Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2019.23421

142 (2019) 252–259
February

Selective adsorption of heavy metals (Co^{2+}, Ni^{2+}, and Cr^{3+}) from aqueous solutions onto natural marne clay

Khadidja Tizaoui, Belkacem Benguella*, Benamar Makhoukhi

Laboratory of Inorganic Chemistry and Environment, Department of Chemistry, University of Tlemcen, P.O. Box 119, Tlemcen, Algeria, email: bbenguella@yahoo.com

Received 28 June 2018; Accepted 2 November 2018

ABSTRACT

Natural marne clay (NMC) is a new clay that was used for the adsorption of heavy metal ions (Co (II), Ni (II), and Cr (III)) from aqueous solutions. Batch method was employed to study the influential parameters such as concentration of metal ions, pH, temperature, and mixing. The adsorption isotherms and kinetic studies were carried out in heavy metal systems. The Langmuir isotherm model fitted to the equilibrium data better than the Freundlich model, with the maximum adsorption capacities for Co^{2+}, Ni^{2+}, and Cr^{3+} are 48.35, 20.64, and 76.62 mg/g, respectively. The thermodynamic data were indicative of the endothermic sorption process of heavy metal ions onto the NMC. The selectivity sequence of the adsorption was found as Co (II) > Cr (III) > Ni (II). The results showed that NMC was a good adsorbent, able to uptake uniquely large quantities of heavy metals from single and binary components, and demonstrate the practical and economic advantages of using NMC in the decontamination of wastewater.

Keywords: Adsorption; Clay; Isotherm; Kinetic; Marne; Selectivity

1. Introduction

Heavy metals are among the important pollutants of water and especially wastewater water decontamination and it has become a public health concern because such pollutants are nonbiodegradable and persistent in nature [1]. Various industries such as metallurgical, tannery, mining, battery manufacturing, and other domestic processes have introduced substantial amounts of potentially toxic heavy metals in water reserves and environments [2]. Because of the industrialization development, many heavy metal ions have been discharged into the environment as waste, which causes soil pollution and water pollution [3].

Various technologies for the treatment of these pollutants in solution have been developed, including physical, chemical, and biological processes such as coagulation-flocculation, precipitation, biodegradation, adsorption, ion exchange, membrane processes, chemical oxidation, and solvent extraction [4,5]. However, all these conventional methods are not comparable with adsorption technique in terms of efficiency, operating cost, process flexibility, and ease of operation. Further, all these techniques were found to be inefficient and incompetent because of the fairly high solubility and stability toward light, oxidizing agents, and aerobic digestion. A comprehensive survey indicates that adsorption technique was the most appropriate and efficient one [6,7].

Activated carbons are widely used as an adsorbent for metal ions from aqueous solutions owing to its excellent adsorption abilities [8]. However, because of its relatively high cost, there have been attempts to utilize low cost and efficient, locally available materials for the removal of metal ions. For instance, some clays such as sepiolite [9], kaolinite [10], montmorillonite [11], smectite [12], bentonite [13], zeolite [14], and alunite [15] have been investigated for this purpose.

Some of the clay minerals possess a high adsorption capacity toward several classes of metal ions, and their adsorption capabilities are comparable with those of activated carbons. From the recent studies of the adsorption of metal

---

* Corresponding author.

1944-3994/1944-3986

ions using clay minerals, it can be seen that some of the natural clay minerals (mostly montmorillonite/bentonite) show significant ion removal capacities, while others still need modification in order to enhance its adsorption capacities.

In this regard, montmorillonite-rich materials like natural marne clay (NMC) exhibit highly interesting properties, e.g. high specific surface area, cation-exchange capacity (CEC), porosity, and tendency to retain water or other polar and nonpolar compounds. The aim of the present study is to evaluate the efficiency of natural clays in removing metal ions, such as Co (II), Ni (II), and Cr (III), from aqueous solutions by the batch adsorption process.

The aim of the present work is to investigate the possibility of NMC as an adsorbent for removal of heavy metal, which is, Co^{2+}, Ni^{2+}, and Cr^{3+}, from aqueous solution by adsorption. Effects of pH and temperature on the adsorption process are also investigated. The adsorption capacity of heavy metal with NMC was carried out using pseudo-second-order model. Finally, the experimental data were compared using two isotherm equations, which are Langmuir and Freudlich.

2. Experimental

2.1. Clay minerals

The NMC is a new clay in the sense that it is used for the first time in Algeria and is extracted from the layer of Hammam-Boughrara (Tlemcen-Algeria). It was washed three times with distilled water, dried in a convection oven at 105°C during 24 h and finally crushed in a mortar.

The chemical composition of bentonite was determined by X-ray fluorescence spectroscopy and was found to be as follows: 44.13% SiO_2, 13.33% Al_2O_3, 5.26% Fe_2O_3, 2.10% MgO, 2.13% K_2O, 10.88% CaO, and 1.14% Na_2O.

The CEC of clay was found to be 25.8 meq/100 g of dry clay.

2.2. Instrumental analysis

The fourier transform infrared spectroscopy (FTIR) of the adsorbent sample were measured as potassium bromide pellets using a Perkin-Elmer Spectrum Two (version 10.4.1) Fourier apparatus.

The thermogravimetric analysis (TGA) was performed under nitrogen flow in the range 50°C–800°C with an ATG Q600 TA instruments, at a heating rate of 10°C/min.

The X-ray diffraction (XRD) pattern was obtained using (Rigaku Miniflex 600) XRD instrument with Cu Kα radiation at ambient temperature operated at 40 kV and 15 mA.

The specific surface area was calculated by the Brunauer, Emmett, and Teller (BET) equation using the adsorption data in the relative pressure. Perkin-Elmer model PinAAcle 900 H atomic absorption spectrometer (AAS) was used for heavy metal analysis.

2.3. Adsorption and procedure

The adsorption of heavy metal ions onto NMC was studied by batch method. Batch experiments were conducted at room temperature (20°C ± 2°C) and at a constant stirring speed of 400 rpm using the optimum conditions of factors that influence adsorption efficiency such as pH (1–10), agitation time (5–180 min), metal ion concentration (100 mg/L), and NMC dosage (1 g). The effect of pH on the adsorption of heavy metal ions over a pH range of 1–10 was investigated, and the pH of the solution was adjusted using HHO_3 (0.1 N) and/or NaOH (0.1 N). The adsorption of Co^{2+}, Ni^{2+}, and Cr^{3+} was also studied in the concentration range of 100 mg/L at different temperatures (10°C, 20°C, 30°C, and 40°C) to elucidate the effect of temperature and adsorption thermodynamic parameters.
The samples were then centrifuged, and the concentration of the supernatant heavy metal solution was analyzed by AAS. It gives the concentration of each sample, based on the calibration curve of the Beer-Lambert law giving the quantity q_t (mg/g) of heavy metals fixed per gram of the adsorbent according to Eq. (1):

$$q_t\left(\text{mg/g}\right) = \frac{C_i - C_t}{m} \times V \tag{1}$$

where C_i and C_t (mg/L) are the concentrations of heavy metal at time $t = 0$ and t, respectively; V (L) is the volume of heavy metal solution; and m (g) is the mass of the adsorbent used.

3. Results and Discussion

3.1. Characteristic results of NMC

3.1.1. FTIR analysis

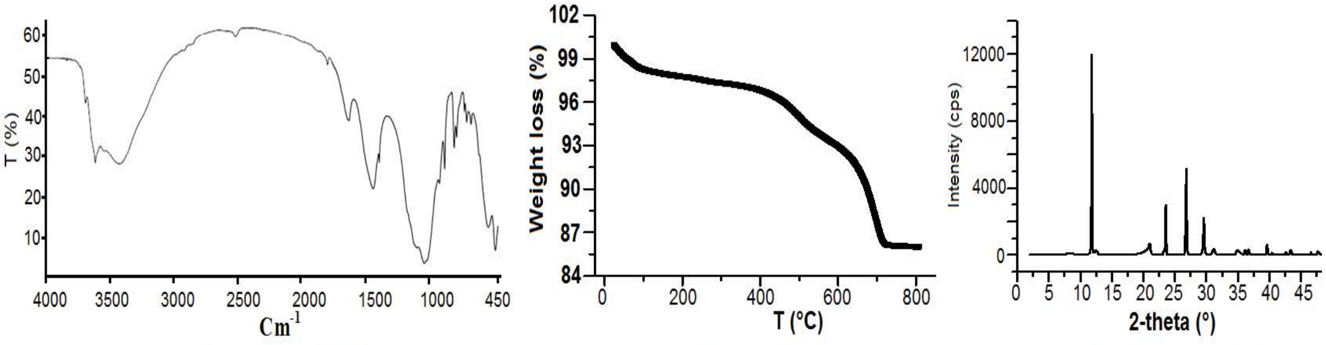
The FTIR spectrum of NMC is shown in Fig. 1(a), the band at 3,621 cm^{-1} corresponds to the stretching vibrations of hydroxyl groups attached to the octahedral layer. The bands between 3,621 and 3,435 cm^{-1} can be associated with the stretching vibrations of OH groups coordinated to Al and Mg atoms or two Al atoms in octahedral sheets of clay [16]. The band at 1,623 cm^{-1} corresponds to the OH deformation of water, because the OH stretching band at 3,621 cm^{-1} suggests the presence of some interlamellar water. The band at 1,432 cm^{-1} corresponds to C–O stretching vibrations while that at the 1,384 cm^{-1} is assigned to calcite. The 1,032 cm^{-1} component of the Si–O stretching band is assigned to the Si–O vibrations within the layer [16,17]. The bands at 523 and 469 cm^{-1} are due to Si–O–Al (where Al is an octahedral cation) [17].

3.1.2. Thermogravimetric analysis

TGA analysis of the NMC samples is illustrated in Fig. 1(b) showing two distinct temperature ranges. The first endothermic phenomenon that took place below 140°C is due to dehydration of clay minerals. The corresponding weight loss of 1.36% was ascribed to the removal of physically bound water [18]. A second broad endothermic phenomenon took place between 400°C and 600°C with an associated mass decrease reaching 5.04% of NMC. This loss resulted mainly from the removal of OH groups of the clay, and the total mass loss at 700°C was 15.59% [19].

3.1.3. XRD analysis

A typical XRD pattern of NMC is given in Fig. 1(c); the prominent peak appears at 2θ = 11.82° with an intensity



a) FT-IR spectra of NMC

b) TGA of NMC

c) XRD pattern of NMC

Fig. 1. Characterization of NMC.

of 1,157, corresponding mainly to calcium magnesium carbonate (dolomite) and calcium hydrogen phosphate at 2θ = 26.82°. The additional peaks at 29.56° and 39.60° correspond essentially to magnesium, gallium, and quartz.

3.1.4. BET analysis

Type IV isotherms in the BET classification indicate mesoporous materials with a limited microporosity [20]. In all cases, capillary condensation occurs during adsorption via "cylindrical meniscus," while capillary evaporation during desorption occurs via "hemispherical meniscus," separating the vapor and capillary-condensed phases. The hysteresis loop confirms the mesoporous structure of the studied clay [20].

The specific surface area of NMC was equal to 52.1 m^2/g. The pore volume at different particle size was found to be as follows: 0–80 nm (0.28), 0–25 nm (0.25), and 0–14 nm (0.21). This material is characterized by high porosity, and total pore volume is 0.701 cm^3/g.

The distribution of the particle size for the clay was found to be as follows: 100% (<15 μm), 95% (<80 μm), 92% (<53 μm), 80% (<45 μm), and 70% (<40 μm). This material has the finest granulometry, since 70% of the particle size is smaller than 40 μm.

3.2. Metal adsorption over NMC

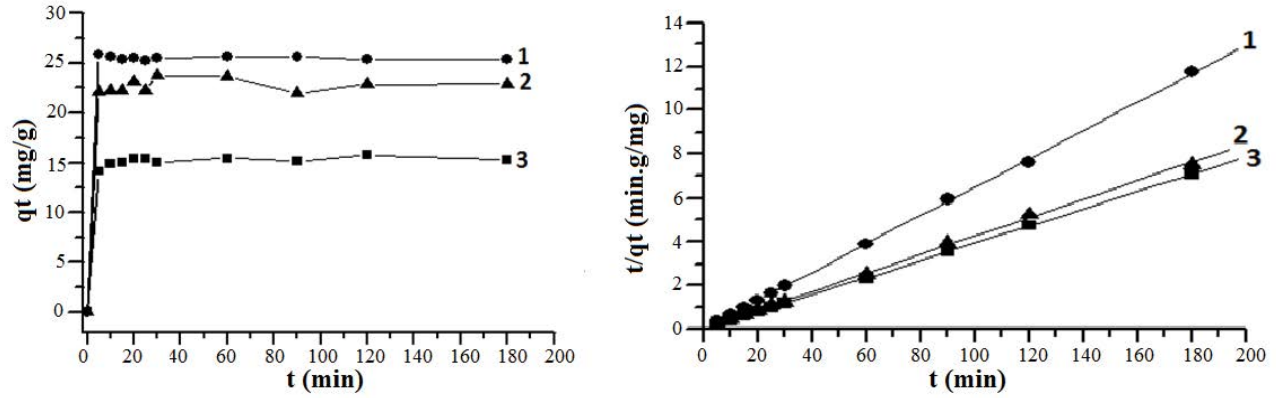
3.2.1. Effect of contact time

The adsorption of heavy metal on NMC was studied as a function of contact time, and the results are shown in Fig. 2(a); the time-dependent adsorption behavior was measured by performing a series of experiments with a range of time 1–180 min; the curves describing the kinetics of adsorption have same forms. They exhibit a strong increase in the first few minutes of contact ions-NMC, that 60% removal of Co^{2+}, Ni^{2+}, and Cr^{3+} was observed in 20 min, followed by a much slow increase until reaching equilibrium.

The fast adsorption at the initial stage was ascribed due to the availability of large number of active sites of the adsorbent. Therefore, 120 min was perched as the optimal contact time for the removal of metal ions using NMC. The adsorption capacity obtained at equilibrium was equal to 25.66 mg/g with cobalt, 15.78 mg/g with nickel, and 23.77 mg/g with chromium.

Similar type of findings has also been reported by other researchers [21].

In order to study the adsorption system heave for metal ions to remove the metal, it is important to establish the appropriate correlation for the kinetic data of



a) Effect of contact time

b) The pseudo second-order rate model

Fig. 2. Kinetics of adsorption of heavy metals by NMC.
1: Co (II), 2: Cr (III), 3: Ni (II)

different systems. The kinetics of metal adsorption can be modeled by the pseudo-second-order rate equation of Lagergren [22].

$$\frac{t}{q_t} = \frac{1}{K_s q_e^2} + \frac{t}{q_e} \tag{2}$$

where K is the pseudo-second-order rate constant of adsorption [(g/mg)/min]; q_e and q_t are the amounts of heavy metal adsorbed per mass unit of adsorbent (mg/g) at equilibrium and at time t, respectively. Fig. 2(b) shows that the curves representing t/q_t vs. t are linear. Hence, the pseudo-second-order reaction rate model adequately describes the kinetics of heavy metal adsorption with a high correlation coefficient. The slopes and intercepts are summarized in Table 1.

It was observed that the pseudo-second-order model agreed with the experimental data better than the pseudo-first and second-order models for the adsorption of dyes (Table 1). High correlation coefficients are obtained when employing the pseudo-second-order model ($R^2 \geq 0.999$), and the calculated equilibrium adsorption capacity is similar to the experimental data, and this indicated that the adsorption of heavy metals onto NMC is controlled by chemical adsorption (chemisorption) involving valence forces through sharing or exchange of electrons between sorbent and sorbate. In chemical adsorption, it is assumed that the adsorption capacity is proportional to the number of active sites occupied on the adsorbent surface [23].

Table 1
Kinetic parameters for Co (II), Ni (II), and Cr (III) adsorption on NMC

Metal ions	Lagergren parameter	
	K (g/mg/min)	R^2
Co (II)	0.365	0.999
Ni (II)	0.247	0.999
Cr (III)	0.044	0.999

3.2.2. Effect of pH

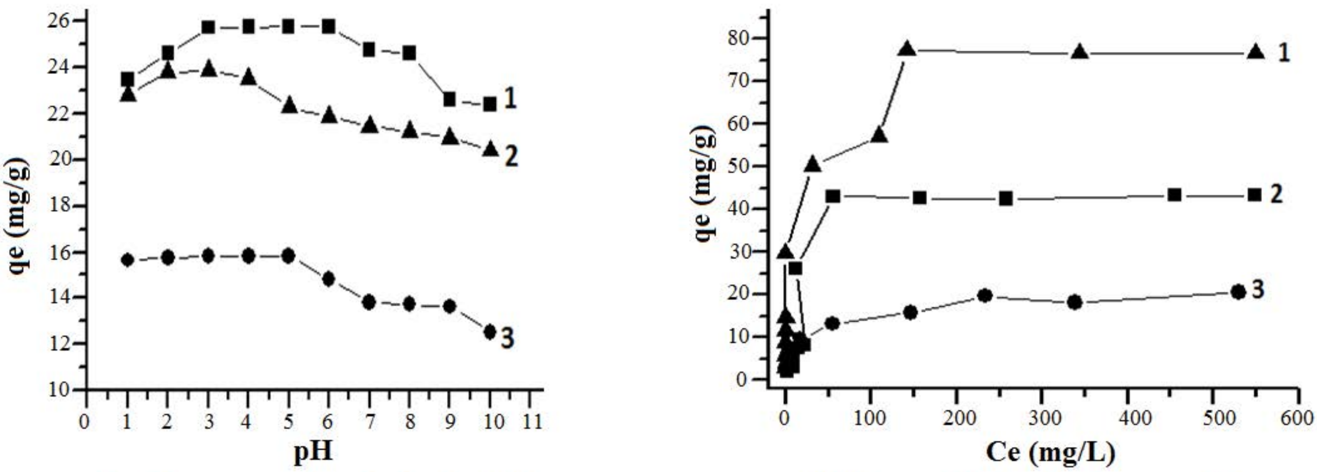
The variations of pH were one of the most important factors affecting the concentration and metal recovery procedure, which was related to the formation of metal complexes (metal hydroxide) and subsequently their stabilities in aqueous solutions [23]. The adsorptions of heavy metals by NMC were studied at different pH values ranging from 1 to 10, and the results are shown in Fig. 3(a); it is seen that the adsorption decreases with increasing initial pH. It reaches a maximum value around pH = 4 for cobalt (85.89%), pH = 5 for nickel (52.8%), and pH = 3 for chrome (79.64%). At low pH, there is large number of H^+ ions, which neutralized the negatively charged adsorbent surface and thereby increased the diffusion of metal ions into the surface of the adsorbent; at higher pH values, decrease in the adsorption may be due to the abundance of OH^- ions, which retarded the diffusion of metal ions.

Hence, pH equal to 3.0, 4.0, and 5.0 were taken as the optimal values for adsorption of Cr (III), Co (II), and Ni (II) onto NMC, respectively.

3.2.3. Equilibrium of adsorption

The equilibrium isotherms were determined by mixing a constant mass of adsorbent to 1 g of NMC, with a solution of volume 0.03 L containing heavy metals in the concentration range of 10–600 mg/L. The experimental conditions were the same as in the kinetics of adsorption.

Fig. 3(b) shows that by increasing the initial concentration in solution, the amount of adsorbed heavy metals gradually increases. The increase in initial metal concentration enhances the interaction force that it is necessary to overcome the resistances to the mass transfer between adsorbate and



a) pH of heavy metals solution in NMC **b) The equilibrium isotherm at 25°C**

Fig. 3. Adsorption of heavy metals by NMC (effect of pH and equilibrium isotherm).
1: Co (II), 2: Cr (III), 3: Ni (II)

the adsorbent [24]. However, as the initial concentration of metals increased, most of the available sorption sites became occupied, leading to a decrease in the removal efficiency; this is why this increase starts to ease off after 400 ppm of initial metal concentrations.

3.3. Modeling of the isotherms of adsorption

Langmuir and Freundlich models were used to fit experimental data when the solute uptake occurs by a monolayer adsorption. This modelling allows determination of the maximum capacity of removal. The fit quality is assessed by the value of the correlation coefficient R^2. The modelling provides the best fit when R^2 is close to one.

3.3.1. Langmuir model

Langmuir modelling of the adsorption of heavy metals on NMC was carried out with the linearized equation [25,26]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{3}$$

where the constants b and q_m are deduced from the slope and intercept of plot of C_e/q_e vs. C_e.
One notes from Fig. 4(a) that the linearization of the isotherms of adsorption of Co (II), Ni (II), and Cr (III) by NMC follows linear trends with a good quality fit. Table 2 summarizes the results by giving the fit parameter for Langmuir and Freundlich isotherms. On the basis of these results, we can say that the Langmuir model is adequate for a good description of these isotherms of adsorption. The values of q_m obtained for each metal confirm the tendency observed previously while following the order of affinity of NMC for heavy metals.

3.3.2. Freundlich model

In the Freundlich model, the isotherm equation can be linearized in logarithmic form as [28]:

$$\text{Ln } q_e = \text{Ln } K + n \text{ Ln } C_e \tag{4}$$

The parameters n and K are deduced from the slope and intercept of the line plots ln (q_e) vs. ln (C_e). The curves of adsorption by Freundlich model are given in Fig. 4(b). The correlation coefficient R^2 shows that the Freundlich model is not adequate for representing the adsorption isotherms of heavy metals by NMC in all these studied concentration domains. The Freundlich constant K, which is related to the adsorption capacity, increased with temperature, indicating that the adsorption process is endothermic. The value of n is an indication of the favorability of adsorption. Values of $n > 1$ represent favorable nature of adsorption [27]. Table 2 summarized the parameters of the Freundlich model.

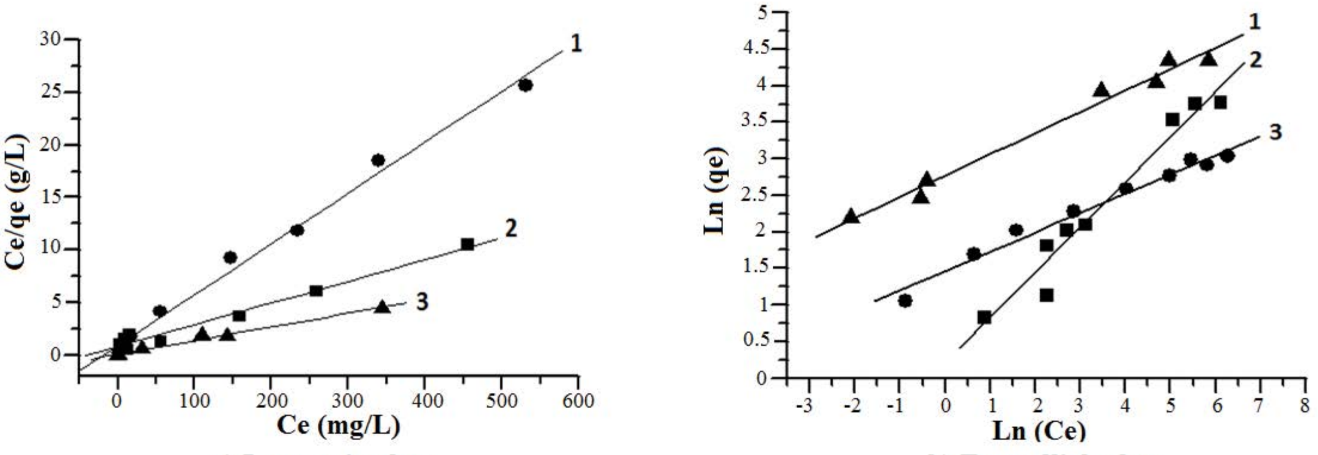
3.4. Thermodynamic parameters

The effect of temperature on the adsorption of heavy metal by NMC at initial pH and concentration of 100 ppm was studied. The thermodynamic parameters, namely, the enthalpy (ΔH) and entropy (ΔS), associated with the adsorption process could be obtained from the slope and intercept of the Vant Hoff plot. The logarithm of the rate constant (K_c), versus the inverse temperature ($1/T$) was computed using the following equation [29]:

$$\text{Ln } K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{5}$$

Table 2
Langmuir and Freundlich parameters for the adsorption of heavy metals onto NMC

	Langmuir parameters			Freundlich parameters		
	q_m (mg/g)	b (L/g)	R^2	n	K	R^2
Co (II)	48.35	0.0248	0.99	0.618	1.226	0.98
Ni (II)	20.64	0.0534	0.99	0.264	4.321	0.98
Cr (III)	76.62	0.1521	0.99	0.291	15.82	0.99



a) Langmuir plots b) Freundlich plots

Fig. 4. Isotherm plots for the adsorption of heavy metals by NMC. 1: Cr (III), 2: Co (II), 3: Ni (II)

where K_c is the distribution coefficient, T is the temperature in Kelvin, and R is the gas constant. Distribution coefficient (mL/g) is also computed using the following equation:

$$K_c = \frac{C_i - C_e}{C_e} \tag{6}$$

where C_i and C_e are the initial and equilibrium concentrations of heavy metal (mg/L) in solution. Fig. 5 shows adsorption of heavy metals onto NMC as a function of the temperature. Table 3 summarizes the thermodynamic data for adsorption of heavy metals onto NMC.

The thermodynamic parameters ΔH and ΔS of heavy metal adsorption on NMC are determined graphically from the plot of log K versus $1/T$ (Fig. 5). The negative values of ΔH for Co (II), Ni (II), and Cr (III) confirm that the adsorption of heavy metals by NMC is an exothermic process; also, the negative values of ΔS for Co (II), Ni (II), and Cr (III) suggest that the randomness in solid/solution interface decreased during the adsorption [30].

Table 3
Thermodynamic data for adsorption of heavy metals onto NMC

Metals	ΔH (KJ/mol)	ΔS (J/mol K)	R^2
Co (II)	–9.697	–46.391	0.82
Ni (II)	–14.950	–50.962	0.96
Cr (III)	–8.537	–39.280	0.98

3.5. Selectivity study

Based on our previous studies and preliminary results of this work, it was demonstrated that Co (II) ions have higher capability to bind with clayey surface than other metal ions. In view of verifying this result, the adsorption of selected metals was carried out with different concentrations. The sorption selectivity of the Co (II) was investigated by competitive loading of Ni (II) and Cr (III) in their binary and tertiary mixtures at the same concentration as Co (II) (100 mg/L). Fig. 6 and Table 4 show the results of this experiment, along

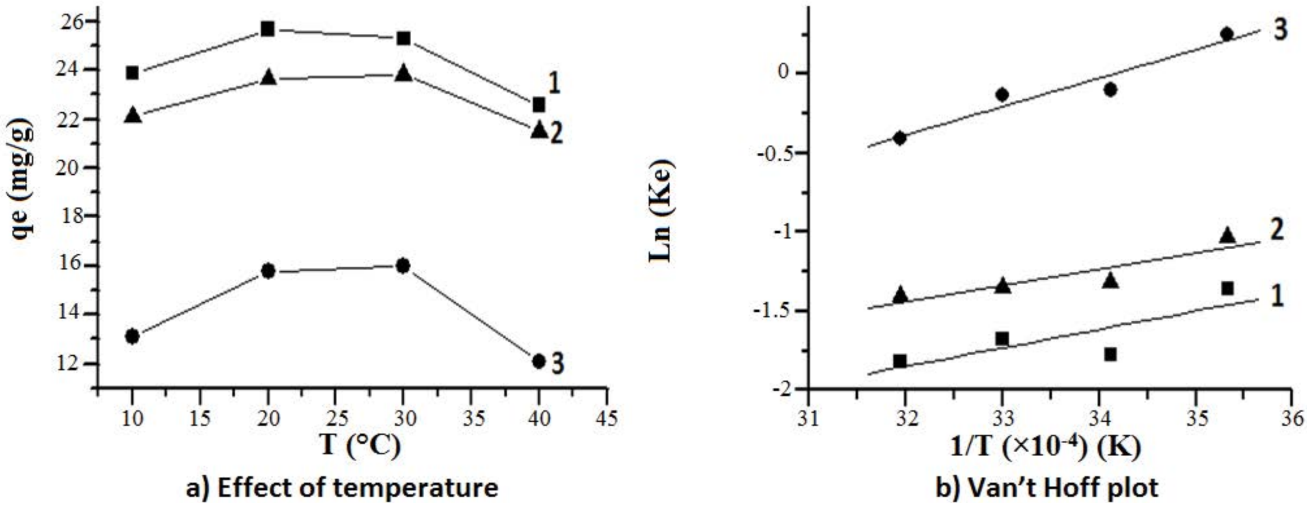


Fig. 5. Thermodynamic plots for the adsorption of heavy metals by NMC.
1: Co (II), 2: Cr (III), 3: Ni (II)

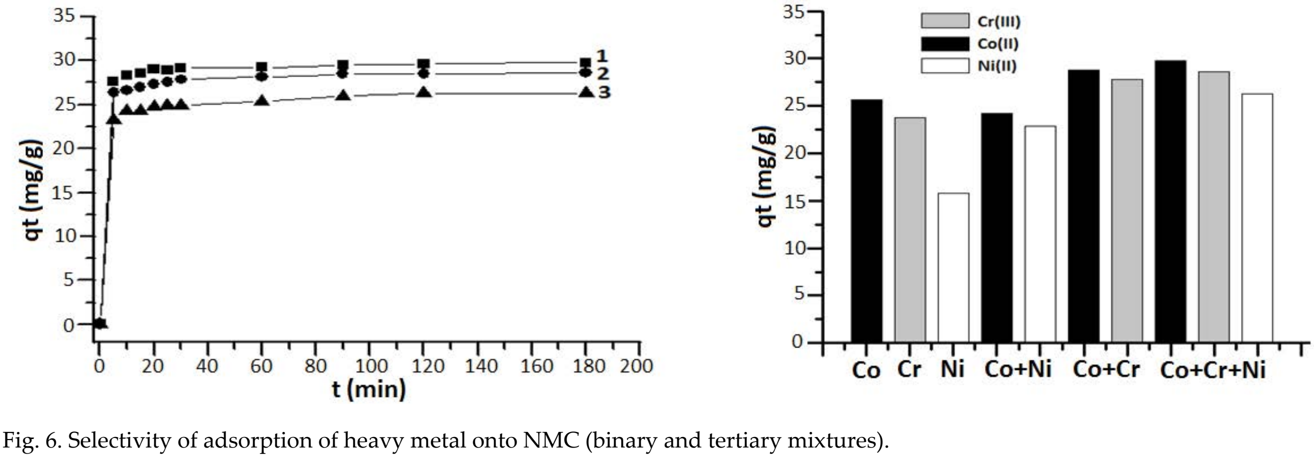


Fig. 6. Selectivity of adsorption of heavy metal onto NMC (binary and tertiary mixtures).
1: Co (II), 2: Cr (III), 3: Ni (II)

Table 4
Selectivity of NMC for mixed ions

Mixed ions	Co (II)	Co (II) + Ni (II)		Co (II) + Cr (III)		Co (II) + Ni (II) + Cr (III)		
		Co (II)	Ni (II)	Co (II)	Cr (III)	Co (II)	Ni (II)	Cr (III)
q_e (mg/g)	25.66	24.21	22.92	28.77	29.76	29.77	28.65	26.25

1: Co (II), 2: Cr (III), 3: Ni (II)

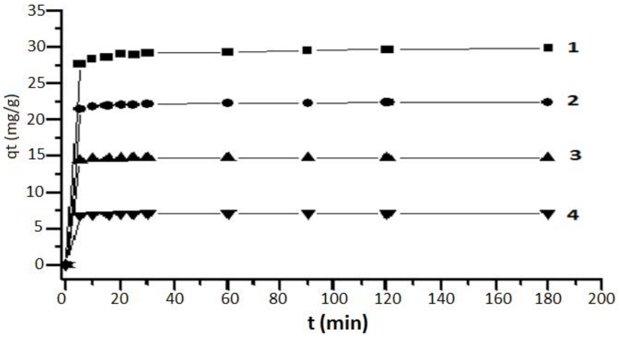


Fig. 7. Selective adsorption of Co^{2+} onto NMC from mixtures (concentration effect).
1: 100 mg/L (Co) + 100 mg/L (Cr) + 100 mg/L (Ni).
2: 75 mg/L (Co) + 100 mg/L (Cr) + 100 mg/L (Ni).
3: 50 mg/L (Co) + 100 mg/L (Cr) + 100 mg/L (Ni).
4: 25 mg/L (Co) + 100 mg/L (Cr) + 100 mg/L (Ni).

with the corresponding efficiencies for the metal adsorption alone, which serves as a reference point; the results demonstrate there was no serious interference in the adsorption of cobalt ions from the mixed solutions with the investigated amounts of coexisting metal ions, Co (II) could be easily separated and fixed from solutions containing Cr (III) and Ni (II) metal ions. Chromium shows better selectivity than Nickel, and thereafter, the abovementioned selectivity order (Co > Cr > Ni) was experimentally confirmed. The main reason might be explained by metal cations presented different adsorptive affinities toward the adsorbent active sites (Brönsted acid sites, oxidizing sites and surface hydroxyl groups bound to Si, Al) [31] and the metal interactions with clay such as charge, radius, and electronegativity [32].

Fig. 7 illustrates the effect of concentration of Co (II) ions as a function of both co-ions: Cr (III) and Ni (II), on the adsorption selectivity by NMC. The results clearly indicate that Cr (III) and Ni (II) have an appreciable effect on cobalt uptake capacity into NMC while inhibit the cobalt sorption.

4. Conclusion

In this study, the results obtained have shown that NMC can be used to remove metal ions such as Co (II), Ni (II), and Cr (III) from aqueous solution in both single and multi-metal ions. The adsorption capacity of Co (II) onto NMC is the largest compound to the other ions tested. There are several factors affecting the adsorption of metal ions onto NMC; however, the adsorption process was affected essentially by physicochemical factors such as pH, NMC content, heavy metal concentration, and temperature. Kinetic data of adsorption were well fitted by the pseudo-second-order kinetic model. The sorption mechanism was a multi-step process, involving adsorption on the external surface, diffusion into the bulk, and electrostatic interactions. Moreover, NMC could selectively adsorb more Co (II) ions than other heavy metal ions including Ni (II) and Cr (III) during competitive adsorption in the binary and tertiary metal species systems, which indicated that it was a selective adsorbent of Co (II) from aqueous solution. Well, equilibrium data were fitted perfectly with the Langmuir isotherm. It indicates the formation of a monolayer of metal ions on the surface of NMC. Detailed characterization of NMC showed that the high surface area resulted in a high percentage of removal by the clay. It also demonstrated that NMC can be used in practical large-scale application of wastewater treatment and heavy metal removal.

References

[1] M. Naushad, T. Ahamad, B.M. Al-Maswari, A.A. 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.

[2] B. Hayati, A. Maleki, F. Najafi, H. Daraei, F. Gharibi, G. McKay, Adsorption of Pb^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+} metal ions from aqueous solution by PPI/SiO_2 as new high performance adsorbent: preparation, characterization, isotherm, kinetic, thermodynamic studies, J. Mol. Liq., 237 (2017) 428–443.

[3] H. Sis, T. Uysal, Removal of heavy metal ions from aqueous medium using Kuluncak (Malatya) vermiculites and effect of precipitation on removal, Appl. Clay Sci., 95 (2014) 1–8.

[4] Z. Zhen, G. Chao, W. Yanliang, S. Lifei, H. Xiaolei, R. Wei, S. Qirong, Removal of heavy metals from aqueous solution by lipopeptides and lipopeptides modified Na-montmorillonite, Bioresour. Technol., 147 (2013) 378–386.

[5] B. Hayati, A. Maleki, F. Najafi, H. Daraei, F. Gharibi, G. McKay, Super high removal capacities of heavy metals (Pb^{2+} and Cu^{2+}) using CNT dendrimer, J. Hazard. Mater., 336 (2017) 146–157.

[6] E. Kenawy, A. Ghfar, M. Naushad, Z.A. AL-Othman, M.A. Habila, A.B. Albadarin, Efficient removal of Co(II) metal ion from aqueous solution using cost-effective oxidized activated carbon: kinetic and isotherm studies, Desal. Wat. Treat., 70 (2017) 220–226.

[7] A. Kumar, C. Guo, G. Sharma, D. Pathania, M. Naushad, S. Kalia, P. Dhiman, Magnetically recoverable ZrO_2/Fe_3O_4/Chitosan nanomaterials for enhanced sunlight driven photoreduction of carcinogenic Cr (VI) and dechlorination and mineralization of 4-chlorophenol from simulated waste water, RSC Adv., 6 (2016) 13251–13263.

[8] Z.A. AL-Othman, M. Naushad, R. Ali, Kinetic, equilibrium isotherm and thermodynamic studies of Cr(VI) adsorption onto low-cost adsorbent developed from peanut shell activated with phosphoric acid, Environ. Sci. Pollut. Res., 20 (2013) 3351–3365.

[9] K.G. Bhattacharyya, S. Gupta, Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite, Adv. Colloid Interface Sci., 140 (2008) 114–131.

[10] M.S. Schaller, C.M. Koretsky, T.J. Lund, C.J. Landry, Surface complexation modeling of Cd(II) adsorption on mixtures of

hydrous ferric oxide, quartz and kaolinite, J. Colloid Interface Sci., 339 (2009) 302–309.

[11] M. Ulmanu, E. Maranon, Y. Fernandez, L. Castrillón, I. Anger, D. Dumitriu, Removal of copper and cadmium ions from diluted aqueous solutions by low cost and waste material adsorbents, Water Air Soil Pollut., 142 (2003) 357–373.

[12] A. Kaya, A. Hakan Oren, Adsorption of zinc from aqueous solutions to bentonite, J. Hazard. Mater., 125 (2005) 183–189.

[13] A.W. Marczewski, M. Seczkowska, A. Deryło-Marczewska, M. Blachnio, Adsorption equilibrium and kinetics of selected phenoxy acid pesticides on activated carbon: effect of temperature, Adsorption, 22 (2016) 777–790.

[14] Z.A. AL-Othman, R. Ali, M. Naushad, Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: adsorption kinetics, equilibrium and thermodynamic studies, Chem. Eng. J., 184 (2012) 238–247.

[15] Y. Gutha, V.S. Munagapati, M. Naushad, K. Abburi, Removal of Ni(II) from aqueous solution by Lycopersicum esculentum (tomato) leaf powder as a low-cost biosorbent, Desal. Wat. Treat., 54 (2015) 200–208.

[16] F.Z. Choumane, B. Benguella, Removal of acetamiprid from aqueous solutions with low-cost sorbents, Desal. Wat. Treat., 57 (2016) 419–430.

[17] B. Benguella, A. Yacouta-Nour, Adsorption of Bezanyl Red and Nylomine Green from aqueous solution by natural and acid-activated bentonite, Desalination, 235 (2009) 276–292.

[18] B. Makhoukhi, D. Villemin, M.A. Didi, Synthesis of bisimidazolium–ionic liquids: characterization, thermal stability and application to bentonite intercalation, J. Taibah Univ. Sci., 10 (2016) 168–180.

[19] B. Makhoukhi, D. Villemin, M.A. Didi, Preparation, characterization and thermal stability of bentonite modified with bis-imidazolium salts, Mater. Chem. Phys., 138 (2013) 199–203.

[20] A. Sdiri, T. Higashi, S. Bouaziz, M. Benzina, Synthesis and characterization of silica gel from siliceous sands of southern Tunisia, Arabian J. Chem., 7 (2014) 486–493.

[21] V.N. Tirtom, A. Dinçer, S. Becerik, T. Aydemir, A. Çelik, Comparative adsorption of Ni(II) and Cd(II) ions on epichlorohydin cross-linked chitosan–clay composite beads in aqueous solution, Chem. Eng. J., 197 (2012) 379–386.

[22] Y.S. Ho, Adsorption of Heavy Metals from Waste Streams by Peat, Ph.D. Thesis, University of Birmingham, Birmingham UK, 1995.

[23] B. Makhoukhi, M. Djab, M.A. Didi, Adsorption of Telon dyes onto bis-imidazolium modified bentonite in aqueous solutions, J. Environ. Chem. Eng., 3 (2015) 1384–1392.

[24] B. Makhoukhi, Application of new organoclays for the adsorption of bemacide dyes from aqueous solutions, Desal. Wat. Treat., 113 (2018) 235–243.

[25] P. Nagan, L. Srinivasan, N. Persu, N. Sudha, R. Gopalan, Influence of clay on the adsorption of heavy metals like copper and cadmium on chitosan, Environ. Sci. Pollut. Res., 20 (2013) 925–938.

[26] S. Yavari, N.M. Mahmodi, P. Teymouri, B. Shahmoradi, A. Maleki, Cobalt ferrite nanoparticles: preparation, characterization and anionic dye removal capability, J. Taiwan Inst. Chem. Eng., 59 (2016) 320–329.

[27] A.A. Alqadami, M. Naushad, Z.A. Al-Othman, A. Ghfar, Novel metal−organic framework (MOF) based composite material for the sequestration of U(VI) and Th(IV) metal ions from aqueous environment, ACS Appl. Mater. Interfaces, 9 (41) (2017) 36026–36037.

[28] J.V. Flores-Cano, R. Leyva-Ramos, F. Carrasco-Marin, A. Aragonn-Pin, J. Salazar-Rabago, S. Leyva-Ramos, Adsorption mechanism of Chromium (III) from water solution on bone char: effect of operating conditions, Adsorption, 22 (2016) 297–308.

[29] M. Naushad, Z.A. AL-Othman, G. Sharma, Inamuddin, Kinetics, isotherm and thermodynamic investigations for the adsorption of Co(II) ion onto crystal violet modified amberlite IR-120 resin, Ionics, 21 (2015) 1453–1459.

[30] I. Belbachir, B. Makhoukhi, Adsorption of Bezathren dyes onto sodicbentonite from aqueous solutions, J. Taiwan Inst. Chem. Eng., 75 (2017) 105–111.

[31] A. Sdiri, M. Khairy, S. Bouaziz, S. El-Safty, A natural clayey adsorbent for selective removal of lead from aqueous solutions, Appl. Clay Sci., 126 (2016) 89–97.

[32] A. Sdiri, T. Higashi, F. Jamoussi, Adsorption of copper and zinc onto natural clay in single and binary systems, Int. J. Environ. Sci. Technol., 11 (2014) 1081–1092.