J. D.," Uptake of various cations by amorphous $CaAl_2Si_2O_8$ prepared by solid-state reaction of kaolinite with $CaCO_3$" J. Mater. Chem., (2003), 13, 550–556.

10. Okada, K., Shimazu, M., Kameshima, Y., Nakajima, A., MacKenzie, K. J. D., " Simultaneous uptake of Ni^{2+}, NH^{+4} and PO_3^{-4} by amorphous $CaO–Al_2O_3–SiO_2$ compounds", J. Colloid Interface Sci., (2007), 305, 229–238.

11. Okada, K., Nemoto, M., Kameshima, Y.,Yasumori, A.,"Uptake of Various Cations by Imperfectly Ordered $KAlSiO_4$ Prepared by Solid-State Reaction of Kaolinite and K_2CO_3". J. Ceram. Soc. Jpn., (2000), 108(10), 898-903.

12. Iqbala, M., Saeeda, A., Zafar, S. I.,"FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd(2+) and Pb(2+) removal by mango peel waste. Hazard, J., Mater., (2009),164, 161–171.

13. Yang, C.,"Statistical Mechanical Study on the Freundlich Isotherm Equation", J. Colloid &Interface Sci., (1998), 208, 379–387.

14. Mobasherpour, I., salahi, E., Pazouki, M., Arabian, J. Chem, " Comparative of the removal of Pb^{2+}, Cd^{2+} and Ni^{2+} by nano crystallite hydroxyapatite from aqueous solutions: Adsorption isotherm study", Arabian Journal of Chemistry, (2012), 5, 439-446.

15. Shen, S., Pan, T., Liu, X., Yuan, L., Zhang, Y., Wanga, J., Guo, Z., "Adsorption of Pd(II) complexes from chloride solutions obtained by leaching chlorinated spent automotive catalysts on ion exchange resin Diaion WA21J", J. Colloid Interface Sci., (2010), 345 12–18.

16. Traore, K., Kabre, T. S., Blanchart, P., " Gehlenite and anorthite crystallisation from kaolinite and calcite Mix", Ceramic internation, (2003), 29, 377-383.