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Application of polypyrrole coated on perlite zeolite for removal of nitrate from wood and paper factories wastewater

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ABSTRACT

Because of its high solubility, nitrate is considered the most common contaminant of groundwater throughout the world: a contaminant that causes cancer and methemoglobinemia in infants. This research intended to study removal of nitrate from the effluent of the Wood and Paper Factory in Sari with the help of a polypyrrole composite on the natural zeolite perlite. This study, which was carried out under laboratory conditions on the effluent of from the Wood and Paper Factory in Sari, considered the effects of the empirical parameters pH, contact duration, adsorbent dose, and temperature on adsorption. FTIR and SEM were used to identify the structure of the synthesized composites. The optimum conditions for nitrate adsorption by polypyrrole coated on perlite (ppy/perlite) were pH = 5, contact time = 20 min, and adsorbent dose = 0.6 g/100 mL of the effluent. The kinetic data for nitrate adsorption matched the pseudo second-order equation and the Freundlich isotherm, and increases in temperature had a positive effect on removal efficiency. Study of the thermodynamics related to the process indicated that it was a spontaneous and endothermic one. The ppy/perlite composite could be used as an effective adsorbent to remove nitrate from aqueous solutions.

Keywords: Polypyrrole; Perlite; Wood and paper factory effluent; Nitrate

1. Introduction

As the most common contaminant of surface and groundwater, nitrate has been a serious concern throughout the world during the past few decades. Water resources are contaminated with nitrate from point and non point sources including urban and agricultural runoff, animal manure, unsuitable disposal of sanitary and industrial wastewater, leakage of septic systems, and NO_x generated in air control equipment [1–3].

Nitrate is converted into nitrite in the stomachs of infants less than six months of age. Nitrite attaches to the hemoglobin in red blood cells and changes it to methemoglobin. This conversion reduces the ability of blood to transfer oxygen and causes a condition called methemoglobinemia (the blue-baby syndrome) [4]. Furthermore there is

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evidence indicating that gastric, bladder, and lymph node cancers develop under conditions of prolonged exposure to nitrate [5]. From the environmental point of view, presence of nitrate in water resources causes the eutrophication phenomenon (that results in algal blooms) [6]. The World Health organization (WHO has set a maximum allowable nitrate concentration of 50 mg/L for drinking water [7]. There are various methods for removing nitrate from drinking water including selective ion exchange, reverse osmosis, electro dialysis, and biological methods. However, these methods involve problems such as high cost, excessive energy consumption, difficult operation, slow process, production of byproducts, etc. [8–15]. Nowadays, use of the adsorption process has expanded as an effective method for removing various contaminants because it has a simple design, low design and utilization costs, and does not produce and dangerous byproducts [16–18].

Various adsorbents are used in the adsorption process including nano-alumina [1], iron/copper nanoparticles [19], chitosan [20], and clay soil [21]. Bhatnagar et al. used alumina nanoparticles as an adsorbent for removing nitrate from aqueous solutions and reported maximum removal was achieved at pH = 4 and contact time = 60 min [1]. Demiral utilized sugarcane bagasse to synthesize activated carbon for removing nitrate and observed the maximum removal efficiency (43%) under acidic conditions [22]. Moreover, Wang et al. used optimized wheat plant residue to remove nitrate from aqueous solutions and found the best results at contact time of 150 min and adsorbent dosage of 2.5 g/L [23]. Iran is the largest perlite producing country in the world. Soil that contains perlite has been utilized to remove various contaminants from water or wastewater because it has high porosity and is low cost, non-toxic, and eco-friendly [24–28].

Polypyrrole is considered one of the most important conductive polymers due to its high electrical conductivity, stability, environmental stability, and ease of synthesis [29]. Perlite is a volcanic rock with Muchporosity and special surface area which low-cost [30].

Therefore, the present research intended to study synthesis of polypyrrole composite on the natural zeolite perlite to improve nitrate removal, and to investigate the effects of the parameters of pH, contact time, adsorbent dosage, and temperature. Moreover, adsorption kinetics and isotherm were also studied and analyzed.

1.1. Materials and methods

This research was carried out to remove nitrogen from the effluent at the Wood and Paper Factory in Sari. Table 1 presents the characteristics of the effluent. All laboratory materials used in the present research were bought from the German Company Merck. Moreover, pyrrole monomer and $FeCl_3$, which were bought from the Merck Company and perlite, purchased from the Afrazand Company, were used to produce the adsorbent.

1.2. Perlite synthesis

The perlite used to coat poly pyrrole on it was bought from the Afrazand Company. It was first washed with double-distilled water and dried in an oven at 110°C for 24 h. The perlite granules were then ground and passed through a 200 mesh sieve. The grounded perlite was then placed in an over at 550°C for five hours to eliminate any possible impurities. To activate the perlite, five grams of it were stirred in 100 mL of 0.06 N sulfuric acid at 87°C for 2 h. The perlite was then washed several times with double-distilled water, and was finally dried in an oven at 110°C for 24 h [31].

Table 1
Characteristics of the effluent wastewater from the Wood and Paper Factory in Sari

Compound	Concentration in waste water before removal
Cu (mg/L)	0.5
Mg (mg/L)	300
Fe (mg/L)	1.5
Zn (mg/L)	16
Total N(NO_3^-, NO_2^-) (mg/L)	33
S^{-2} (mg/L)	21
SO_4^{-2} (mg/L)	155
Color (absorbance at 600 nm)	0.3612
COD (mg/L)	2700

1.3. Synthesis of ppy/perlite

Five grams of $FeCl_3$ were added to 100 mL of water and the mixture was stirred until a uniform solution was obtained. One gram of perlite was then added to the solution followed by 1 g of the polypyrrole monomer. The solution was put on a stirrer at room temperature for four hours and then passed through filter paper. The obtained precipitate was washed several times with twice-distilled water and then put on watch glass at room temperature to dry [32,33].

2. Materials and methods

All adsorption experiments were conducted discontinuously on the laboratory scale. The effects of the various parameters including the initial pH of the solution (4–10), contact duration (4–28 min), adsorbent dosage (0.1–0.8 g/100 mL) and temperature (20–40°C) on the extent of nitrate removal by the ppy/perlite composite were determined.

The optimum pH was determined first. For this purpose, pH values of effluent solutions with known concentrations and volume of 100 mL were adjusted in the range of 4–10 by using 0.1 N HCl and NaOH. Following that, 0.6 g of the adsorbent was added to each effluent sample and the samples were stirred by a stirrer at 400 rpm for 20 min. They were then passed through filter paper and the concentrations of the residual nitrate were measured using a UV/Vis spectrophotometer at the wavelengths of 220–270 nm.

In the next stage, the effects of contact time were studied in the range of 4–28 min and at the optimum pH (which was determined in the previous stage). After optimizing the pH and contact time, the effects of various adsorbent doses (0.6–0.8 g/100 mL) were analyzed. In all stages of the experiments, removal efficiencies and adsorption capacities were calculated using Eqs. (1) and (2):

$$\text{Removal percentage} = \frac{C_i - C_t}{C_i} \quad (1)$$

$$q_e = \frac{C_0 - C_e}{m} \times v \quad (2)$$

In the above equations, C_i is the initial concentration of the solution (mg/L), C_t shows the concentration at time t (mg/L), q_e nitrate adsorption capacity (mg/L), *m* the adsorbent dose (g), and *V* the sample volume (L) [34,35].

2.1. Determining the temperature and thermodynamics of the nitrate adsorption process

Experiments were carried out in this stage at various temperatures (20, 30, and 40°C) while keeping all the other parameters (pH, contact duration, adsorbent dose) constant at their optimum values determined in the previous stages. A water bath was used to maintain a uniform temperature throughout the samples. The parameters of Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated from Eqs. (3)–(5) (2).

$$\Delta G^0 = -RT\ Ln(k) \quad (3)$$

$$Ln\left(\frac{\text{K2}}{\text{K1}}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T2} - \frac{1}{T1}\right) \quad (4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S \quad (5)$$

In the above equations, *R* is the Universal Gas Constant (8.314 J/mol·k), *T* (K) is the absolute temperature, and K_c the thermodynamic equilibrium constant (2).

Finally, the adsorption isotherm and kinetics were determined for the optimum conditions as follows [16,36].

2.1.1. Langmuir isotherm

Langmuir's theory explains the formation of a single layer by adsorption on a homogeneous surface of the adsorbent. The linear equation of this theory is as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (6)$$

In the above relation, C_e is the nitrate equilibrium concentration (mg/L); q_e the amount of the nitrate adsorbed at the equilibrium time (mg/g), K_L the Langmuir constant (L/mg), and q_m the maximum monolayer adsorption (mg/L).

A line is obtained by plotting C_e/q_e against C_e. The slope (q_0) and y-intercept of this line can be used to determine K_L.

2.1.2. Freundlich isotherm

Contrary to the Langmuir model, this model is based on non-homogeneous (heterogeneous) surfaces, and its equation is as follows:

$$ln(q_e) = ln(k_f) + \frac{1}{n} ln(c_e) \quad (7)$$

In the above relation, C_e and q_e are as defined before, k_f and *n* are Freundlich constants that depend on adsorption capacity: *n* is the indicator of adsorption intensity and k_f the intensity of adsorption capacity of the adsorbent (mg/g (L/mg) 1/n). By plotting the linear diagram of Ln q_e against Ln C_e and calculating the slope and y-intercept of the diagram, *n* and K_L can be derived, respectively.

2.1.3. Dubinin-Radushkevich isotherm

This model, which is usually used to estimate porosity and adsorption free energy, assumes that adsorption curves are related to the porous structure of the adsorbent. The linear equation for this model is as follows:

$$ln(q_e) = ln(Q_m) - \beta\varepsilon^z \quad (8)$$

In the above relation, q_e is as defined before, q_m the adsorption capacity of the monolayer, β (the equation constant) the porosity factor, and ε is called the Polanyi potential and is derived from Eq. (9):

$$\varepsilon = RT\,ln\left[1 + \left(\frac{1}{C_e}\right)\right] \quad (9)$$

In the above relation, *R* is the Universal gas constant, *T* temperature (in Kelvin), and c_e as defined before.

2.2. Determining adsorption kinetics

Various kinetic models such as the pseudo first-order and second-order models and the Maurice-Weber model were used to calculate the data obtained from the experiment for predicting the kinetic parameters of nitrate adsorption.

The pseudo first-order and second-order models are presented below in Eqs. (10) and (11), respectively [37]:

$$log(q_e - q_t) = log q_e - \frac{K_1 t}{2.303} \quad (10)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \quad (11)$$

In the above relation, *t* is time (min), q_e and q_t nitrate adsorption capacity at equilibrium time and at time *t* (mg/g), k_1 the constant of the pseudo first-order model (min^{-1}), and k_2 is the constant of the pseudo second-order model (g/mg·min^{-1}). The Maurice-Weber equation is written as follows [38]:

$$q_t = K_{id} t^{0.5} + C \quad (12)$$

In the above equation, q_t is the quantity adsorbed (mg /g^{-1}) at time *t* (min), K_{id} the constant of internal infiltration intensity (mg/ (g·min^{½}), and *C* a constant of the boundary layer thickness

3. Results and discussion

3.1. Adsorption characteristics

Figs. 1 and 2 present the morphology of perlite before and after it was coated with polypyrrole. The polymer coated on perlite can be clearly seen in the figures. Fig. 3, at greater magnification, shows the coated particles are in polymeric form and of nano size.

The structure of ppy/perlite was studied using FTIR (Fig. 4). The peaks in FTIR clearly indicate that the material coated on perlite is polypyrrole. The peak at 1641 cm^{-1} represents the C=C and C–C bonds and that at 1429 cm^{-1} the C-N bond. The C-H and N-H bonds have their peaks at 1292 cm^{-1} and 1064 cm^{-1}, respectively, and those at 781 cm^{-1} and 632 cm^{-1}represent the external C-H bonds. All these indicate the presence of polypyrrole in the composite [33,36–39].

3.1.1. Effects of pH

One of the important parameters in the adsorption process is pH. Therefore, the effects of this parameter on nitrate removal efficiency by ppy/perlite were studied in the 4–10 range in 100 mL of the effluent. Results are presented in Fig. 5. As shown in this figure, removal efficiency improved and reached its maximum when pH value was raised from 4 to 5, but declined at pH ≥ 6. The reason for the increase in removal efficiency at low pH values is the increase in the number of available protons and the decrease in the number of OH^- ions, which increase the positive charge on the surface of the adsorbent and (consequently) increase

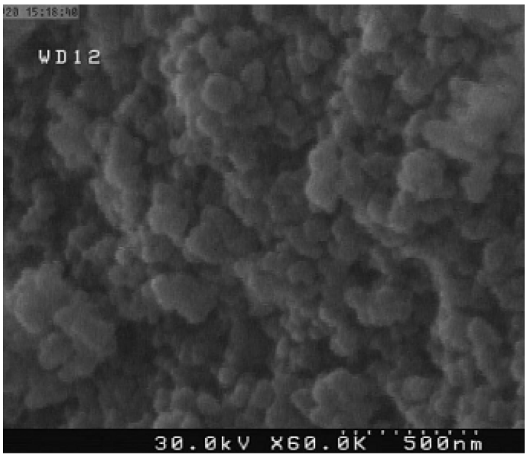

Fig. 1. SEM image of perlite before being coated with polypyrrole.

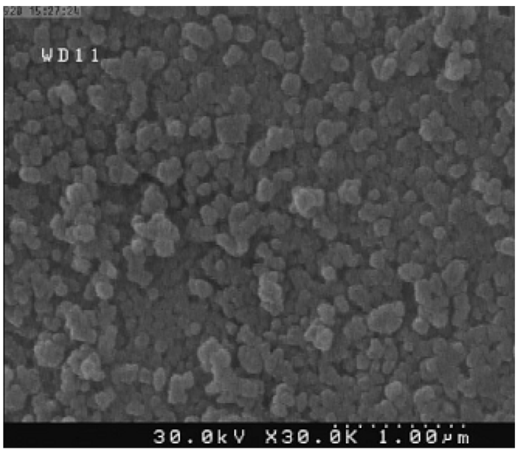

Fig. 2. SEM image of perlite after being coated with polypyrrole.

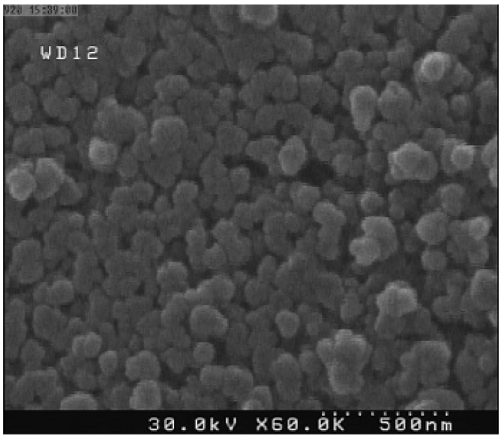

Fig. 3. SEM image of perlite after being coated with polypyrrole (shown at greater magnification).

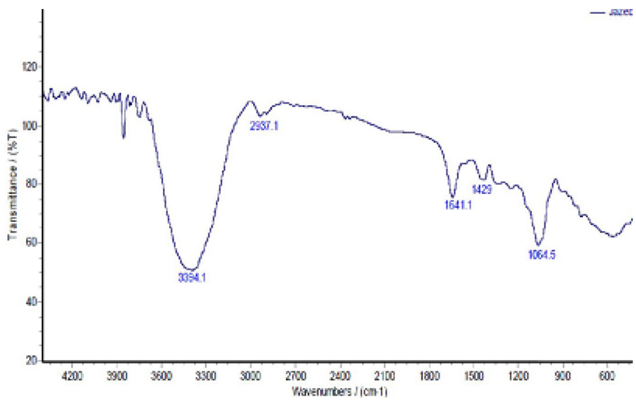

Fig. 4. FTIR spectrum of ppy/perlite.

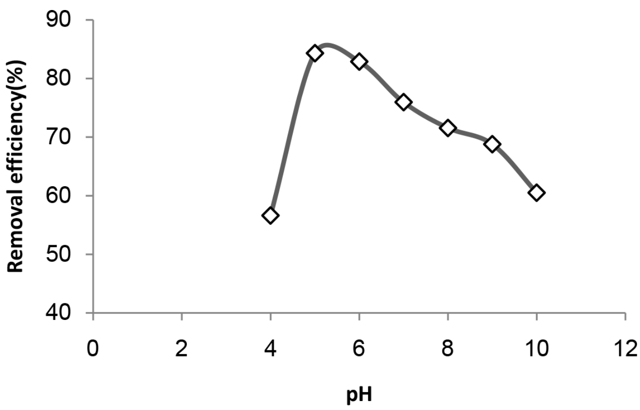

Fig. 5. The effects of pH on efficiency of nitrate removal by ppy/perlite.

nitrate adsorption in the acidic environment. However, the negative charge increases close to the adsorbent surface in basic environments, which leads to increased electrostatic repulsion of nitrate and (consequently) to lower removal efficiency [1,37]. The study carried out by Bhatnagar et al. in 2010 showed that nitrate removal efficiency declined with increases in pH value. Furthermore, as in our research, Ozturk et al. noticed in their study that the highest nitrate removal efficiency achieved by activated Sepiolite happened at the pH value of five [1,37].

3.1.2. Effects of contact time

One hundred mL samples of the effluent were prepared to study the effects of contact duration on efficiency of nitrate removal by ppy/perlite. Their pH values were adjusted to pH = 5 and adsorbent dose of 0.6 g in 100 ml was prepared and stirred by the stirrer at 400 rpm to study the effects of contact duration (in the 4–28 min range) on nitrate removal efficiency. The remaining nitrate concentrations were measured at the end of the contact durations. Fig. 6 shows the effects of reaction durations on efficiency of nitrate removal by ppy/perlite. As seen in the figure, removal efficiency reached 84.2% after 20 min after which there was little change in removal efficiency. Therefore, the optimum contact time was 20 min. Compared to the study conducted by Ensie and Samad in 2014, equilibrium was reached in a shorter time in the present research, which indicated the effectiveness of the adsorbent [8].

3.1.3. Effects of adsorbent dose

One hundred ml samples of the effluent were prepared to study the effects of adsorbent dose on efficiency of nitrate removal by ppy/perlite. Their pH values were adjusted to 5, various adsorbent doses (0.1–0.8 g/100 mL) were added to the samples, the solutions were stirred by the stirrer at 400 rpm for 20 min, and the remaining concentrations of the nitrates in the solutions were measured at the end of the contact duration. Results concerning the effects of adsorbent dose on efficiency of nitrate removal by ppy/perlite are presented in Fig. 7. As shown in this figure, removal efficiency improved when adsorbent dose in 100 ml of the effluent increased from 0.1 to 0.6 g. The reason for this improved efficiency was the increase in the number of available sites for nitrate adsorption. However, at doses higher than 0.6 g little change in removal efficiency was observed because the adsorption sites on the surface of the adsorbent overlapped, which reduced removal efficiency and the adsorbed amount. Therefore, nitrate adsorption in the present research depended on adsorbent dosage. This is in agreement with results obtained in the study conducted by Naghizadeh et al. [40].

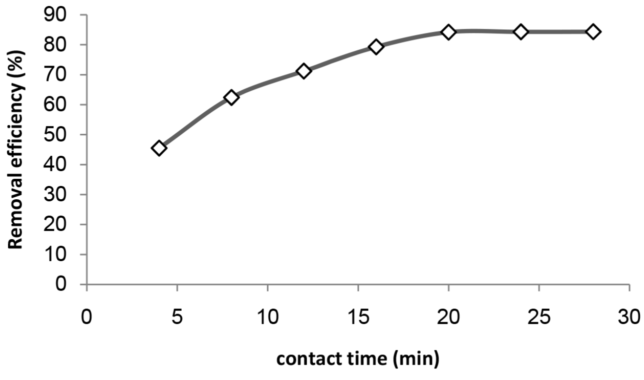

Fig. 6. Effect of contact time on efficiency of nitrate removal by ppy/perlite.

3.1.4. Effects of temperature

One hundred ml samples of the effluent at known concentration, pH = 5, and with adsorbent dose of 0.6 g were prepared and stirred by a stirrer at 400 rpm for 20 min to study the effects of temperature on efficiency of nitrate removal by ppy/perlite at various temperatures (20, 30, and 40°C). Concentrations of the remaining nitrate were measured at the end of the contact times. A water bath was employed to adjust the temperature of the solution so that it remained constant throughout the solution. Table 3 presents results of the thermodynamic studies on nitrate removal at the various temperatures. Study of the effects of temperature indicated that ΔG for this process was negative, which showed it was a spontaneous process. The positive ΔH also suggested that the process was an endothermic one. Furthermore, the value of ΔH can show the adsorption type: values of 0–42 kJ /mol (as in the case of present study) indicate physical adsorption of nitrate on ppy/perlite. Positive ΔS values also revealed that there was an increase in the randomness at the solid/solution interface during the adsorption of the ions. Results of the study Ren et al. conducted in 2016, and those of the research carried out by Bhatnagar et al. in 2010, are similar to those found in the present study [1,41].

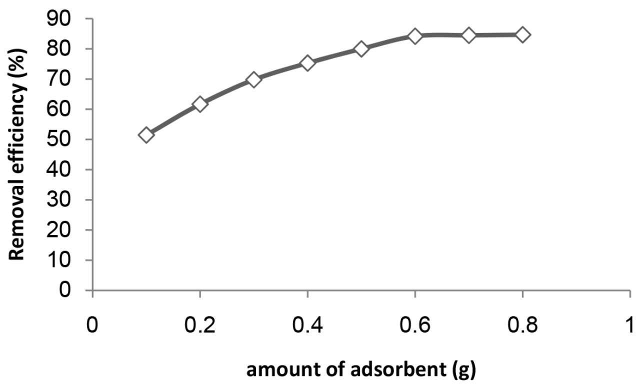

Fig. 7. Effects of adsorbent dose on efficiency of nitrate removal by ppy/perlite.

Table 2
Thermodynamic parameters of nitrate adsorption on ppy/perlite

NO_3	ΔH (kJ/mol)	ΔS (kJ/mol)	T·C	Δ (kJ/mol)	R^2
	35.22	0.267	20	–4.03	0.98
			30	–4.69	
			40	–5.35	

Table 3
Results concerning isothermal studies of nitrate adsorption

Langmuir equation		
	$Y = -0.003x + 0.358$	R^2
		0.225
Freundlich parameter		
K	*n*	R^2
0.71	1.71	0.981
D-R parameter		
Q_m (mg/g)	β	R^2
28.44	0.0025	0.88

Table 4
Results concerning kinetic studies of nitrate adsorption

	R^2	K (min^{-1})
Morris Weber	0.981	1797
Pseudo-first-order	0.874	0.25
Pseudo-second-order	0.997	0.18

3.2. *Adsorption isotherms*

Table 4 presents results obtained from Langmuir, Freundlich, and Dubinin Radushkevich isotherms for nitrate adsorption on ppy/perlite. As shown in this table, the obtained data follow Freundlich isotherm more closely (R^2 = 0.981) compared to Langmuir model (R^2 = 0.225) and Dubinin Radushkevich model (R^2 = 0.88). This indicates that the regions on the surface of the adsorbent were not uniform and had different adsorption capacities and energies. The value of 1/n was between 0 and 1 that indicate sorption of nitrate into ppy/perlite was favorable [42]. This conforms to the results that Mohsenipour et al. and to those Asl et al. found in their studies [43,44].

3.3. *Adsorption kinetics*

Pseudo first- and second-order and Maurice-Weber kinetic models were used to investigate the kinetics of nitrate adsorption on ppy/perlite. Results are presented in Table 4. Comparison of the data readily indicates that the results match the pseudo second-order model well and we can say that the adsorption process was controlled by the pseudo second-order equation. Of course, the Maurice-Weber model also matched the results well. Results obtained from the kinetic studies of Golestanifar et al. and Zheng et al. conform to those obtained in the present research [45,46].

4. Study of the adsorbent by using SEM after the adsorption process

SEM images taken after the adsorbent was used to treat the effluent of the Paper and Wood Factory are presented in Fig. 8. The particles shown in the images represent the adsorbed materials.

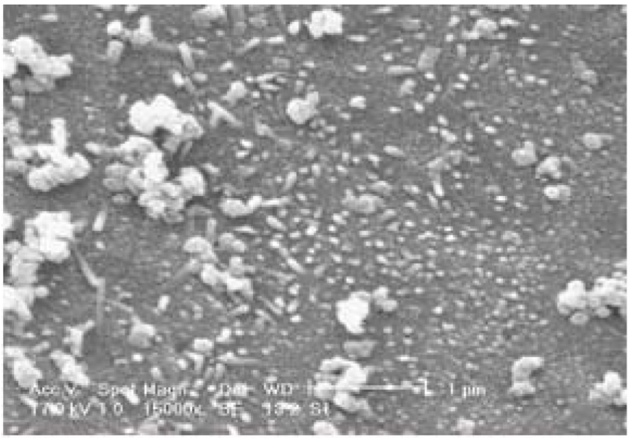

Fig. 8. SEM images of ppy/perlite after treatment of the effluent from the Paper and Wood Factory.

5. Conclusions

The optimum pH for the adsorption process was five, the optimum contact duration 20 min, and the optimum adsorbent dose 0.6 g/100 mL of the effluent from the factory.

The kinetic data for nitrate adsorption matched the pseudo second-order equation and the Freundlich isotherm.

Study of the effects of temperature on the adsorption process and the thermodynamic study of this process revealed that it was a spontaneous and endothermic process.

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