Asian Journal of Chemistry; *Vol. 36, No. 1 (2024), 120-124*

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2024.30682

Adsorption and Kinetic Studies of Nickel(II) Ions onto Vermiculite based Ionite

Obid Tursunmurativ[1,*], Suyun Khushvaktov[1], Murod Jurayev[1],
Davronbek Bekchanov[2] and Mukhtarjan Mukhamediev[2]

[1]Chirchik State Pedagogical University, Chirchik, Uzbekistan
[2]National University of Uzbekistan named after Mirzo Ulugbek, Tashkent, Uzbekistan

*Corresponding author: E-mail: obidosiyo@gmail.com

Received: 6 October 2023; *Accepted*: 18 November 2023; *Published online*: 31 December 2023; AJC-21493

Using vermiculite based ionite, the absorption efficiencies of Ni^{2+} ions from synthetic solutions were investigated. The effects of pH and initial concentration of Ni^{2+} ions their absorption capacity were investigated to optimize process conditions using pseudo-first and pseudo-second-order. The results obtained from the sorption of Ni^{2+} ions on vermiculite based ionite show the kinetic characteristics close to the pseudo-second order. The high Ni^{2+} ions sorption is attributed due to the the complexation of metal ions with $-NH_2$ groups present in the absorbent, which results in the strong coordination bonds.

Keywords: Vermiculite, Sorption, Ionite, Nickel(II) ion, Kinetics.

INTRODUCTION

Wastewater treatment is a crucial industry that faces significant challenges due to increasing high quantities of heavy metal ions in the wastewater, which poses the acute complex problems for the ecology and the environment. In order to maintain the ecosystem, several types of strategies are utilized to diminish the amount of metal cations, which are present in the contaminated water. Early methods such as filtration and reverse osmosis, electrodialysis, oxidation-reduction and ion-exchangers are used to separate the metal ions from wastewater [1].

Materials with ion-exchange hydrostatic properties are widely used in various fields, such as pharmaceuticals, petrochemicals and metallurgy, water treatment. Among all their fields of application, the most important are the treatment of natural water and wastewater, and the separation of rare and precious metals [2]. The primary reason for focusing on natural sorbents is their cost-effectiveness and ready availability. Clay minerals are one of the most extensively used classes of sorbents among any of these naturally occurring materials that are capable of absorbing ions [3]. The most important factor in the use of clay minerals is their ease of extraction and naturalness, low cost of production and durability and heat tolerance [4].

There are two types of adsorbents namely synthetic and natural adsorbents. Initially, synthetic adsorbents were regarded as waste material or byproducts of industrial processes rather than as materials for sorption. The majority of sorbents currently on the market are synthetic sorbents, characterized by their hydrophobic qualities that make them highly effective at absorbing various petroleum-based chemicals [5]. Examples of synthetic sorbents include polystyrene, poly-propylene and polyvinyl chloride. In addition to its low density, high hydrophobicity and oleophilicity, it possesses drawbacks such as high expense, non-biodegradability, and ecological hazards to the environment and living things [6].

A few examples of natural adsorbents include biosorbents, biochars, clay and zeolite (abundant and inexpensive). Natural adsorbents are divided into organic materials such as peat moss or wood products and inorganic materials such as silt or clay. Examples of biosorbents derived from agricultural waste include date pits, walnut shells, corn husks, banana peels, egg shells and palm leaves. The advantage of natural adsorbents is that they are easy to find, natural, ecologically clean, inexpensive and their sorption properties are comparable to synthetic adsorbents. Table-1 below illustrates the results of recent study on the sorption of heavy metals to soil minerals, which differs from the sorption properties of clay minerals [7]. According to Table-1, each of the soil minerals is selective for specific metal ions, indicating that the sorption process effectively absorbs the particular metal ions.

Normally, clay or clay minerals are a group of hydrous alumino-silicates that make up the bulk of the phyllosilicate family and usually have a particle size of 2 to 4 mm. Their small size and large surface area give clay minerals a number of unique properties, including high cation exchange capacity, catalytic properties [7,8].

There is a classification of the origin and distribution of vermiculite, which are mainly divided into three classes: kaolin, smectite and illite group. Examples of the smectite group include bintonite or vermiculite [8]. These mineral mainly contains magnesium and iron silicates and considered as one of the good adsorbents for removing the heavy metal ions [9,10]. Vermiculites are usually brown in colour and bronze in appearance. In fact, the colour depends on the amount of ingredients. Depending on the type and proportions of the components, it varies from black to dark brown and even green, yellow and yellowish-brown. Differences in the composition of minerals affect not only colour, but also some other properties [11].

Vermiculite has aluminum and magnesium silicic acid salts with bound water; when heated to 650-1000 ºC, due to the separation of layers and bound water, vermiculite expands several tens of times. After cooling, expanded vermiculite cannot retain its original size, it swells and forms a new size. Vermiculite has high acid resistance and stable deformation properties. Resized vermiculite has a very low density and is very light. It can be used in the production of polymer-based compositions [12].

So far, the sorption properties of vermiculite have been limited studied in wastewater treatment, and it is an excellent adsorbent for the removal of non-ferrous metal ions such as copper(II), lead(II) and cadmium(II) from wastewater [13-15]. Absorption of heavy and rare metal ions into vermiculite is accompanied by heat absorption. The mechanisms of sorption of metal cations of natural "silicates" have been studied, considered in various works, and it has been established that the most important sorption centers are basal and hydroxide centers [16].

Previous studies [17] have shown that the sorption capacity of vermiculite for metal ions depends on the environment of the solution (acidic or alkaline environment) and the sorption capacity increases with the pH of the solution. It was also found that the sorption capacity of metal cations on a modified vermiculite based ion exchanger increases with increasing temperature. In this work, the adsorption process of using modified vermiculite (vermiculite with polyethylene polyamine, ionites) as a sorbent for nickel ions was investigated. The mechanisms of Ni^{2+} ion sorption processes were studied and analyzed.

EXPERIMENTAL

As a result of the modification of vermiculite with polyethylene polyamine, ionites were prepare and analytically pure substances were used to study the sorption of nickel (II) ions on ion-exchange materials.

Preparation of Ni(II) stock solution: Nickel(II) solution was prepared from analytical grade $Ni(NO_3)_2 \cdot 6H_2O$ by dissolving 58.16 g in 2 L distilled water to obtain 0.1 mol/L concentration. Then, aliquot solutions of 0.05, 0.025 and 0.0125 mol/L were prepared by diluting the 0.1 mol/L Ni^{2+} solution.

Preparation of ion exchangers based on vermiculite: In order to obtain ionic material, vermiculite was first heated at high temperature. Then polyethylenepolyene and vermiculite were mixed in different proportions and left at room temperature for 30 min. The resulting mixture was then placed into a vessel, which was sealed tightly and heated in a muffle furnace at 403 K for 300 min. The obtained ionite was washed with distilled water and the value of static exchange capacity (SEC) against HCl was determined to be 2.5 mgequiv./g.

Experiments on the sorption process

Study of sorption kinetics: For this purpose, using 0.1 mol/L of Ni^{2+} ions, the aliquotes of 0.05; 0.025 and 0.0125 mol/L

TABLE-1
PERCENTAGE OF OXIDES IN SOIL MINERALS, CATION EXCHANGE CAPACITY, SURFACE AREA AND SORPTION OF HEAVY METALS

	Oxides	Natural soil minerals						
		Kaolinite	Halloysite	Bentonite	Montmorillonite	Vermiculite	Attapulgite	Sepiolite
Elemental composition (mass fraction, %)	SiO_2	53.7	46.86	50.08	65.34	39.00	58.38	55.21
	Al_2O_3	43.6	34.10	17.40	12.39	12.00	9.50	0.43
	Fe_2O_3	2.00	2.27	6.00	2.38	8.00	–	0.15
	TiO_2	0.1	2.72	–	0.52	–	0.56	0.05
	Na_2O	–	0.05	1.39	0.53	–	–	0.10
	K_2O	0.5	0.8	0.84	1.54	4.00	–	0.15
	CaO	–	0.13	0.28	0.24	3.00	0.40	0.20
	MgO	–	0.08	3.95	0.95	20.00	12.10	24.26
Cation exchange capacity and surface area	Cation exchange (mg/g) (pH = 7)	3-15	40-50	80-90	40-90	100-150	40-60	3-20
	Surface area g/m^2	5-40	110	200	140-170	760	160	40-180
Absorption properties of metals		Pb(II)	Cs, U(VI)	Pb(II), Cu(II)	Cr(VI), Cu(II)	Cu(II), Cr(VI), Co(II)	Cr(VI), Co(II)	Hg(II), Cd(II), As(III)

were prepared and the duration of sorption of metal ions from the prepared solutions was studied at 30, 60, 90, 120, 150, 180, 210, 240, 270, 300 min and 12, 24 h. For this, 0.3 g of dried sorbent was added to 100 mL of metal solutions and shaked virgrously and left for atleast 2 h in a static manner. Changes in the Ni^{2+} concentrations, before and after absorption were determined using a spectrophotometer (Microplate reader Perkin-Elmer, USA).

The Ni^{2+} ion absorbed by the vermiculite-based ionite was calculated by the following formula:

$$Q_e = \frac{V}{m} \times C_o - C_e \quad (1)$$

where, Q_e = concentration of absorbed Ni^{2+} ion; C_o = initial concentration of Ni^{2+} in mol/L; C_e = equilibrium concentration of Ni^{2+} in mol/L; V is the volume of solution, l; m = dry weight (g) of the ion exchanger.

Sorption kinetic models: The solute absorption rate, which defines the equilibrium time necessary to complete the adsorption reaction, can be determined *via* kinetic analysis. Two well known kinetic models *viz*. pseudo-first order and pseudo-second order models were employed to describe the adsorption process.

RESULTS AND DISCUSSION

FT-IR studies: The obtained sorbent was analyzed using the FT-IR spectroscopic method. The IR of vermiculite based ionite shows that the absorption peak at 2933.99 and 2855.10 cm^{-1}, which corresponds to the symmetric and asymmetric $-CH_2-$ group (Fig. 1). The polymeric compound has penetrated the interlayers of vermiculite, indicating the successful formation of vermiculite based ionite. The absorption at 3013.37 cm^{-1} is due to $-NH_2-$ groups, which confirms the presence of the polymeric compound *i.e.* polyethylene polyamine, whereas the absorption peak at 1276.45 cm^{-1} corresponds to $Si-CH_3$. The absorption peak belonging to the C=O group appeared at 1658.31 with high intensity. As a result, it can be concluded that the organic compound modified composite was effectively achieved between the vermiculite layers.

The kinetics results of adsorption of Ni(II) ions of the ion-exchange material obtained by modifying vermiculite was studied by spectrophotometerically. It is clearly observed that adsorption capacity of the modified vermiculite was increased. This The increase in adsorption efficiency was due to the increase in porosity and saturation of negatively charged $-NH_2$ anions, which enhanced the adsorption of positively charged metal ions through electrostatic force of attraction.

Effect of pH: The effect of pH on adsorption of Ni^{2+} ions on vermiculite based ionite was also studied. The adsorption experiment was performed in the pH range of 1-5, since the precipitation of Ni^{2+} ions occurred at pH above 5. The adsorption of Ni^{2+} ions increased significantly as the pH increased from 2.0 to 5.0 with optimum removal efficiency of 86.2%. As the pH was increased from 5.0 to 5.5, the rate of adsorption decreased due to hydrolysis of Ni^{2+} ion at higher pHs.

Effect of inital Ni^{2+} ion concentration: Intially, the adsorption capacity of the adsorbent increases as the initial concentration increases due to an enhanced driving force of the metal

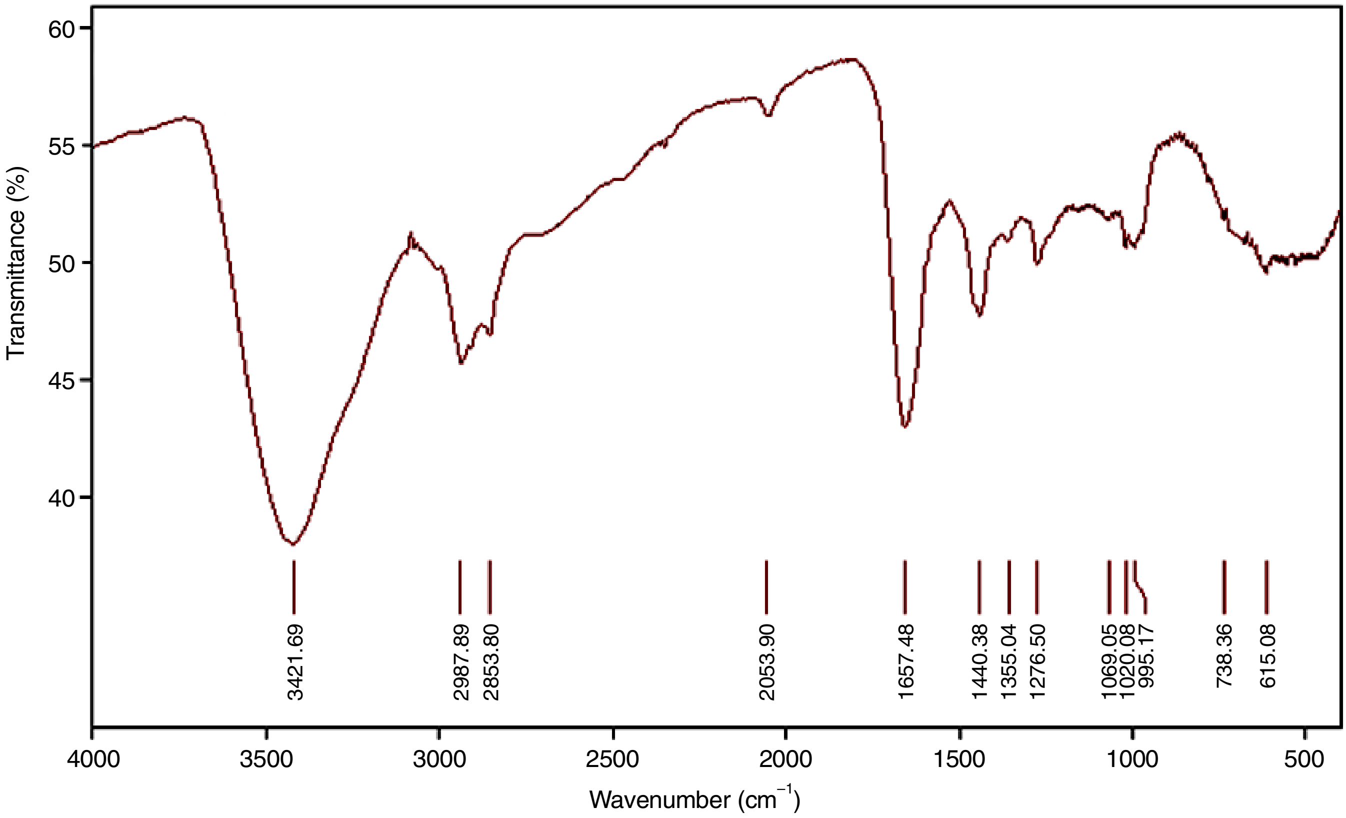

Fig. 1. FT-IR spectrum of ion-exchanger composite containing vermiculite and polyethylene polyamine

ion towards the active sites. The removal rate of Ni^{2+} ions was maximum at the initial concentration of 25 mg/L indicating the high percentage adsorption. However, a decrease in the percentage removal as the initial concentration increased from 25 mg/L onwards can be attributed to more metal ions competing for the fixed binding sites available for interaction.

Adsorption kinetics: The adsorption data obtained for Ni^{2+} ions on modified vermiculite while studying the effect of temperature were analyzed using pseudo first-order and pseudo second-order models.

First-order sorption kinetics is expressed by the following equation [10]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t$$

where q_t and q_e are the mass of Ni^{2+} (mg/g) absorbed at a certain time and at equilibrium; k_1 is the rate constant of the first-order sorption process (1/min) and the angular value of the slope of the intersection in the linear graph of log $(q_e - q_t)$ *versus* time is $k_1/2.303$ (Fig. 2).

The second-order sorption kinetics can be represented by the following:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t$$

At the initial Ni^{2+} absorption rate (t = 0) is found by the following formula:

$$h = k_2 \cdot q_e^2$$

where, k_2 is the second-order sorption rate constant, q_e is the mass of Ni^{2+} ions absorbed by a certain mass of sorbent (mg/g), and t is the time (min).

From the results (Table-2), the pseudo second-order model best fit the data for adsorption of Ni^{2+} ions with regression coefficient (R^2) values of 0.9967-0.9988 at the optimum temperature as a function of contact time (Fig. 3). It can be suggested that the interaction between sorbent and Ni(II) is the result of weak bonding with amine ($-NH_2$) group through donor-acceptor bond and mutual electrostatic interaction (Fig. 4).

Conclusion

In summary, the modified vermiculite based ionite using poly-ethylene polyamine significantly increased the adsorption capacity for Ni^{2+} ions and thus can be used as effective adsor-

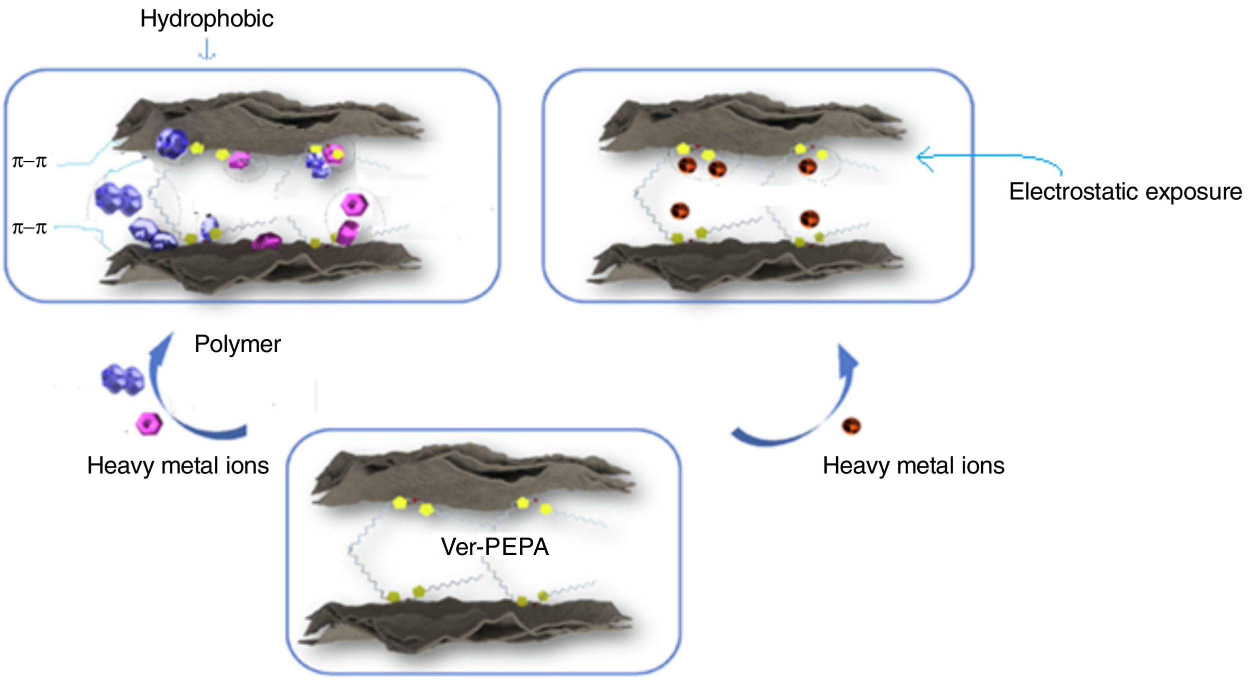

Fig. 2. Sorption scheme of metal ions on vermiculite (Ver) and vermiculite and polyethylene polyamine (Ver + PEPA) composite

TABLE-2
KINETIC SORPTION PARAMETER DATA OF Ni^{2+} IONS ON AN ION EXCHANGER BASED ON VERMICULITE

Sorbent	Metal cation	Initial concentration (mol/L)	First-order sorption kinetics			Second-order sorption kinetics			
			Equilibrium adsorption amount q_e (mg/g)	k_1 (min^{-1})	R^2	Equilibrium adsorption amount q_e (mg/g)	k_2 (mg/g min^{-1})	R^2	E_a (kj/mol)
Based on vermiculite ionite	Ni^{2+}	0.0125	92.8	0.4097	0.796	97.4	0.4368	0.997	19.8
		0.0250	121.2	0.4138	0.812	143.4	0.4467	0.997	
		0.0500	145.9	0.4383	0.841	152.5	0.4907	0.998	
		0.1000	164.8	0.4670	0.863	178.4	0.5668	0.9988	

Average k_1 = 0.4323; k_2 = 0.50876

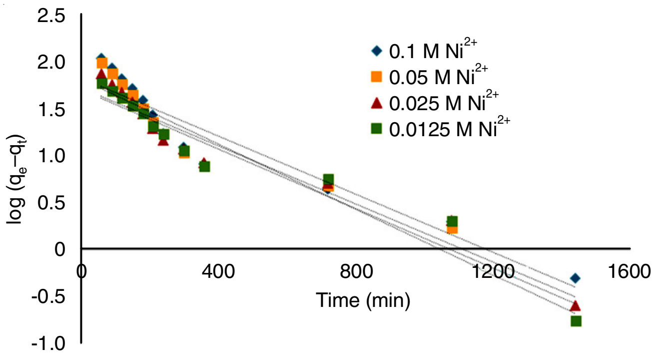

Fig. 3. Kinetic model of pseudo-first order sorption of Ni^{2+} ions on an ion-exchanger based on vermiculite

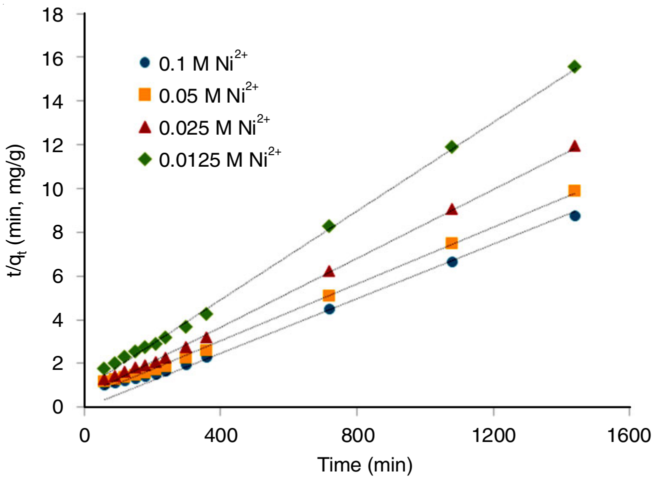

Fig. 4. Kinetic model of pseudo-second order sorption of Ni^{2+} ions on an ion-exchanger based on vermiculite

bent for the removal of Ni^{2+} ions from the synthetic solutions. The experimental data were fitted to the pseudo-second order kinetic model ($R^2 = 0.9967$-0.9988). The sorption capacity of Ni^{2+} ions at equilibrium was calculated to be 0.0814 mg g^{-1}.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. D. Bekchanov, H. Kawakita, M. Mukhamediev, S. Khushvaktov and M. Juraev, *Polym. Adv. Technol.*, **32**, 2700 (2021); https://doi.org/10.1002/pat.5209
2. M.G. Mukhamediev and D.Z. Bekchanov, *Russ. J. Appl. Chem.*, **92**, 1499 (2019); https://doi.org/10.1134/S1070427219110053
3. B.O. Otunola and O.O. Ololade, *Environ. Technol. Innov*., **18**, 100692 (2020); https://doi.org/10.1016/j.eti.2020.100692
4. A.G. Olaremu, *Chem. Res. J.*, **6**, 157 (2021).
5. B. Davron, M. Mukhtar, K. Nurbek, X. Suyun and J. Murod, *Int. J. Technol.*, **11**, 794 (2020); https://doi.org/10.14716/ijtech.v11i4.4024
6. M.G. Mukhamediev, D.Z. Bekchanov, M.M. Juraev, P. Lieberzeit and D.A. Gafurova, *Russ. J. Appl. Chem.*, **94**, 1594 (2021); https://doi.org/10.1134/S1070427221120041
7. M. Debure, C. Tournassat, C. Lerouge, B. Made, J.C. Robinet, A.M. Fernandez and S. Grangeon, *Sci. Total Environ.*, **642**, 216 (2018); https://doi.org/10.1016/j.scitotenv.2018.06.037
8. M. Kotti, A. Papafilippaki, P. Prassa and A. Xirouhaki, *Comput. Water, Energy Environ. Eng.*, **7**, 111 2018); https://doi.org/10.4236/cweee.2018.73007
9. P. Lieberzeit, D. Bekchanov and M. Mukhamediev, *Polym. Adv. Technol.*, **33**, 1809 (2022); https://doi.org/10.1002/pat.5656
10. X.L. Su, L.Y. Ma, J.M. Wei and R.L. Zhu, *Appl. Clay Sci.*, **132-133**, 261 (2016); https://doi.org/10.1016/j.clay.2016.06.011
11. F. Koksal, O. Gencel and M. Kaya, *Constr. Build. Mater.*, **88**, 175 (2015); https://doi.org/10.1016/j.conbuildmat.2015.04.021
12. D.S. Moraes, E.M.S. Rodrigues, C.N. Lamarao, G.T. Marques and A.F.S. Rente, *J. Hazard. Mater.*, **366**, 34 (2019); https://doi.org/10.1016/j.jhazmat.2018.11.086
13. A. Wegrzyn, L. Chmielarz, P. Zjezdzalka, A. Kowalczyk, M. Jablonska, X.B. Tolosa and M. Michalik, *Acta Geodyn. Geomater*., **10**, 353 (2013); https://doi.org/10.13168/AGG.2013.0034
14. M. Bugarcic, Z. Lopicic, T. Šoštaric, A. Marinkovic, J.D. Rusmirovic, D. Miloševic and M. Milivojevic, *J. Environ. Chem. Eng*., **9**, 106020 (2021); https://doi.org/10.1016/j.jece.2021.106020
15. N.C. Das and M. Bandyopadhyay, *Water Environ. Res.*, **64**, 852 (1992).
16. J. Feng, M. Liu, L. Fu, K. Zhang, Z. Xie, D. Shi and X. Ma, *RSC Adv.*, **10**, 7635 (2020); https://doi.org/10.1039/D0RA00223B
17. K. Vijayaraghavan and F.D. Raja, *Clean Soil Air Water*, **43**, 1174 (2015); https://doi.org/10.1002/clen.201400423