Predominant mechanisms for the removal of nickel metal ion from aqueous solution using cement kiln dust

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Abstract: The experimental methodology achieved in the present study signified that the adsorption and precipitation were mainly mechanisms occurred together in the removal of nickel from aqueous solutions by sorption using cement kiln dust (CKD) byproduct as sorbent. Finding the contribution of each mechanism in the removal process and derivation an analytical model for finding the portion of precipitation were the focal points of this work. Results proved that the pure precipitation was increased with the increase of CKD dosage and metal concentration where total removal (adsorption-precipitation) ranged from 45 to 100%. The SEM micrographs of the CKD sorbent before and after sorption process certified that there was a crystal precipitates on the surface of the CKD. Also, these graphs in combination with FT-IR tests proved that $[Ni(OH_2)^n]^{+2}$ (n=4-6) species were bonded with CKD and insoluble hydroxide species may be precipitated onto the CaO surfaces by co-precipitation, while K-O, Si-O and Ca-O groups enhanced the adsorption mechanism.

Declarations of interest: none.

1. Introduction

Tremendous industrial and economic developments give rise to produce massive quantities of different construction materials worldwide [1]. Portland cement is one of the fundamental materials in construction industry [2]. During production processes of cement clinker, cement kiln dust (CKD) is resulted as a by-product waste solid in form of particulate mixture of dust with incompletely calcined and unreacted raw materials (clay, limestone, iron ore, and silica), ash, augmented with alkali sulfates, halides, and other volatiles [3,4]. Typically, CKD is generated at the central process stage of intermediate cement clinker production when the raw inorganic substances burn at temperatures around 1500°C [5]. In general, CKD is removed from the cement kiln exhaust gases by scrubbers and/or electrostatic precipitators which are generally composed of micron-sized particles. Therefore, CKD is defined as a heterogeneous by-product dust with fine-grained solid of highly alkaline constituent with mineralogical–based composition resources of carbonate from limestone component and other raw materials of acid as clay component [6,7].

Disposal of huge quantities of CKD has been recognized as a problematical issue in terms of economic, environmental and public health considerations. The annual created CKD amount about fifteen million tons in the United States in production of around a hundred million tons of cement, however, the estimated international annual quantity of by-product CKD in 2006 was about 2.5 billion tons as mentioned in the previous studies [1–4]. In Iraq, about two million tons of Portland cement produced annually from fifteen cement factories generated more than 350,000 tons of CKD. In Oman, the annual amount of produced CKD from Oman Cement Company has been accounted about 25,000 tons [8]. The cement productions in Saudi Arabia, Yemen and Egypt have reached around 20-30 million tons per year, with corresponding creation

of CKD about 1.4, 2.0 and 3.0 million tons per year, respectively [9–11]. Although, the figures on CKD production could not be exactly, but this significant amount of CKD can aggravate the environment [11].

Nowadays, recycle of industrial waste products such as CKD has been successively practiced in alleviate the engineering and environmental challenges in sustainable and economic strategies [2]. Since, the CKD is classified as non-hazardous by-product waste solid [12]. Although, some of applications unaccepted elevated levels of alkali substances such as agricultural landfill and reinforced concrete structures [8]. However, CKD has been utilized in several purposes such as in the United States where approximately 60% of the total produced CKD returned to cement manufacturing after further process [6]. In the last decades, considerable researches have been focused on the reuse of CKD for the treatment of industrial wastes and wastewater, cement enhancement, asphalt pavement, soil stabilization and landfill which have significant environmental and financial benefits [2,6,8,11]. An attempt has been directed towards re-engineering the CKD in production of a high-quality, sustainable and eco-friendly alternative materials to be reused as an adsorbent for removal of inorganic dissolved contaminants, such as heavy metals from water and groundwater [13–15], [16], [17].

Industrial and mining activities can be caused a serious contamination for surface water and groundwater resources due to spillage of inorganic/organic contaminants like copper, lead, cadmium, nickel, dyes and other trace elements [18], [19], [20], [21]. These metals are considered toxic elements for components of ecosystem and, contrast to organic pollutants, heavy metals can be removed from contaminated water by separation or converted to chemically inert state [22], [23]. Suitability of alkaline substances for adsorption, stabilization and solidification of heavy metals essentially

appears when react chemically to produce less soluble compounds as hydroxides and silicates of heavy metals [24].

Legislation has been introduced strictly to manage the water pollution especially from industrial wastewater before disposal to water body. Risk of heavy metals accumulation in biological system could be minimized the metal concentration effects for the potential long-term contamination. Since, compounds of some heavy metals such as nickel are recognized as human carcinogens [25], [26]. Where, a little concentration of accumulated nickel ion could cause dangerous symptoms, diseases and irregular angiogenesis through enhancing the peroxidation of lipid followed by decreasing in glutathione peroxidase and increasing the biological activity of iron in tissues producing lung and nasal cancer [27]. In the nature, contamination with nickel occurred typically through supplies of the groundwater from chalk aquifers as in the south-western Sweden and Denmark, where nickel can be found as a solid solution in pyrite nodules. Nickel ions are released with concentration ranged from 40×10^{-5} to 140×10^{-5} mol of Ni/mol of pyrite due to oxidize of pyrite with drawdown of the water table [28,29].

Concentrations of nickel in the groundwater system can vary from barely detectable to a few hundred ppm which will greater than the Danish acceptable limit and the World Health Organization (WHO) recommended value of 0.02 mg/L. Anthropogenic contamination mostly results from the industrial activities through the production or usage of nickel in the manufacturing process. Also, degradation of radioactive waste repositories in the long time scale can be caused a secondary contamination. ^{59}Ni and ^{63}Ni are resulted from neutron activation of ^{58}Ni and ^{62}Ni (naturally occurring and stable isotopes) in the steel structures and internal constituents of nuclear reactor vessels. These radionuclides represent important

activation products and more active from the other activation products. Moreover, spent fuel rods can be disposed within stainless-steel containers and, beyond the decay of the waste, the containers would become radioactive and corrosion could risk release to the ecosystem [29,30].

Practically, there are several techniques used for treatment of the water contaminated with metal ions such as chemical precipitation, ion exchange, solvent extraction, air flotation, adsorption and membrane filtration [31], [32–34]. These two mechanisms are adsorption/desorption and precipitation/dissolution. The last one is the predominant in the long time scale especially the metal ions can be incorporated with the structure of the CKD and this has great role in the inhibition of re-entrance of metals to the groundwater. Previous studies for interaction of CKD and heavy metals are divided mainly into three categories. The first one assumed that the CKD is behaved as adsorbent material and its oxides components as well as the fine texture can be the control concept for pure adsorption process within certain values of pH. The second category proved that the pure adsorption is not accurate description for interaction of CKD and heavy metals because this interaction can be changed as a function of pH due to the presence of lime in CKD with high percentage. This means that the pH of the contaminated water may be raised and, consequently, the hydroxides of the metals can be generated. Accordingly, the studies of this category assumed that the pure precipitation is the predominant mechanism in the removal process [35,36]. Finally, the studies in the last category don't recognized between the mechanisms that are responsible of contaminants removal due to their interactions with CKD and it is just the removal regardless the contribution of adsorption and precipitation mechanisms [27].

Unfortunately, there is an obvious gap in the previous literatures about the more predominant mechanism and finding the contribution of each mechanism in the removal process. Derivation of a mathematical expression for representing the total sorption in combination with the role of each mechanism described previously when occurs simultaneously is a unique task that will play a significant role in the filling of this gap. This expression can be used effectively for determining the value of retardation factor that has a potential effect in the plotting the front of the contaminant plume through the migration of contaminated water in the subsurface environment. Hence, the focal point of the present study was derived an analytical model for formulating simultaneous sorption–precipitation mechanisms and finding the quantity of contaminant removed by each mechanism. Distinguishing between these mechanisms was conducted through the applied of derived model on the set of experimental data measured from the interactions of nickel and CKD under different operational conditions.

2. Mathematical description of sorption-precipitation mechanisms

The principle derivation of analytical model for description the sorption-precipitation mechanisms is based on the representation of the total removal and the precipitation processes. The difference between the two processes can be represented the sorption process and the step wise of operation manner can be adopted in the derivation of the model as follows [37]:

Precipitation by metal (M) hydrolysis

$$X_2O + H_2O \rightarrow 2X(OH) \tag{1}$$

$$MSO_4 + 2X(OH) \rightarrow M(OH)_2\downarrow + X_2SO_4 \tag{2}$$
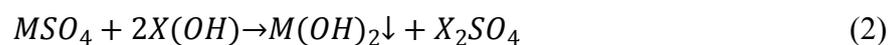
Where, X: K or Na, and M: Cu or Zn

The metal ions removed from aqueous solution, R_p, because of pure precipitation can be calculated [38]:

$$R_p = \frac{(C_o - C_p)}{C_o} * 100\% \tag{3}$$

Where, C_o is the initial concentration of metal ions in the solution (mg/L), C_p is the remaining concentration of metal ions in the solution (mg/L) after precipitation. Sorption of metal ions onto CKD particle is written as:

$$M(OH)_n^{+m} + CKD \rightarrow CKD - \{M(OH)_n^{+m}\} \tag{4}$$
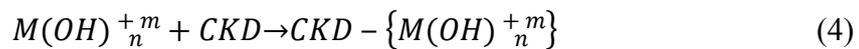
The retained of metal ions in the CKD phase, R_{sr}, because of pure sorption can be calculated [38]:

$$R_{sr} = \frac{(C_o - C_{sr})}{C_o} * 100\% \tag{5}$$

Where, C_{sr} is the concentration of metal ions remaining in the solution (mg/L) after sorption. The total removal (R) by sorption-precipitation processes can be calculated by following equation:

$$R = \frac{(C_o - C_t)}{C_o} * 100\% \tag{6}$$

Where, C_t is the concentration of metal ions remaining in the solution (mg/L) at time t (min). Also, the value of R can be calculated from the summation of the metal ions retained by sorption (Eq. (5)) and removed by precipitation (Eq. (3)) as follows:

$$R = R_{sr} + R_p \tag{7}$$

$$\frac{(C_o - C_t)}{C_o} * 100\% = \frac{(C_o - C_{sr})}{C_o} * 100\% + \frac{(C_o - C_p)}{C_o} * 100\%$$

$$(C_o - C_t) = (C_o - C_{sr}) + (C_o - C_p)$$

$$(C_o - C_{sr}) = (C_o - C_p) - (C_o - C_t)$$

$$C_{sr} = C_o - C_t + C_p \tag{8}$$

Substituting of Eq. (8) into Eq. (5), the final equation will be:

$$R_{sr} = \frac{(C_t - C_p)}{C_o} * 100\% \qquad (9)$$

The description of dissolved contaminant in the column packed with reactive material as in the many applications of industrial wastewater treatment or migration of this contaminant in the subsurface environment can be achieved by applying advection-dispersion equation. The one main variable appeared in this equation beside the advection and hydrodynamic dispersion is the source/sink. The sink item in the transport of contaminant in the porous medium is the quantity of dissolved contaminant removed from aqueous solution and adsorbed on the solid particles. Accordingly, it is very important to separate between the quantities of contaminant removed by adsorption and precipitation because the proportion of first mechanism can be incorporated with solute transport equation for describing the value of retardation factor. This factor is the main core for representing the transport of reactive contaminant and this represents the focal point for the present study. Consequently, the developed model can be used in the future studies for finding the effect of retardation factor on the distribution of contaminant. In addition, this model can be incorporated with solute transport codes such as COMSOL Multiphysics software and it is inserted as default option beside the Langmuir and Freundlich models. The modification of COMSOL software aims to find the spatially and temporally propagation of the contaminant front which can be very helpful in the protection of water resources through the estimation the time required to reach for these resources and, accordingly, the remedial program that must be adopted.

3. Material and methods

3.1. Mediums and contaminants

The CKD is collected from Al-Kufa cement factory, Al-Najaf city, Iraq (Latitude: 31°57'44.81"; Longitude: 44°25'59.89") and batch experiments were

applied to test its ability in the removal of nickel from aqueous solution. The primary reason for selection of CKD was the composition of this material that contained a high percentage of CaO. This constituent (= 46.25%) can be caused a dramatic change in the status of the aqueous solution from acidic to basic state depended on the quantity of added CKD. This is very important for evaluation of the mechanism responsible of the removal process when sorption–precipitation occur together. However, the composition test for four different batch samples proved that there were SiO_2, Al_2O_3, Fe_2O_3, MgO, and SO_3 with average values of 11.72, 3.82, 2.76, 2.49, 11.05%, respectively. The chemical constituents of the CKD composition mentioned previously such as CaO and others were measured by X-ray fluorescence.

Nickel was selected as representatives of heavy metal contaminants. To simulate the water's Ni^{+2} contamination, a solution of $Ni(NO_3)_2.6H_2O$ (manufactured by SD Fine-Chem. Limited, India) was prepared and dilution was applied to prepare the required concentration.

3.2. Batch experiments for sorption and precipitation processes

Batch experiments were conducted to measure the pure precipitation and total removal (sorption-precipitation) mechanisms under different values of contaminant concentrations and CKD dosages. A series of 250 mL conical-flasks were employed, and each flask was filled with 50 mL of solution contaminated with nickel (Ni^{+2}) at pH 3. The total (sorption–precipitation) mechanisms were investigated with different values of dosage (0.03, 0.1, 0.5, 1, 2, 3 and 5 g CKD/50 mL) of contaminated solution and different prepared values of initial concentrations of contaminant (1, 10, 50, 100, 500 and 1000 mg Ni^{+2} /L). On set of 7 flasks contained 50 mL of contaminated solution of 1 mg Ni/L, each flask got a single dosage of 0.03, 0.1, 0.5, 1, 2, 3 and 5 g of CKD, and the same test strategy was operated for contaminated solutions of

concentrations 10, 50, 100, 500 and 1000 mg Ni/L. The solution in each flask was kept stirred on a high-speed orbital shaker at 200 rpm for 4 h to obtain equilibrium state.

Pure precipitation mechanism was studied by adding different quantities of CKD into 50 mL of acidic clear water (pH = 3) and the solution was kept stirred at high-speed (200 rpm) using orbital shaker for 4 h. Then, separation of CKD particles from aqueous solution was achieved by filtration using "tea-bag" procedure [39]. The clear solution was mixed with the Ni^{+2} solution for 4 h and the resultant solution was filtered using filter paper type (Wattmann No. 1). The nickel concentration still present in the filtered solution was measured by using atomic absorption spectrophotometer (AAS) (AA-7000 Shimadzu, Japan). The pH meter (WTW, Bench model, German) was used to measure the pH of the aqueous solutions at each step of the applied processes and the same conditions of the total sorption (sorption-precipitation) can be applied. However, the concentration of precipitated contaminant was determined by the mass balance. The initial concentration of nickel was achieved by addition the certain quantity of the nickel salt to 5 mL of the solution, while the "tea bag" test was completed with 45 mL of the sample. The 50 mL (summation of two previous solutions) of CKD-pretreated solution will be contaminated with the required initial concentration of nickel ions.

4. Results and discussion

4.1. Influence of contact time and initial metal concentration

To establish the equilibrium time for sorption-precipitation of Ni^{+2}- contaminated water by certain dosage of CKD, influence of contact time over the process evolution was investigated until achieved the equilibrium. Fig. 1 proved that the removal efficiency was increased rapidly in the first 50 min either due to the formation of

Ni(OH)$_2$ or the removal by surface of CKD (as a result of adsorption/co-precipitation), however, gradually decrease was recognized up to 120 min. Additional increase in contact time was not enhanced the sorption-precipitation process. For practical reasons, the equilibrium contact time was extended to be 360 min for further experiments to ensure that the processes responsible of metal removal arrived at equilibrium status regardless the variation of other operation conditions.

4.2. Batch equilibrium studies

Fig. 2 shows the influence of CKD dosages on the removal efficiencies of nickel ions and final pH of aqueous solution at different values of concentration. The more than 80% of contaminant could be removed from the aqueous solution with CKD quantity of greater than 3 g for 50 mL. Also, Fig. 2 (b) signified that the high quantity of CKD has a significant effect on the pH of the water and it is increased from 3 (acidic) to reach 10.8 (basic) at dosage of 2 g/50 mL for water contaminated with low concentration. Values of final pH for interaction of contaminated water with sorbent material were almost constant between 10.8 and 11 as the weights of CKD increased beyond 2 g/50 mL and this means that the solution had reached to its saturation value [40,41]. Increase in pH (alkaline condition) may be due to the high quantity of CKD (i.e. high amount of quicklime content (CaO) and this can play a significant role in the change of the solution status towards the alkalinity (Eqs. (10 & 11)). This result is consistent with previous studies [42,43].

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{10}$$

$$Ca(OH)_2 \leftrightarrow Ca^{+2} + 2OH^{-1} \tag{11}$$
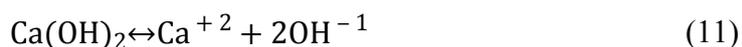
The high concentration of nickel ions (1000 mg/L) has low pH in comparison with other aqueous solutions (Fig. 2) and this may be due to consume of hydroxide ions ($2Ni^{+2} + OH^{-1} \rightarrow Ni(OH)_2$). However, the low concentration of metal ions (1

mg/L) can be caused an increase in the final pH to be identical for control water (i.e. uncontaminated water) because the nickel hydroxide precipitation will not be the predominant. Fig. 3 shows the variation of removal efficiencies of contaminant by pure precipitation mechanism and the increase of CKD mass will enhance the removal percentage due to high amount of quicklime dissolved in water.

4.3. Predominant mechanisms

The results of pure precipitation (Fig. 3) showed that there was a lag in nickel removal by pure precipitation for high concentrations; specifically, 100 and 1000 mg/L in comparison with contaminant removed by total sorption–precipitation (Fig. 2 (a)). This can be attributed to the direct contact between the sorbent and contaminant in the total sorption–precipitation case. This will increase the probability of attachment of metal ion (or hydroxide ion) to the CKD sorbent and this result agrees with Sulaymon et al. in 2017 [14]. Fig. 4 is a histogram plot drawn the portion of metal ions removed due to pure sorption onto CKD. This portion can be calculated by applying Eqs. (8 & 9) in conjunction with measured values of total sorption–precipitation and precipitation portion described previously. This figure signified that the total sorption–precipitation and portion of pure sorption were increased with increasing of sorbent dosage. The results showed that the pure precipitation was the predominant for high concentrations of metal ions; conversely, the predominant mechanism will be pure sorption for low concentrations. This result is consistent with results of Aziz et al. in 2008 [40], but not in agreement with Sulaymon et al. in 2017 [14].

4.4. Identification of removal mechanisms

The fact that the CKD gives the highest removal of heavy metals from aqueous solutions can be attributed to the two mechanisms. The first mechanism is the rough

surface of the sorbent which can be resulted in the chemi-sorption process at low metal concentrations and this is in line with various workers such as [44,45]. The second mechanism is resulted from the presence of dissolved calcium oxide which increase the pH of the solution above the solubility point and metals would be precipitated as metals hydroxide, however, these results are consistent with study of Liu et al. in 2016 [46] on manganese.

The SEM micrographs of the CKD sorbent before and after nickel sorption at initial pH of 3, initial metal concentration of 1000 mg/L and sorbent dosage of 5g /50 mL are illustrated in Fig. 5. By magnification of the graph resulted from the contact of CKD and nickel ions, it can be observed that there is a crystal precipitates on the surface of the CKD. Precipitation of the metal hydroxides is also possible; generally, metal become insoluble at higher pH values and this is in compatible with Aziz et al. in 2008 [40].

FT-IR test was conducted for one CKD sample before contact with contaminated water and two others after the interaction with 1 and 1000 mg/L solution which corresponded to the low and high concentrations respectively as shown in Fig. 6. The broad bands at high frequency (3580–3400 cm^{-1}) indicate the presence of hydroxyl groups [47,48], [49–52]. The vibration frequencies proved that [Ni $(OH_2)^n$] $^{+2}$ (n=4 - 6) complexes are scaled by 0.96 as suggested by Scott and Radom 1996 [53] and Curtiss et al. in 1997 [54]. According to the IR spectra for formed complexes, there were two main bands of the vibration transitions. The first one, in the 2700 - 3100 and 1000 - 1100 cm^{-1} region for the four-, five- and six-coordinated complexes respectively, involves the symmetric where vibrations are recognized to shift for higher wavenumbers due to increase the coordination number of the complexes. In the range of (600-800 cm^{-1}), the second band can be observed and it is contained Ni-O-H

group. Thus, distinguishing the coordination geometry of the $[Ni (OH_2)^n]^{+2}$ (n=4-6) complexes can be achieved by the position of IR bands. IR spectra elucidate that there is an extra characteristic sharp band at 1384 cm^{-1} associated with the δ(OH) stretching vibrations of metal hydroxides and/or oxyhydroxides [32,55]. The results of this test certified that the adsorption and co-precipitation are the main mechanisms responsible of nickel retention on the CKD sorbent where poly-nuclear / mono-nuclear insoluble hydroxide species can be bonded to the CaO surfaces by co-precipitation. Also, the shifts in the IR frequencies certified that K-O, Si-O and Ca-O groups within wavelengths ranged from 590 to 830 cm^{-1} are responsible for the adsorption of nickel onto CKD.

5. Conclusions

The results signified that the removal of nickel ions using CKD sorbent was achieved primarily by two mechanisms; namely sorption and precipitation. These two mechanisms occurred simultaneously and finding a procedure for separation between them were a unique task. This study was presented an experimental procedure for evaluation the total removal of nickel due to sorption–precipitation and share of nickel removed by pure precipitation, however, these measurements in conjunction with derived analytical model was used to predict the proportion of pure sorption. The results proved that the sorptive mechanism was an important component of the total sorption–precipitation which was increased due to the increase of reactive material and decrease of metal concentration. The other task was finding the mechanisms of sorption responsible of nickel removal onto CKD sorbent and this was achieved through the SEM and FT-IR tests. These tests proved that the adsorption and co-precipitation were main mechanisms that occurred together in the removal of nickel by sorption. FT-IR results proved that the most species to be chemisorbed on the

surface of CKD was $[Ni(OH_2)^n]^{+2}$ (n=4-6). Poly-nuclear and/or mononuclear insoluble hydroxide species could be bonded to the CKD sorbent by co-precipitation, while the adsorption process might be occurred through the shifts in the K-O, Si-O and Ca-O groups.

Acknowledgement

References

[1]   EPA, Cement Kiln Dust (CKD): Materials Characterization Paper, in Support of the Advanced Notice of Proposed Rulemaking–Identification of Non–hazardous Materials that are Solid Waste, 2008.

[2]   A.M. Mosa, A.H. Taher, L.A. Al-Jaberi, Improvement of poor subgrade soils using cement kiln dust, Case Stud. Constr. Mater. 7 (2017) 138–143. doi:10.1016/j.cscm.2017.06.005.

[3]   R. Siddique, Utilization of cement kiln dust (CKD) in cement mortar and concrete-an overview, Resour. Conserv. Recycl. 48 (2006) 315–338. doi:10.1016/j.resconrec.2006.03.010.

[4]   W.S. Adaska, D.H. Taubert, Beneficial uses of cement kiln dust, in: IEEE Cem. Ind. Tech. Conf., 2008: pp. 210–228. doi:10.1109/CITCON.2008.24.

[5]   A. Cipurkovic, I. Trumic, Z. Hodžic, V. Selimbašic, A. Djozic, Distribution of heavy metals in Portland cement production process, Adv. Appl. Sci. Res. 5 (2014) 252–259.

[6]   EPA, Appendix a summaries of state guidelines and regulations on reuse of industrial by-products, 2002.

[7]   Van Oss, Cement. Technical report., US Geological Survey, Washington, DC, 2012.

[8]   W. Alnahhal, R. Taha, H. Al-Nasseri, S. Nishad, Effect of Using Cement Kiln Dust as a Nano-Material on the Strength of Cement Mortars, KSCE J. Civ. Eng. 22 (2018) 1361–1368. doi:10.1007/s12205-017-0010-6.

[9]   T.O. Al-Refeai, A.A. Al-Karni, Experimental Study on the Utilization of Cement Kiln Dust for Ground Modification, J. King Saud Univ. - Eng. Sci. 11 (1999) 217–231. doi:10.1016/S1018-3639(18)30999-1.

[10] M.E.S.I. Saraya, M.E.S. Aboul-Fetouh, Utilization from cement kiln dust in removal of acid dyes, Am. J. Environ. Sci. 8 (2012) 16–24.

[11] K.M. Hussein, E. Ahmed, Formulation of the cement kiln dust (CKD) in concrete: Studies of the physical-chemical and mechanical properties, Int. J. ChemTech Res. 9 (2016) 695–704.

[12] Z.A. Baghdadi, M.N. Fatani, N.A. Sabban, Soil modification by cement kiln dust, J. Mater. Civ. Eng. 7 (1995) 218–222. doi:10.1061/(ASCE)0899-1561(1995)7:4(218).

[13] A.H. Sulaymon, A.A.H. Faisal, Q.M. Khaliefa, Cement kiln dust (CKD)-filter sand permeable reactive barrier for the removal of Cu(II) and Zn(II) from simulated acidic groundwater, J. Hazard. Mater. 297 (2015) 160–172. doi:10.1016/j.jhazmat.2015.04.061.

[14] A.H. Sulaymon, A.A.H. Faisal, Q.M. Khaliefa, Dominant Mechanisms for Metal Removal from Acidic Aqueous Solutions by Cement Kiln Dust, Mine Water Environ. 36 (2017) 209–216. doi:10.1007/s10230-016-0416-2.

[15] A.A.H. Faisal, A.H. Sulaymon, Q.M. Khaliefa, A review of permeable reactive barrier as passive sustainable technology for groundwater remediation, Int. J. Environ. Sci. Technol. 15 (2018) 1123–1138. doi:10.1007/s13762-017-1466-0.

[16] M. Naushad, S. Vasudevan, G. Sharma, A. Kumar, Z.A. Alothman, Adsorption kinetics, isotherms, and thermodynamic studies for Hg2+ adsorption from aqueous medium using alizarin red-S-loaded amberlite IRA-400 resin, Desalin. Water Treat. 57 (2016) 18551–18559. doi:10.1080/19443994.2015.1090914.

[17] M. Naushad, A. Mittal, M. Rathore, V. Gupta, Ion-exchange kinetic studies for Cd(II), Co(II), Cu(II), and Pb(II) metal ions over a composite cation exchanger, Desalin. Water Treat. 54 (2015) 2883–2890.

doi:10.1080/19443994.2014.904823.

[18] M. Naushad, G. Sharma, A. Kumar, S. Sharma, A.A. Ghfar, A. Bhatnagar, F.J. Stadler, M.R. Khan, Efficient removal of toxic phosphate anions from aqueous environment using pectin based quaternary amino anion exchanger, Int. J. Biol. Macromol. 106 (2018) 1–10. doi:https://doi.org/10.1016/j.ijbiomac.2017.07.169.

[19] A.A. Alqadami, M. Naushad, M.A. Abdalla, T. Ahamad, Z. Abdullah ALOthman, S.M. Alshehri, A.A. Ghfar, Efficient removal of toxic metal ions from wastewater using a recyclable nanocomposite: A study of adsorption parameters and interaction mechanism, J. Clean. Prod. 156 (2017). doi:10.1016/j.jclepro.2017.04.085.

[20] M. Naushad, Surfactant assisted nano-composite cation exchanger: Development, characterization and applications for the removal of toxic Pb2+ from aqueous medium, Chem. Eng. J. 235 (2014) 100–108. doi:10.1016/j.cej.2013.09.013.

[21] M. Naushad, G. Sharma, Z.A. Alothman, Photodegradation of toxic dye using Gum Arabic-crosslinked-poly(acrylamide)/Ni(OH)2/FeOOH nanocomposites hydrogel, J. Clean. Prod. 241 (2019) 118263. doi:https://doi.org/10.1016/j.jclepro.2019.118263.

[22] T.A. Kurniawan, G.Y.S. Chan, W.-H. Lo, S. Babel, Physico–chemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J. 118 (2006) 83–98. doi:10.1016/j.cej.2006.01.015.

[23] G. Sharma, D. Pathania, M. Naushad, N.C. Kothiyal, Fabrication, characterization and antimicrobial activity of polyaniline Th(IV) tungstomolybdophosphate nanocomposite material: Efficient removal of toxic

metal ions from water., Chem. Eng. J. (Amsterdam, Netherlands). 251 (2014) 413–421. doi:10.1016/j.cej.2014.04.074.

[24] G. Eker, Immobilization of Heavy Metals in Waste Phosphate Coating Sludge Using Kiln Dust as Portland Cement Substitute, Civ. Eng. Archit. 6 (2018) 65–70. doi:10.13189/cea.2018.060203.

[25] I. Beryllium, cadmium, mercury, and exposures in the glass manufacturing industry, 1993.

[26] I. Mironyuk, T. Tatarchuk, M. Naushad, H. Vasylyeva, I. Mykytyn, Highly efficient adsorption of strontium ions by carbonated mesoporous TiO2, J. Mol. Liq. 285 (2019) 742–753.

[27] M.G. Klimantavièiûtë, D. Virbalytë, V. Pakðtas, R. Juðkënas, A. Pigaga, Interaction of heavy metal ions with cement kiln dust, Ekologija. 1 (2005) 31–36.

[28] F. Larsen, D. Postma, Nickel Mobilization in a Groundwater Well Field: Release by Pyrite Oxidation and Desorption from Manganese Oxides, Environ. Sci. Technol. 31 (1997) 2589–2595. doi:10.1021/es9610794.

[29] L.Z. Lakshtanov, S.L.S. Stipp, Experimental study of nickel(II) interaction with calcite: Adsorption and coprecipitation, Geochim. Cosmochim. Acta. (2007). doi:10.1016/j.gca.2007.04.006.

[30]. P. Adams, M.L. Carboneau, W.E. Allred, Selected radionuclides important to low-level radioactive waste management, Idaho Natl. Eng. Environ. Lab. Idaho Falls, Idaho, USA. (1996) 1–413.

[31] Q. Chen, Z. Luo, C. Hills, G. Xue, M. Tyrer, Precipitation of heavy metals from wastewater using simulated flue gas: Sequent additions of fly ash, lime and carbon dioxide, Water Res. 43 (2009) 2605–2614.

doi:10.1016/j.watres.2009.03.007.

[32]   A.A.H. Faisal, H.K. Jasim, Adsorption-precipitation mechanisms for cadmium removal from polluted water, Assoc. Arab Univ. J. Eng. Sci. 25 (2018) 110–125.

[33]   A.A.H. Faisal, Z.T. Abd Ali, Groundwater protection from lead contamination using granular dead anaerobic sludge biosorbent as permeable reactive barrier, Desalin. Water Treat. (2016). doi:10.1080/19443994.2014.990928.

[34]   A.A.H. Faisal, Z.A. Hmood, Groundwater protection from cadmium contamination by zeolite permeable reactive barrier, Desalin. Water Treat. 53 (2015) 1377–1386. doi:10.1080/19443994.2013.855668.

[35]   N. Zaki, I. Khattab, N. Abdelmonem, Removal of some heavy metals by CKD leachate, J. Hazard. Mater. 147 (2007) 21–27. doi:10.1016/j.jhazmat.2006.12.057.

[36]   A.L. Mackie, M.E. Walsh, Bench-scale study of active mine water treatment using cement kiln dust (CKD) as a neutralization agent, Water Res. 46 (2012) 327–334. doi:10.1016/j.watres.2011.10.030.

[37]   M.H. El-Awady, T.M. Sami, Removal of Heavy Metals by Cement Kiln Dust, Bull. Environ. Contam. Toxicol. 59 (1997) 603–610. doi:10.1007/s001289900522.

[38]   L. Vinet, A. Zhedanov, A "missing" family of classical orthogonal polynomials, Biotechnol. Adv. 27 (2010) 195–226. doi:10.1088/1751-8113/44/8/085201.

[39]   B. Volesky, Sorption and Biosorption, 2004. doi:0973298308.

[40]   H.A. Aziz, M.N. Adlan, K.S. Ariffin, Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: Post treatment by high quality

limestone, Bioresour. Technol. (2008). doi:10.1016/j.biortech.2007.04.007.

[41] A.A.H. Faisal, L.A. Naji, Simulation of Ammonia Nitrogen Removal from Simulated Wastewater by Sorption onto Waste Foundry Sand Using Artificial Neural Network, Assoc. Arab Univ. J. Eng. Sci. 26 (2019) 28–34. doi:10.33261/jaaru.2019.26.1.004.

[42] M. Islam, R.K. Patel, Evaluation of removal efficiency of fluoride from aqueous solution using quick lime, J. Hazard. Mater. (2007). doi:10.1016/j.jhazmat.2006.09.030.

[43] W. Wang, Y. Hua, S. Li, W. Yan, W. Zhang, Removal of Pb (II) and Zn (II) using lime and nanoscale zero-valent iron (nZVI): A comparative study, Chem. Eng. J. 304 (2016) 79–88. doi:10.1016/j.cej.2016.06.069.

[44] S.M. Shaheen, F.I. Eissa, K.M. Ghanem, H.M. Gama El-Din, F.S. Al Anany, Metal ion removal from wastewaters by sorption on activated carbon, cement kiln dust, and sawdust, Water Environ. Res. (2015). doi:10.2175/106143015X14212658614630.

[45] A.E.-E.A.Z. Amin, S.A.H. Selmy, Effect of pH on Removal of Cu, Cd, Zn, and Ni by Cement Kiln Dust in Aqueous Solution, Commun. Soil Sci. Plant Anal. 48 (2017) 1301–1308. doi:10.1080/00103624.2017.1341914.

[46] F. Liu, J. Zhou, T. Jin, S. Zhang, L. Liu, Effect of calcium oxide on the efficiency of ferrous ion oxidation and total iron precipitation during ferrous ion oxidation in simulated acid mine drainage treatment with inoculation of Acidithiobacillus ferrooxidans, Water Sci. Technol. 73 (2016) 1442–1453. doi:10.2166/wst.2015.600.

[47] P. Tiwari, R. Verma, S.N. Kane, T. Tatarchuk, F. Mazaleyrat, Effect of Zn addition on structural, magnetic properties and anti-structural modeling of

magnesium-nickel nano ferrites, Mater. Chem. Phys. 229 (2019) 78–86. doi:10.1016/j.matchemphys.2019.02.030.

[48] I. Mironyuk, T. Tatarchuk, H. Vasylyeva, V.M. Gun'ko, I. Mykytyn, Effects of chemosorbed arsenate groups on the mesoporous titania morphology and enhanced adsorption properties towards Sr(II) cations, J. Mol. Liq. 282 (2019) 587–597. doi:10.1016/J.MOLLIQ.2019.03.026.

[49] D. Pathania, D. Gupta, A.H. Al-Muhtaseb, G. Sharma, A. Kumar, M. Naushad, T. Ahamad, S.M. Alshehri, Photocatalytic degradation of highly toxic dyes using chitosan-g-poly(acrylamide)/ZnS in presence of solar irradiation, J. Photochem. Photobiol. A Chem. 329 (2016) 61–68. doi:10.1016/j.jphotochem.2016.06.019.

[50] M. Naushad, T. Ahamad, G. Sharma, A.H. Al-Muhtaseb, A.B. Albadarin, M.M. Alam, Z.A. ALOthman, S.M. Alshehri, A.A. Ghfar, Synthesis and characterization of a new starch/SnO2 nanocomposite for efficient adsorption of toxic Hg2+ metal ion, Chem. Eng. J. 300 (2016) 306–316. doi:10.1016/j.cej.2016.04.084.

[51] M. Naushad, T. Ahamad, Z.A. AlOthman, A.H. Al-Muhtaseb, Green and eco-friendly nanocomposite for the removal of toxic Hg(II) metal ion from aqueous environment: Adsorption kinetics & isotherm modelling, J. Mol. Liq. (2019). doi:https://doi.org/10.1016/j.molliq.2019.01.090.

[52] M. Naushad, T. Ahamad, B.M. Al-Maswari, A. Abdullah Alqadami, S.M. Alshehri, Nickel ferrite bearing nitrogen-doped mesoporous carbon as efficient adsorbent for the removal of highly toxic metal ion from aqueous medium, Chem. Eng. J. 330 (2017) 1351–1360. doi:10.1016/J.CEJ.2017.08.079.

[53] A.P. Scott, L. Radom, Harmonic Vibrational Frequencies: An Evaluation of

Hartree−Fock, Møller−Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors, J. Phys. Chem. 100 (1996) 16502–16513. doi:10.1021/jp960976r.

[54] L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople, Investigation of the use of B3LYP zero-point energies and geometries in the calculation of enthalpies of formation, Chem. Phys. Lett. 270 (1997) 419–426. doi:10.1016/S0009-2614(97)00399-0.

[55] A. Godelitsas, D. Charistos, A. Tsipis, C. Tsipis, A. Filippidis, C. Triantafyllidis, G. Manos, D. Siapkas, Characterisation of zeolitic materials with a HEU-type structure modified by transition metal elements: Definition of acid sites in nickel-loaded crystals in the light of experimental and quantum-chemical results, Chem. - A Eur. J. (2001). doi:10.1002/1521-3765(20010903)7:17<3705::AID-CHEM3705>3.0.CO;2-5.
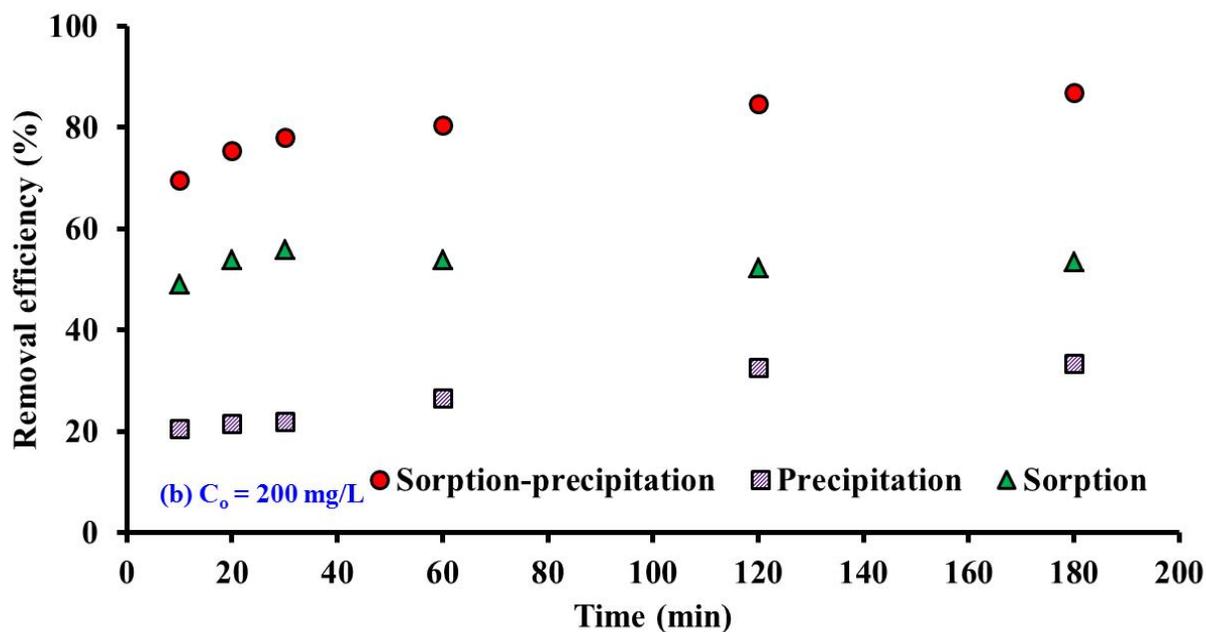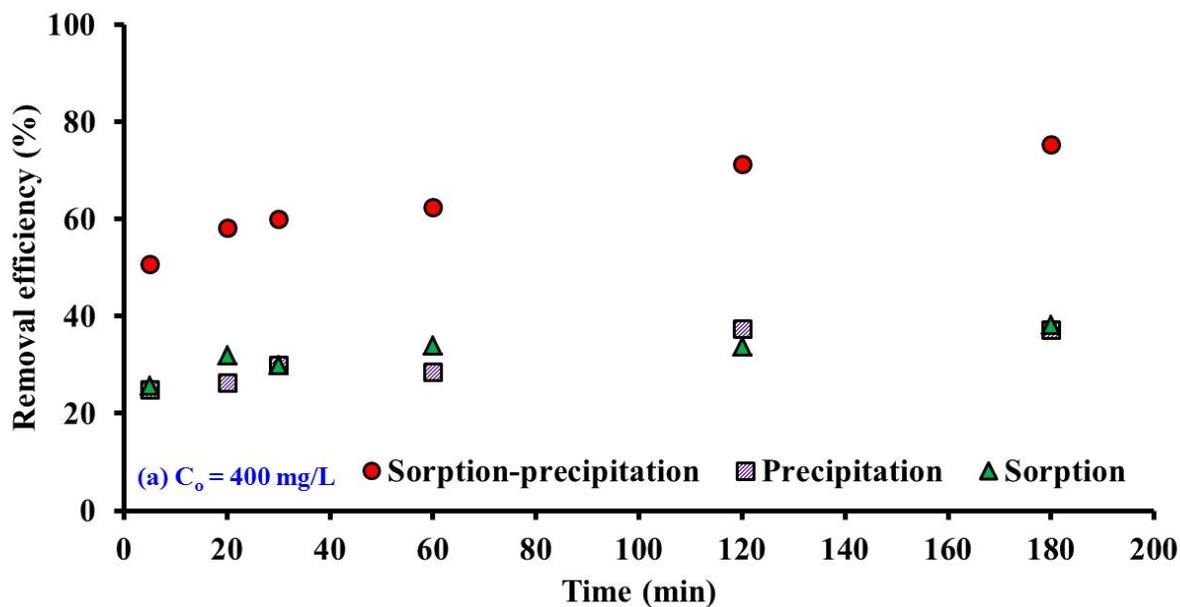
Fig. 1. Effect of contact time on the removal efficiency of nickel due to sorption-precipitation, pure precipitation and surface sorption mechanisms (dosage = 0.5 g/50 mL, initial pH=3 and temperature=25°C).
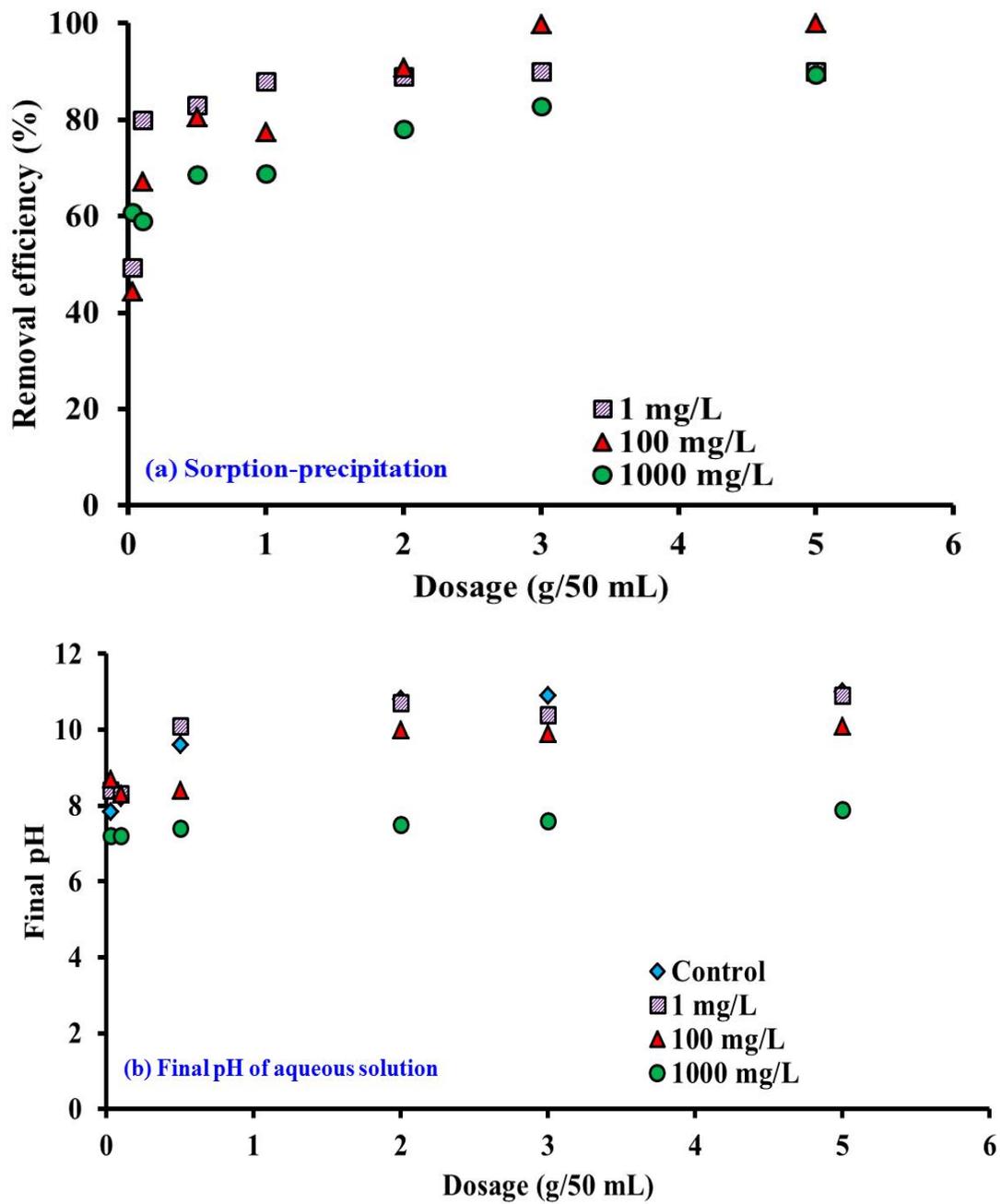
Fig. 2. Influence of the CKD quantity on the (a) nickel removal and (b) final pH of aqueous solution for different concentrations (contact time=4 h, initial pH=3 and temperature=25°C).
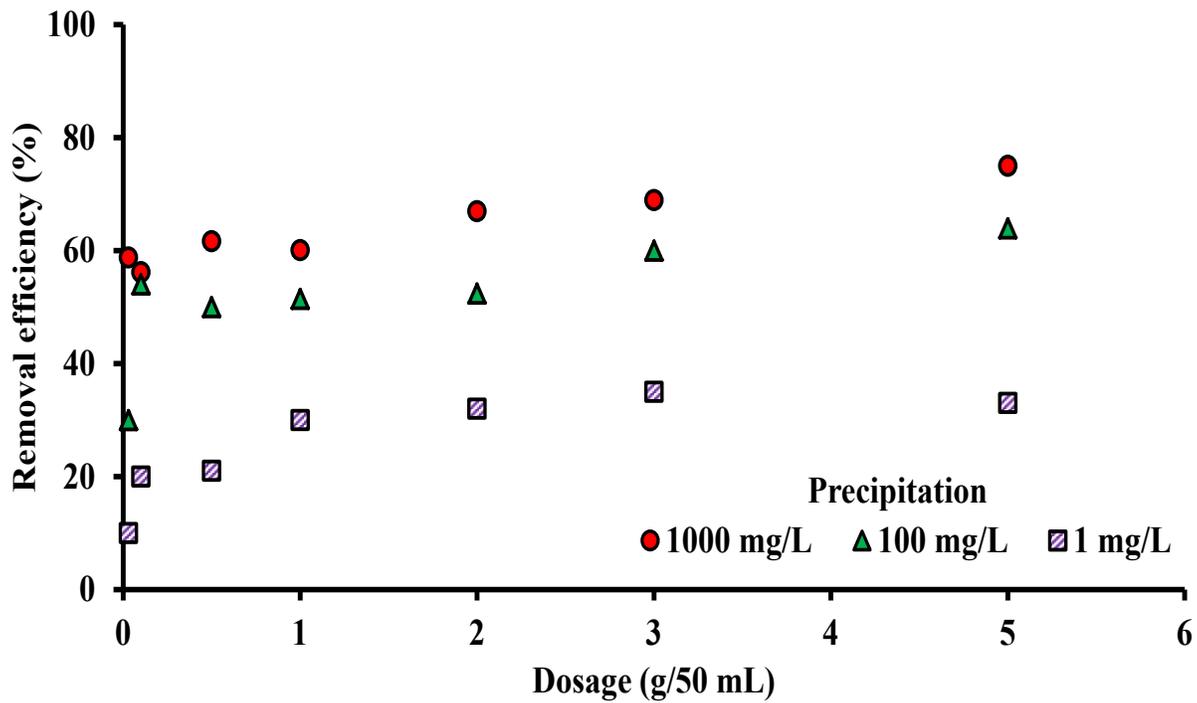
Fig. 3. Removal of nickel ions from aqueous solutions due to pure precipitation mechanism using CKD sorbent for different initial concentrations (contact time=4 h; initial pH= 3 and temperature= 25°C)
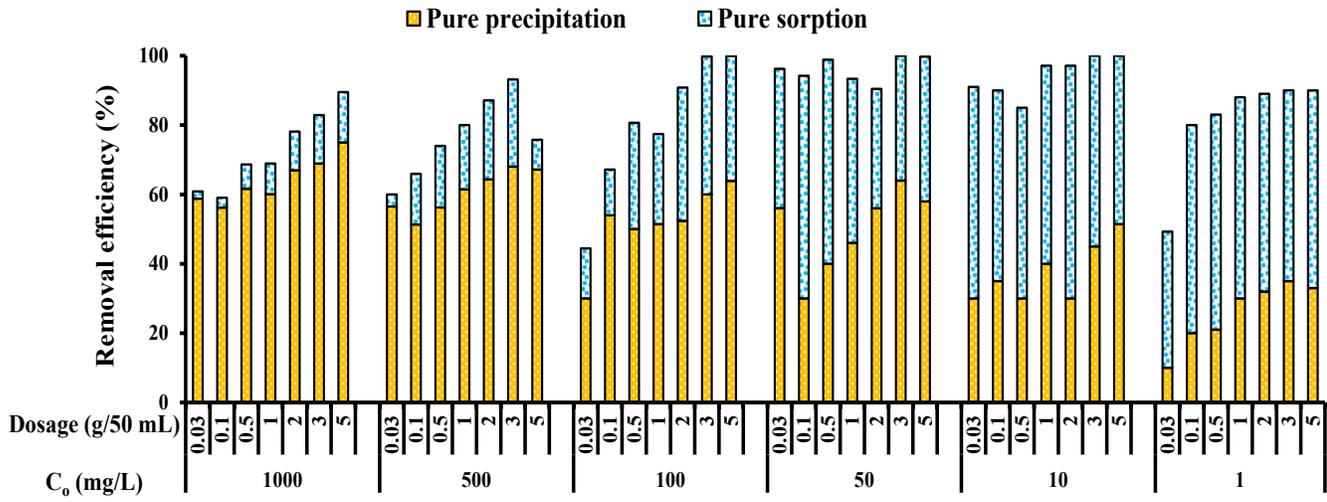
Fig. 4. Removal efficiencies of nickel from aqueous solution due to precipitation and sorption mechanisms using CKD sorbent
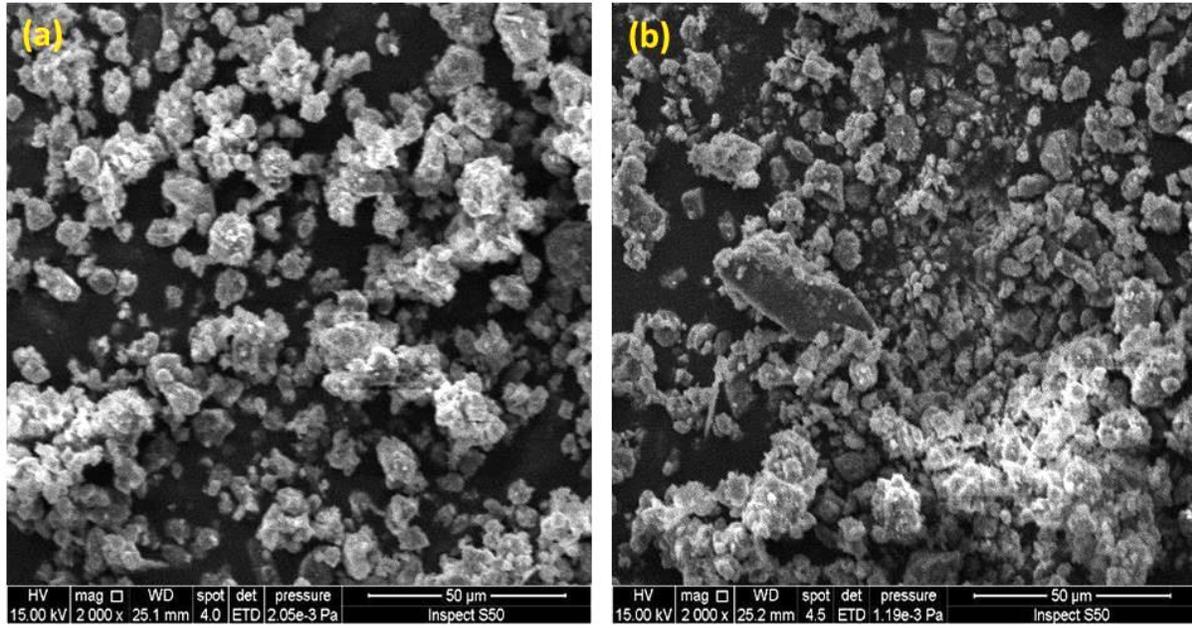
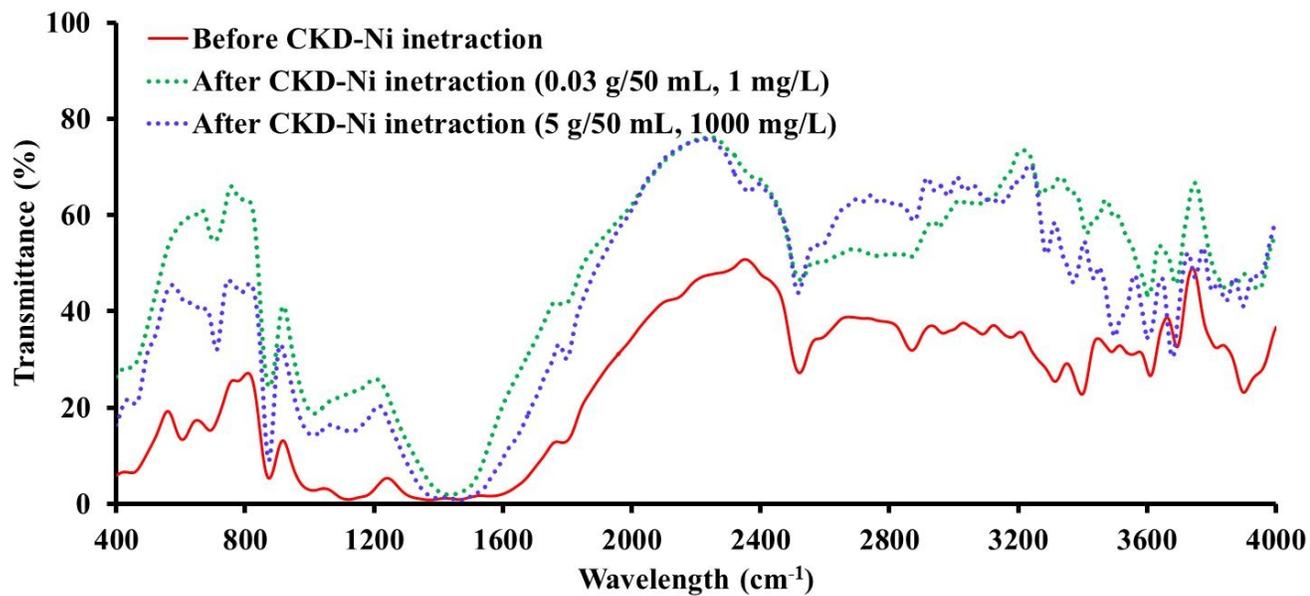**Fig. 5.** SEM images of CKD (a) before and (b) after sorption experiments

Fig. 6. FTIR spectra for CKD before and after sorption of nickel ions