



STUDYING LIVESTOCK BREEDING WASTEWATER TREATMENT WITH BENTONITE ADSORBENT

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ABSTRACT

The possibility of using adsorbents (bentonite, diatomite and kaolinite) for obtaining adsorptive materials effective in livestock breeding wastewater treatment has been assessed. It has been shown on the example of ions of ammonia (NH_4^+) and phosphate (PO_4^{3-}) that particles of bentonite have relatively high adsorption capacity. For these systems, the time of establishing the adsorption balance at room temperature has been determined equalling to 24 h at pH 8 for NH_4^+ and 2 hours at pH 6 for PO_4^{3-} . The data about adsorption kinetics have been processed with the use of first and second-order kinetic models. It has been revealed that the second-order kinetic model described better adsorption of ammonia and phosphate from aqueous solutions by particles of bentonite. Adsorption isotherms have been built and analyzed. The maximum adsorption for particles of bentonite in relation to ions NH_4^+ and PO_4^{3-} has reached 17.24 mg/g and of 5.37 mg/g, respectively.

Keywords: bentonite, diatomite, kaolinite, ammonium, phosphate, adsorption.

INTRODUCTION

As a result of tectonic processes on the surface of the Earth, a wide variety of promising mineral reserves was formed in the South Central Coast of Vietnam field. The results of the study revealed 25 types of minerals on the South Central coast such as kaolinite, lignite, peat, iron, tin, lead, zinc, gold, ruby, sapphire, opal, quartz crystal, etc. Of these, kaolinite, bentonite and diatomite are very important in the industry [1].

In industrial wastewater treatment, kaolinite, bentonite and diatomite are widely used as materials for studying and production of adsorbents that are insoluble in water, which is of great importance [2].

Adsorption is considered to be a simple, efficient and reliable method, which is used for industrial and domestic wastewater treatment in industry, and for improving quality of drinking water. Depending on the resolved task and the nature of the substances removed from the water, a wide range of hundreds of adsorbents is used.

The aim of this work was studying the choice of clay adsorbents for purification of livestock breeding wastewater.

MATERIALS AND METHODS

Samples of sorbents (bentonite, diatomite and kaolinite) were collected. The montmorillonit-containing clays of the South Central Coast of Vietnam field were used as raw material. For the experiment, insoluble in water bentonite was used, then bentonite was mixed with liquid glass (Na_2SiO_3) in the ratio of 1: 1 (by weight). Next, Na_2SiF_6 15% (by weight of the liquid glass) was added, mixed and crushed to particles with the size of 0.3

cm. Then the samples were heated at 500 °C for 3 hours [1].

The adsorption capacity of the samples was tested in relation to ions of ammonia and orthophosphate by the static method. Concentration of ammonium ions in the solutions was determined spectrophotometrically with Nessler's reactant [3-4], and of phosphate ions - with ammonium molybdate reactant [4-5]. pH of the solutions was maintained at 8 (ammonium ions) and 6 (phosphate ions) by adding 0.01 M of HCl and 0.01 M of NaOH. Then the solutions were centrifuged at 3000 rpm for 15 min, and their optical density (A) was measured on spectrophotometer in UV and visible light. According to the obtained data, the residual concentration, efficiency of adsorption (N) and adsorption capacity (q) were determined, calculated by equations (1), (2):

$$H(\%) = \frac{(C_{init} - C_{conc})}{C_{init}} \times 100 \quad (1)$$

$$q(\text{mg/g}) = \frac{(C_{init} - C_{conc}) \cdot V}{m} \quad (2)$$

where C_{init} was the initial concentration of ammonium and phosphate ions in the solution (mg/l);

C_{conc} was the concentration of ammonium and phosphate ions in the solutions after the adsorption process (mg/l);

V was the volume of the solution (ml); and m was adsorbent weight (g).

All experiments were performed at room temperature (22 ± 2 °C).

Photomicrographs of bentonite particles were obtained with scanning electronic microscope Quanta 200



3D. The accelerating voltage of the electron gun was 5 kV. The images were obtained at magnification of 2000x. Images were taken with a CCD camera with the use of Hough conversion.

The specific surface area, the volume and the average pore size of the materials were determined by the method of Bruner-Emmett-Teller (BET) [6].

The phase composition of the samples was determined by x-ray diffraction (XRD) [7]. Survey was made with the use of diffractometer Rigaku Ultima IV (Japan) with detector D/teX Ultra. Generator parameters were the following: accelerating voltage of 40 kV, tube current of 40 mA. Survey options included the interval of angles equal to $2\theta=5-85^\circ$, increments of $2\theta=0.02^\circ$, spectra recording speed of $3^\circ/\text{min}$.

The functional groups of bentonite particles were studied by the method of IR spectroscopy, absorption of the samples was recorded in the range of $400 - 4,000 \text{ cm}^{-1}$ with the following parameters: the number of scans of the sample was 32; the number of scans equalled to 32; resolution was 4.000; amplification was 8.0; mirror speed equalled to 0.6329; aperture was 100.00. The obtained IR spectra were analyzed, and the values of wave numbers

were determined with the use of software suite OMNIC (version 7.3) with AutoFilter and baseline correction.

RESULTS AND DISCUSSIONS

The results of studying samples (bentonite, diatomite and kaolinite) using X-Ray Fluorescence (XRF) and BET showed that the main interplanar distance (d_{001}) and specific surface (S) of the bentonite were higher compared to those of diatomite and kaolin (Table-1 and Figure-1). Thus, bentonite has higher adsorption capacity and is a promising adsorbing material for wastewater treatment.

Table-1. Comparison of the value of d_{001} , Å and S, m^2/g of kaolinite, diatomite and bentonite.

Sample	d_{001} , Å	S, m^2/g
Kaolinite	7.15	23.17
Diatomite	9.68	48.47
Bentonite	10.13	52.34

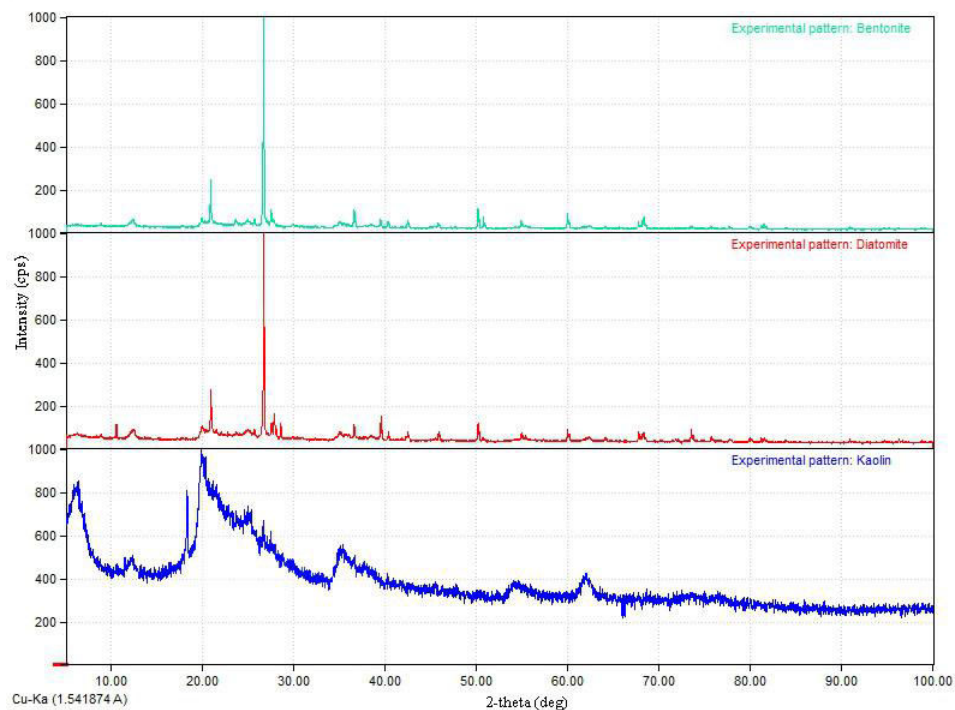


Figure-1. XRF spectrum of bentonite, diatomite and kaolin.

Studies with a scanning electron microscope (SEM) showed that the size of bentonite agglomerates was 10 to $30 \mu\text{m}$. Crystals of montmorillonite are shown in Figure-2 in the form of plates of irregular shape obtained

by the laser particle size analyzer Microtrac S3500. Both individual crystals of montmorillonite (m) and their aggregates (M) were observed.

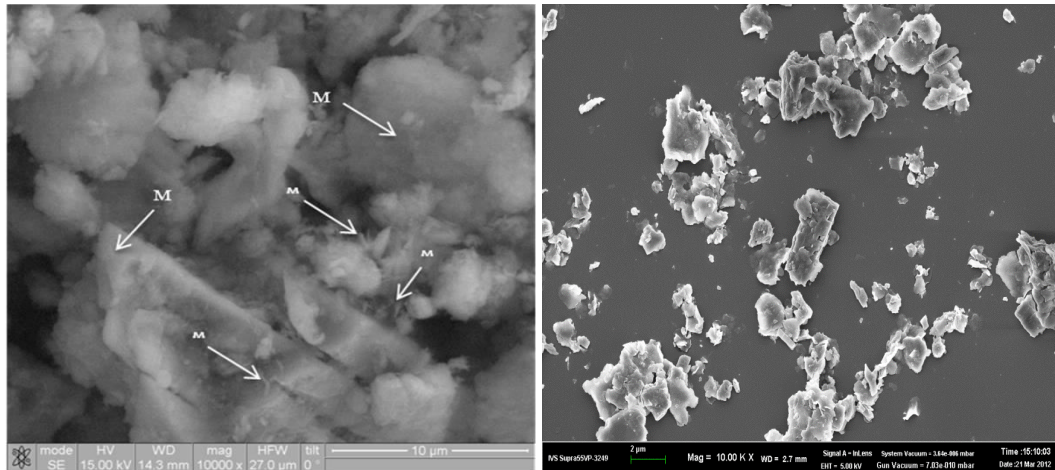


Figure-2. Morphological characteristics of particles.

Based on the x-ray phase analysis with the use of the ARL 9900 series x-ray workstation with a Co anode and $K_{\alpha 1}$ radiation, $U=60$ kV, and energy dispersive analysis (EDAX analyzer combined with ion-electron

microscope Quanta 200 3D), the chemical composition of the studied bentonite had been determined, presented in the form of oxides (Table-2).

Table-2. The oxide chemical composition of bentonite from the South central coast of Vietnam.

Content of oxides, % wt.							
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂
59.02	26.41	7.31	1.14	1.39	0.48	2.77	1.48

Analysis of the elemental composition of bentonite by the method of energy dispersive analysis is shown in Table-3.

Table-3. Elemental chemical composition of bentonite from the South central coast of Vietnam.

Element	Content, % wt.	Content, % atom.
O	47.65	62.95
Na	0.36	0.33
Mg	0.69	0.60
Al	14.08	11.03
Si	27.84	20.95
K	2.32	1.25
Ca	1.01	0.53
Ti	0.90	0.40
Fe	5.16	1.95
Total	100	100

The mineralogical composition of bentonite samples from the South central coast of Vietnam were determined using the x-ray diffraction method of powder materials with the use of an ARL 9900 series x-ray workstation. The results of analysis of the mineralogical composition of samples are shown in Figure-3.

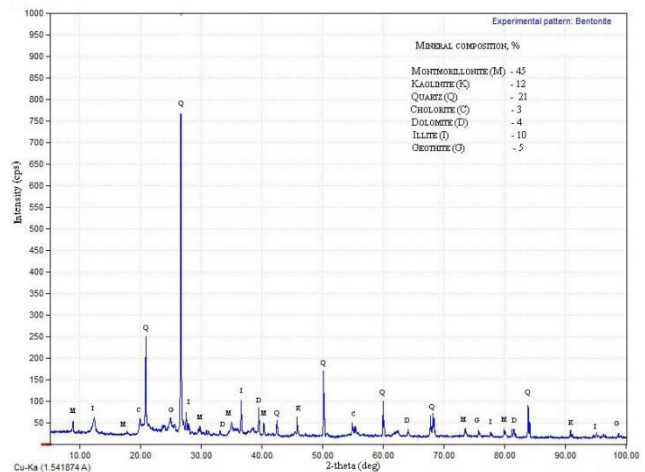


Figure-3. X-ray powder diffraction pattern of a bentonite sample.

The specific surface of the samples was determined on specific surface analyzer TriStar II 3020 using the method of low-temperature nitrogen adsorption. The area of specific surface of bentonite was equal to 52.34 m²/g, the specific pores volume was 0.065 cm³/g, and the average pore size was 50.24 Å.

To determine the mechanism of interaction between ammonium cations (NH_4^+) and anions of phosphate (PO_4^{3-}) with the bentonites, kinetic curves of sorption were obtained (Figure-4) [8-11]. It was found that



the time of reaching sorption equilibrium by ions of ammonium (NH_4^+) was about 8 hours. Further increasing of the exposure time up to 3 days did not result in any significant changes in the equilibrium concentration NH_4^+ . In further experiments, adsorption was prolonged for 24 hours. For anions of phosphate (PO_4^{3-}), the time of reaching sorption equilibrium was approximately 2 hours.

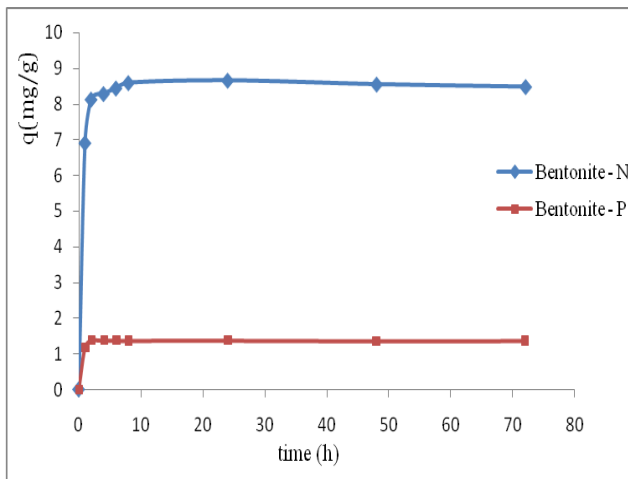


Figure-4. Kinetics of ammonium (25mg/l) and phosphate (5mg/l) ions adsorption.

For analytical expression of the kinetic curves, the method was chosen that consisted in processing the kinetic curves by the equations of inner diffusion kinetics and equations of chemical kinetics (pseudo - first order, pseudo - second order) [12-14]. The results the graphical processing of experimental data in relevant coordinates are shown in Figures.5-6.

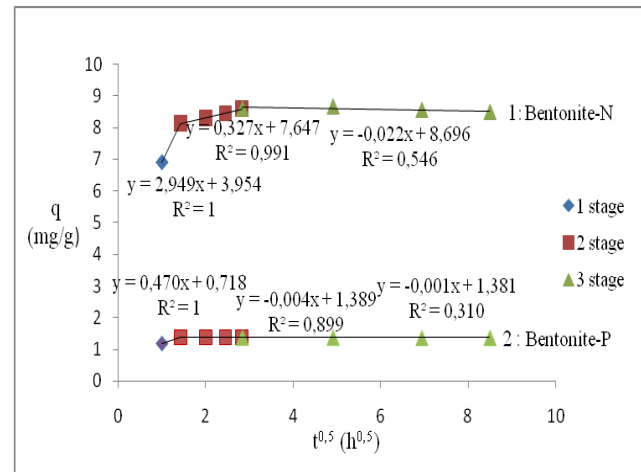


Figure-5. Intradiffusional curve of kinetics of ammonium and phosphate ions adsorption.

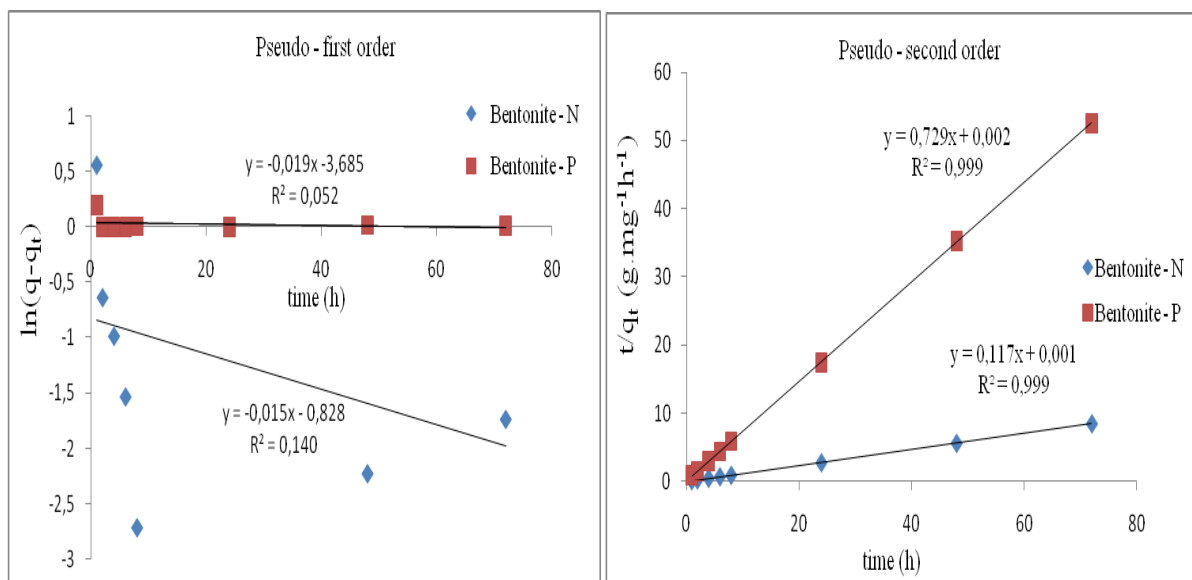


Figure-6. Kinetics of pseudo-second order and second-order adsorption of ammonium and phosphate ions.

Figure-5 shows that in the intradiffusional process between bentonites and ammonium and phosphate ions, three stages of mass transfer of sorbate on preparations may be allocated [15]. The first step section describes diffusion of molecules of ammonium and phosphate ions from the bulk of the solution through the outer diffusion layer to the surface of the bentonite (extradiffusional mass transfer). The second section relates to diffusion of ammonium and phosphate ions into bentonite

towards active centers (intradiffusional mass transfer). The third and final plateau relates to the process of ion exchange.

Figure-6 shows that at different initial concentrations of ions of ammonium and phosphate, the kinetic model of the pseudo-first order does not describe sufficiently well the kinetics of adsorption of ammonium and phosphate ions by bentonites, as evidenced by the relatively low correlation coefficients (R^2) obtained in



processing of kinetic curves in coordinates $\ln(q_e - q_t) - t$. Processing kinetic straight lines of adsorption by the

model of pseudo-second order kinetics in coordinates $t/q_t - t$ showed high correlation coefficients (R^2) (Table-4).

Table-4. Kinetic parameters for adsorption NH_4^+ (25mg/l) and PO_4^{3-} (5mg/l) by bentonites.

Sample	q_e , mg/g	Kinetics pseudo - first order			Kinetics pseudo - second order		
		K_1 , $g \cdot mg^{-1} \cdot h^{-1}$	G_t , mg/g	R^2	K_2 , $g \cdot mg^{-1} \cdot h^{-1}$	G_t , mg/g	R^2
Bentonite - NH_4^+	8.650	0.015	0.149	0.140	13.69	8.547	0.999
Bentonite - PO_4^{3-}	1.383	0.019	0.0002	0.052	177.1	1.372	0.999

Thus, kinetics of NH_4^+ and PO_4^{3-} adsorption by bentonite is described by the kinetic model of pseudo - second order.

Figure-7 shows isotherms of NH_4^+ and PO_4^{3-} adsorption by bentonites. The shape of the isotherms suggests that adsorption is limited to the monolayer.

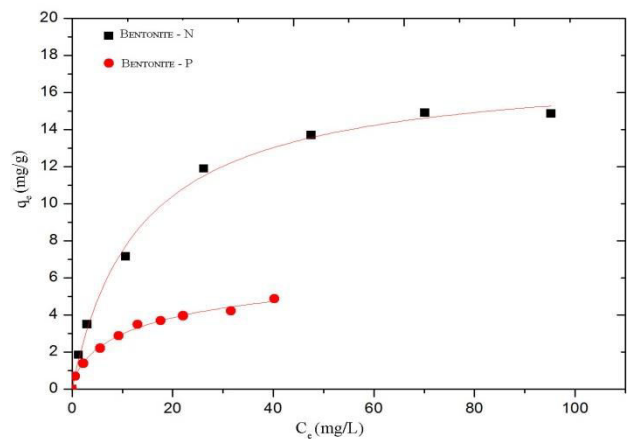


Figure-7. Isotherms of NH_4^+ and PO_4^{3-} adsorption by bentonites.

Analysis of adsorption isotherms is important for developing a model that can be used for describing the adsorption process. In the present paper, models of Langmuir and Freundlich were used for elucidating the mechanism of NH_4^+ and PO_4^{3-} adsorption by bentonites. Both models had been used for calculating the parameters of isotherms [16-22]. The data are shown in Table-5.

Table-5. Parameters of NH_4^+ and PO_4^{3-} adsorption by bentonites by Langmuir and Freundlich models.

Sample	Model by Langmuir			Model by Freundlich		
	K	q_{max} , mg/g	R^2	K_F	$1/n$	R^2
Bentonite - NH_4^+	0.082	17.24	0.997	1.909	0.496	0.963
Bentonite - PO_4^{3-}	0.052	5.37	0.982	1.093	0.184	0.880

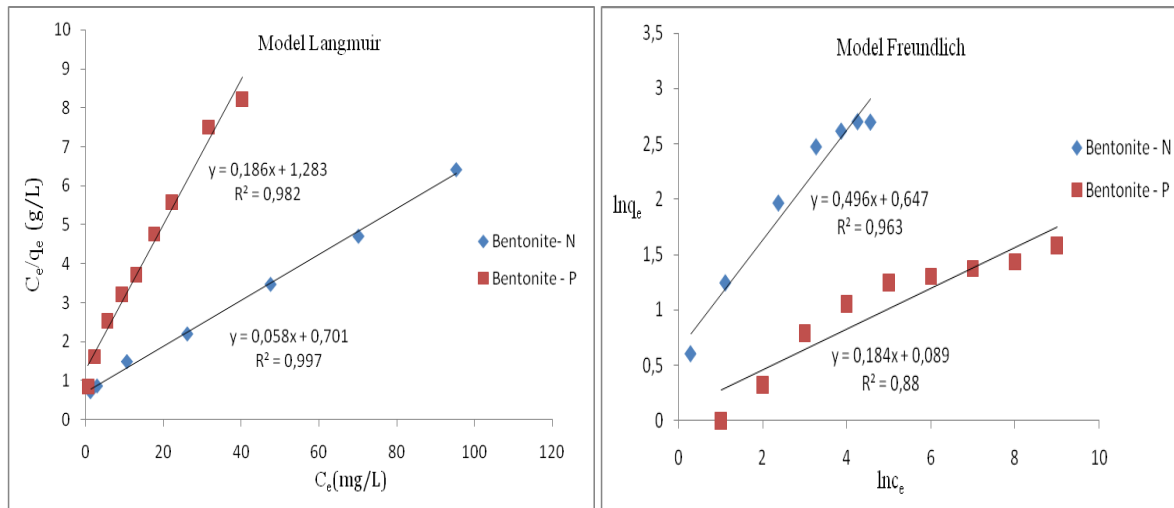


Figure-8. Linearized isotherms of NH_4^+ and PO_4^{3-} adsorption by bentonites.

The data in Table-4 show that NH_4^+ and PO_4^{3-} adsorption by bentonite is well described by the Langmuir equation. Probably, the surface of sorbents may be considered quite homogeneous. This is also evidenced by value $1/n$ from the Freundlich equation.

In the study, the optimum pH condition for desorption was found [23-25]. Figure-9 shows that efficient desorption of NH_4^+ (N_d : 32.06 %) is at pH 2, and an efficient desorption of PO_4^{3-} is 43.20 % at pH 10.

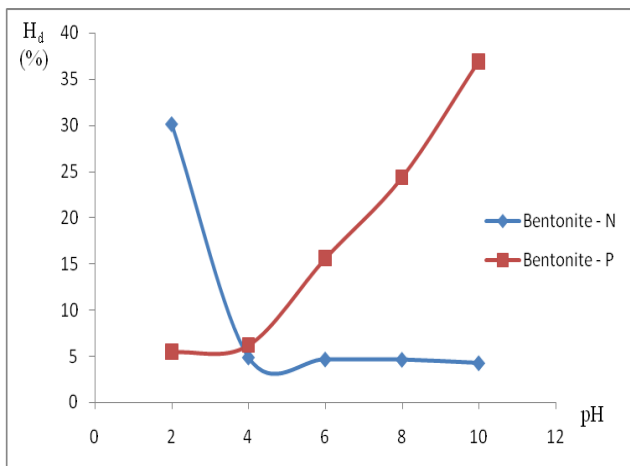


Figure-9. Dependence of efficient desorption on the pH value.

CONCLUSIONS

The experimental study of adsorption of wastewater from livestock breeding in the field of the "South-Central Coast of Vietnam" has shown the following results.

- During the experiment, water-insoluble bentonite has been synthesized being the main basis for recovery of the used sorbent.

- The time of establishment of adsorption balance at room temperature has been determined equalling to 24 h at pH 8 for NH_4^+ and 2 hours at pH 6 for PO_4^{3-} .
- The maximum adsorption for particles of bentonite in relation to ions NH_4^+ and PO_4^{3-} has reached 17.24 mg/g and of 5.37 mg/g, respectively.

According to the results of the research, a conclusion can be made that bentonite may be a promising adsorptive material with high adsorption capacity, ability to regenerate, which can be used for treatment of water from livestock breeding.

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