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Dedicated to Professor Liviu Literat
On the occasion of his 85th birthday

ADSORPTIVE CHARACTERISTICS OF HISTOSOL MODIFIED BY SIMPLE CHEMICAL TREATMENTS FOR Ni(II) REMOVAL FROM AQUEOUS MEDIA

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ABSTRACT. The adsorptive characteristics of Ni(II) from aqueous media on histosol modified by simple chemical treatments was investigated. The chemical treatments have been achieved by mixing histosol with aqueous solution of common chemical reagents (HNO_3, NaCl and NaOH, respectively), without the addition of supplementary additives. The influence of initial Ni(II) concentration and equilibrium contact time was studied in a series of batch experiments, in comparison with untreated histosol. An increase of adsorption capacity of histosol in case of treatments with NaCl and NaOH (15.58 % and 24.19 %, respectively) was obtained, and this is mainly attributed to the increase of functional groups availability from adsorbent surface. In addition a significant decrease of equilibrium contact time in case of modified histosol was also found. The experimental data were analyzed using two isotherm models (Langmuir and Freundlich) and three kinetics models (pseudo-first order, pseudo-second order and intra-particle diffusion model). The Langmuir model provides best correlation of equilibrium experimental data, and the pseudo-second order describes well the adsorption kinetics of Ni(II) on untreated and modified histosol. The histosol modified by considered simple chemical treatments has potential for serving as Ni(II) adsorbent, and the cost of these treatments is very low.

Keywords: *adsorption, Ni(II) ions, histosol, chemical treatment, kinetics, isotherm*

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INTRODUCTION

Unlike organic pollutants that are susceptible to biological degradation once they are discharged into environment, the heavy metals cannot be degraded into harmless end products. In addition, due to their toxicity, mobility and accumulating tendency, the contamination of aqueous environment with heavy metals is an important source of pollution with serious human health consequences [1,2]. Consequently, heavy metals should be eliminated or at least reduced from industrial wastewater before discharge into environment.

Nickel is one the common heavy metals that is present into environment mostly due to the industrial activities. Thus, many industries (such as: metal plating, mining, tanneries, etc.) produce large quantities of waste stream containing nickel along with other metal ions from process. In most of cases, Ni(II) ions are added to waste stream at a much higher concentration that the permissible limits, leading to health hazard and environment degradation [3,4].

Several methods can be employed to remove Ni(II) ions from industrial wastewater, including chemical precipitation, flotation, ion exchange, membrane-related processes, biological techniques [5-9]. Unfortunately, in many cases the applicability of these methods is limited because are expensive, have low selectivity, high energy consumption or generate large amounts of sludge that are also difficult to treat [10].

Adsorption provide potential alternative to overcome the disadvantages of conventional methods for wastewater treatment containing heavy metals. Well-design adsorption process has high efficiency and lead to getting a high-quality effluent that can be recycled. In addition, if the adsorbents have a low-cost or the adsorbents regeneration is feasible, then the adsorption process is inexpensive and accessible [11]. The natural materials or waste products from industrial or agricultural activities, which are available in large quantities, may have potential as low-cost adsorbents in the control of environmental pollution [12,13].

The histosol could be especially useful because this material is fairly abundant in many regions of the world, has a greatly metal removal potential and large surface area [14,15]. The excellent binding capacity of histosol is determined by the presence of various functional groups of lignin, cellulose and humic substances on they structure [16,17], but also to the small and uniform distribution of binding sites [18].

Nevertheless, there are still many aspects that need to be solved before that the histosol to be used in real applications in wastewater treatment. The most important is the fact that the adsorption capacity of histosol should be improved, mainly because low adsorption capacity may cause large amounts of wastes loaded with heavy metals, which are also a source of environmental pollution [19]. The studies from literature show that the adsorption capacities of histosol for different heavy metals do not exceed 2.5 mmol/g, which are significant lower that those obtained for commercial adsorbents, such as activated carbon. In consequence, new preparation methods of adsorbents derived from histosol should be developed, and the cost of preparation should be kept low. In order to improved the adsorption characteristics of histosol for Ni(II) ions, several simple chemical treatments were used. These treatments suppose the mixing of histosol with aqueous solution of several common chemical reagents (HNO_3, NaCl and NaOH), and the main advantage of these procedures is that the enhancement of adsorption characteristics of histosol is done without adding expensive additives, and thus the cost of adsorbent preparation remains low.

In this study, the adsorptive characteristics of Ni(II) from aqueous media on histosol modified by simple chemical treatments was examined, at laboratory scale. The influence of initial Ni(II) ions concentration and equilibrium contact time was studied at room temperature (25 ±0.5 °C) in batch experiments, in comparison with untreated histosol. Two isotherm models (Langmuir and Freundlich) and three kinetics models (pseudo-first order, pseudo-second order and intra-particle diffusion model) were used for the mathematical description of experimental data, and various model parameters have been calculated in each case.

RESULTS AND DISCUSSION

The histosol is usually considered as a complex material, which contains organic matter in various decomposition stages [20,21]. The major constituents (lignin, cellulose and humic substances) contains in their structure various functional groups (-OH, -COOH, -C=O, $-NH_2$, etc.), that can be involved in specific chemical interactions (ion-exchange or complexation) with metal ions from aqueous solution, during the adsorption.

FT-IR spectrum (Figure 1) was used to characterize the histosol. Several important peaks, at 3452, 2920, 1728, 1633, 1514, 1381 and 1037-1058 cm^{-1} are observed in the spectrum of histosol used as adsorbent in this study.

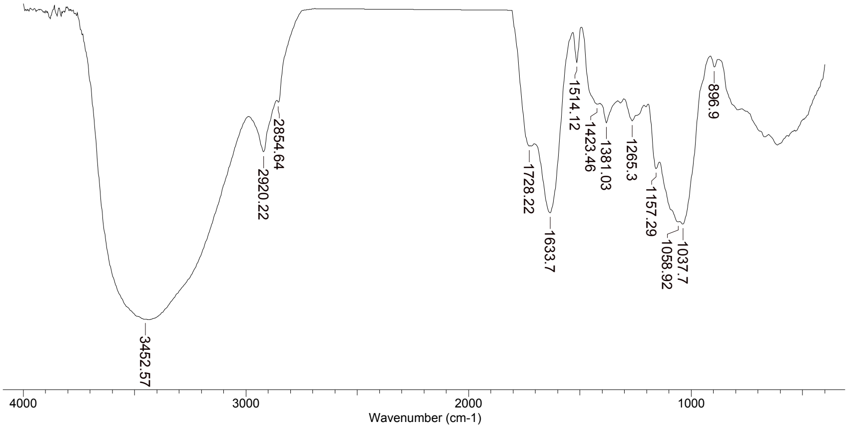

Figure 1. FT-IR spectrum of histosol used as adsorbent in this study.

The broad and strong band from 3452 cm^{-1} is attributed to the overlapping of O–H and N–H stretching vibrations. Peak at 2920 cm^{-1} is the C–H stretching vibration. The peaks at 1728 and 1633 cm^{-1} can be assigned to C=O stretching vibrations. Thus, the absorption band from 1633 cm^{-1} corresponding to carbonyl bond from carboxylic groups (-COO^{-}), while the band from 1728 cm^{-1} corresponds to the carbonyl bond from esters and carboxylic acid compounds. The peak at 1514 cm^{-1} is assigned to N–H vibrations. The peak at 1381 cm^{-1} is O–H bending vibration in alcohols. The strong band at 1058-1037 cm^{-1} indicates the presence of organic compounds with two or more hydroxyl groups. On the basis of these observations, it can be concluded that in the structure of histosol numerous functional groups (hydroxyl, amine, carbonyl, carboxylic groups, etc.) are present, and these can interact with Ni(II) ions during the adsorption process.

In consequence, it is expected that the efficiency of adsorption process to depend both on the affinity of metal ions for the superficial functional groups of histosol, and on the availability of these groups to interact with metal ions from aqueous solution. In case of a given metal ion, the increase of adsorption efficiency can be achieved by increasing of the availability of superficial functional groups of histosol, using specific treatments.

Starting from these observations, for the treatment of histosol three common chemical reagents (HNO_3, NaCl and NaOH), have been selected because: (i) a strong mineral acid can remove the metal ions that are already bonded on superficial functional groups of histosol, and thus these become free; (ii) a neutral salt with high mobile cation, can replace the low mobile metal ions already bonded on superficial functional groups; and (iii) a strong base that will increase the dissociation degree of the functional superficial groups from adsorbent surface, without the histosol structure to be significant affected.

In order to evaluate the performances of histosol modified by these treatments on Ni(II) adsorption efficiency, the influence of initial metal ion concentration and equilibrium contact time was studied in comparison with untreated histosol, under optimum experimental conditions (pH = 6.0 (acetate buffer), 5 g adsorbent/dm^3), established previously [22].

Effect of initial Ni(II) concentration

The influence of initial Ni(II) concentration on its adsorption efficiency on untreated histosol and modified histosol was studied in the 24.45 – 244.52 mg/dm^3 concentration range. The experimental results, presented in Figure 2, shows that the amount of metal ion retained on mass unit of adsorbent (q, mg/g) increase with increasing of initial Ni(II) concentration from aqueous solution, in all cases.

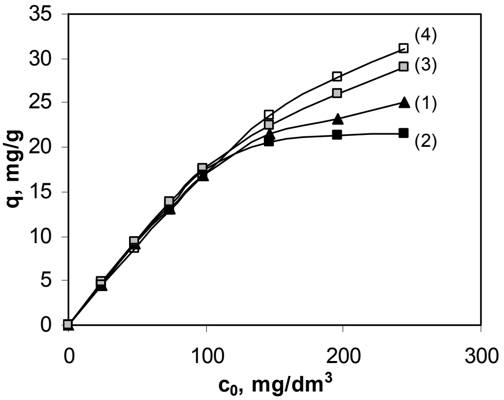

Figure 2. Influence of initial Ni(II) concentration on its removal on: (1) untreated histosol; (2) histosol treated with HNO_3; (3) histosol treated with NaCl; (4) histosol treated with NaOH (pH = 6.0 (acetate buffer); 5 g adsorbent/dm^3).

It can also be observed from Figure 2 that in the studied Ni(II) concentration range the adsorption efficiency depends by the type of treatment used for histosol modification, and follows the order: histosol treated with NaOH (q = 31.11 mg/g) > histosol treated with NaCl (q = 28.95 mg/g) > untreated histosol (q = 25.04 mg/g) > histosol treated with HNO_3 (q = 21.49 mg/g), for an initial concentration of 244.51 mg/dm^3.

The obtained experimental results suggest that the adsorption of Ni(II) from aqueous solution on untreated histosol and modified histosol occurs predominantly by electrostatic (ion-exchange) interactions, and the efficiency of adsorption process depends by the availability and dissociation degree of functional groups from adsorbent surface. Thus, when the histosol is treated with NaCl or NaOH, some functional groups, which are not active in the metal-binding process become available, and so the adsorption capacity increase. The change in availability of superficial functional groups of histosol by these simple chemical treatments determined an enhancement of adsorption capacity with 15.58 % in case of histosol treated with NaCl, and with 24.19 % in case of histosol treated with NaOH, respectively.

In case of histosol treated with HNO_3, even if the number of free functional groups is increased, most of these are un-dissociated. This makes that the number of electrostatic interactions with Ni(II) ions from aqueous solution to be low, and in consequence a decrease of adsorption capacity with 14.21 % in comparison with untreated histosol was obtained.

Equilibrium modelling

The adsorption isotherms of Ni(II) on untreated histosol and modified histosol, used for equilibrium modelling are presented in Figure 3.

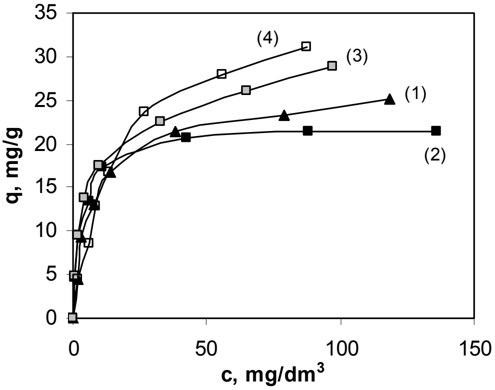

Figure 3. Adsorption isotherms of Ni(II) onto: (1) untreated histosol; (2) histosol treated with HNO_3; (3) histosol treated with NaCl; (4) histosol treated with NaOH (pH = 6.0 (acetate buffer); 5 g adsorbent/dm^3).

The adsorption isotherm represents the equilibrium distribution of the Ni(II) ions between phases of solid adsorbent and aqueous solution, and are characterized by definite parameters, whose values express the surface properties and affinity of adsorbent for metal ions. In this study, two isotherm models were selected to fit the experimental data, namely Langmuir and Freundlich models.

The Langmuir isotherm model is based on the assumption that the adsorption occurs at specific homogeneous sites on the adsorbent surface, by adsorption forces similar to the forces on chemical interactions [23,24], and is used to estimate the maximum adsorption capacity (q_{max}, mg/g) corresponding to the adsorbent surface saturation. The linear form of the Langmuir isotherm model can be expressed by:

$$\frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} \cdot K_L} \cdot \frac{1}{c} \tag{1}$$

where: q_{max} is the maximum adsorption capacity (mg/g), corresponding to the complete monolayer coverage of surface, c is the Ni(II) concentration at equilibrium (mg/dm^3) and K_L is the Langmuir constant, related to the adsorption / desorption energy (dm^3/g).

The Freundlich isotherm model is derived from multilayer adsorption and adsorption on heterogeneous surface [24,25], and was chosen to estimate the adsorption intensity of Ni(II) ions on untreated histosol and modified histosol. The linear form of this model is:

$$\lg q = \lg K_F + \frac{1}{n} \lg c \tag{2}$$

where: K_F is the Freundlich constant and represent an indicator of adsorption capacity ($mg \cdot dm^{3/n}/g \cdot mg^{1/n}$) and *n* is a constant that characterized the surface heterogeneity. The 1/n value between 0 and 1 indicate that the adsorption process is favourable under studied experimental conditions [24].

The obtained values of Langmuir and Freundlich isotherm parameters, evaluated from the slope and intercept of the corresponding plots (1/q vs. 1/c, and lg q vs. lg c, respectively) are summarized in Table 1, together with the linear regression coefficients (R^2), which were used to settle the best fit isotherm model.

Table 1. Isotherm parameters for the adsorption of Ni(II) on untreated histosol and modified histosol

Langmuir isotherm model			
Adsorbent	R^2	q_{max}, mg/g	K_L, dm^3/g
Untreated histosol	0.9992	25.4451	0.1832
Histosol treated with HNO_3	0.9991	21.9784	0.3315
Histosol treated with NaCl	0.9929	29.4126	0.1873
Histosol treated with NaOH	0.9975	36.6303	0.0625
Freundlich isotherm model			
Adsorbent	R^2	1/n	K_F, $mg \cdot dm^{3/n}/g \cdot mg^{1/n}$
Untreated histosol	0.9246	0.4437	5.2612
Histosol treated with HNO_3	0.8945	0.1881	9.4363
Histosol treated with NaCl	0.9798	0.2604	9.0095
Histosol treated with NaOH	0.9334	0.4472	4.6968

The values of correlation coefficients (R^2) show that the adsorption isotherm data are very well represented by the Langmuir model, indicating the formation of monolayer coverage of Ni(II) ions on the other surface of adsorbent. The maximum adsorption capacity, which is a measure of the adsorption capacity to form a monolayer is higher in case of Ni(II) adsorption on histosol treated with NaCl and NaOH respectively, and lower in case of Ni(II) adsorption on histosol treated with HNO_3, than those obtained by using untreated histosol as adsorbent. The increase of the maximum adsorption capacity, calculated according with equation (4) was by 15.59 % in case of histosol treated with NaCl and by 43.96 % in case of histosol treated with NaOH, while in case of histosol treated with HNO_3 a decrease with 13.62 % was obtained. This is another argument that sustain the hypothesis that after treating the histosol with NaCl and NaOH respectively, more many superficial functional groups from histosol surface become available for interactions with Ni(II) ions, therefore which make that the amount of metal ions required to form a complete monolayer on such modified histosol is higher. In addition, the K_L values follows the same order, and indicate that between functional groups of adsorbent surface and Ni(II) ions from aqueous solution strong interactions occurs.

The fractional values of 1/n constant from Freundlich isotherm model (Table 1) suggests that untreated histosol and histosol modified by considered chemical treatments have an heterogeneous surface, but the adsorption process of Ni(II) ions on these adsorbents is a favorable process.

Effect of equilibrium contact time

The effect of equilibrium contact time between adsorbent (untreated histosol and modified histosol) and Ni(II) aqueous solution with an initial concentration of 48.90 mg/dm^3, at pH = 6.0 (acetate buffer) is presented in Figure 4.

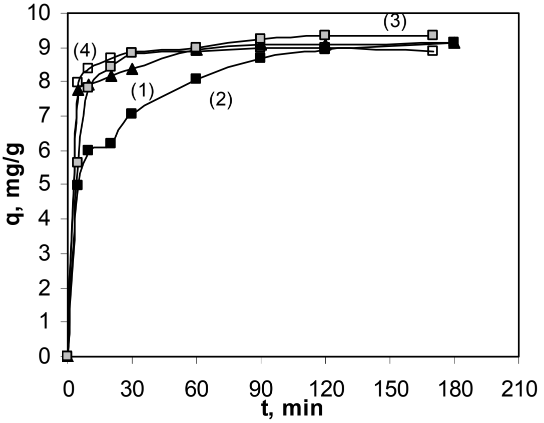

Figure 4. Effect of equilibrium contact time on Ni(II) adsorption onto: (1) untreated histosol; (2) histosol treated with HNO_3; (3) histosol treated with NaCl; (4) histosol treated with NaOH (pH = 6.0 (acetate buffer); 5 g adsorbent/dm^3).

It can be observed that in all the cases the amount of Ni(II) ions retained on mass unit of adsorbent increase with increasing of contact time. The adsorption process is very fast during of initial stage, when in the first 20 min around of 80 % of Ni(II) is retained (84.54 % in case of untreated histosol, 63.74 % in case of histosol treated with HNO_3, 86.63 % in case of histosol treated with NaCl and 89.71 % in case of histosol treated with NaOH, respectively). After this initial step, the rate of adsorption process become slower, near to equilibrium, which is practically obtained after 60 min in case of untreated histosol, 90 min in case of histosol treated with HNO_3, 25 min in case of histosol treated with NaCl and 20 min in case of histosol treated with NaOH, respectively. These results show that in case of histosol treated with

NaCl and NaOH respectively, the required time for to attain the equilibrium of adsorption process is lower than case of untreated histosol. This is because after these treatments, most of functional groups from histosol surface become dissociated, and the electrostatic interactions with Ni(II) ions from aqueous solution occurs more easily. The fast adsorption on histosol treated with NaCl and NaOH respectively, makes these adsorbents suitable for continuous flow rate treatment systems.

Kinetics modelling

The kinetics modeling is important in the design of wastewater treatment system, and allows the selection of optimum conditions for operating in full scale process, as it provide valuable insights into the process pathways and adsorption mechanism. In order to analyze the adsorption kinetics of Ni(II) on untreated histosol and modified histosol, three kinetics models (pseudo-first order, pseudo-second order and intra-particle diffusion model) were tested to fit the experimental data. The linear expressions of the pseudo-first order (Eq. (3)) and pseudo-second order (Eq. (4)) kinetics models can be written as [26,27]:

$$\lg(q_e - q_t) = \lg q_t - \frac{k_1}{2.303} \cdot t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{4}$$

where: q_e and q_t are the amounts of Ni(II) retained on mass unit of adsorbent at equilibrium and at time t respectively, (mg/g), k_1 is the rate constant of pseudo-first order kinetic model (1/min), and k_2 is the rate constant of the pseudo-second order kinetic model (g/mg·min).

The kinetics parameters of the pseudo-first order and pseudo-second order kinetics models, calculated from the linear dependences $\lg(q_e-q_t)$ vs. t and t/q_t vs. t respectively, together with the corresponding correlation coefficients (R^2) are summarized in Table 2.

The obtained results showed that the adsorption capacities (q_e, mg/g), calculated from the pseudo-first order equation, are very different from the experimental values (q_e^{exp}, mg/g) in all cases. This means that the pseudo-first kinetic model is not adequate to describe the kinetics data of Ni(II) adsorption on untreated histosol and modified histosol.

The experimental data were further fitted to the pseudo-second order kinetic model, when a better fitting was obtained with high correlation coefficients ($R^2 > 0.999$), in all cases. Also, the adsorption capacity values, calculated from the pseudo-second order kinetic model (q_e, mg/g) have similar values with those obtained experimentally (Table 2).

Table 2. Kinetics parameters for the adsorption of Ni(II) on untreated histosol and modified histosol

Pseudo-first kinetic model				
Adsorbent	q_e^{exp}, mg/g	R^2	q_e, mg/g	k_1, 1/min
Untreated histosol	9.1424	0.9701	1.6462	$3.11\cdot10^{-2}$
Histosol treated with HNO_3	9.1350	0.9942	4.6676	$1.15\cdot10^{-2}$
Histosol treated with NaCl	9.3412	0.9094	2.4294	$1.57\cdot10^{-2}$
Histosol treated with NaOH	9.8631	0.9201	3.0904	$2.15\cdot10^{-2}$
Pseudo-second kinetic model				
Untreated histosol	q_e^{exp}, mg/g	R^2	q_e, mg/g	k_2, g/mg·min
Histosol treated with HNO_3	9.1424	0.9995	9.2421	$3.40\cdot10^{-2}$
Histosol treated with NaCl	9.1350	0.9996	9.0551	$1.29\cdot10^{-2}$
Histosol treated with NaOH	9.3412	0.9999	9.4971	$3.93\cdot10^{-1}$
Untreated histosol	9.8631	0.9999	9.8431	$2.12\cdot10^{-1}$

The pseudo-second kinetics model is based on the assumption that the rate controlling step in the adsorption process is the chemical interaction between metal ions from aqueous solution and superficial functional groups of adsorbent [27]. The good fitting of experimental data by this model indicate that in case of untreated histosol and modified histosol, the rate of adsorption process depends by the availability of Ni(II) ions and superficial functional groups to interact. If the availability of functional groups is higher, the rate of adsorption process is also higher. Thus when the histosol is treated with NaCl or NaOH respectively, the availability of superficial functional groups is increased (mainly due to the increase of dissociation degree of these), and the obtained values of rate constants are higher even with one order of magnitude than in case of untreated histosol. Contrary, by treating the histosol with HNO_3 solution, the availability of superficial functional groups to interact with Ni(II) ions from aqueous solution decrease (due to the decrease of dissociation degree of functional groups) and the obtained values of rate constant is lower than in case of untreated histosol.

The intra-particle diffusion model was used to determine the participation of diffusion process in the adsorption of Ni(II) on untreated histosol and modified histosol. The mathematical equation of the intra-diffusion model can be expressed as [28]:

$$q_t = k_{diff}\cdot t^{1/2} + c \qquad (5)$$

where: k_{diff} is the intra-particle diffusion rate constant (mg/g·min$^{1/2}$) and c is the concentration of Ni(II) ions solution at equilibrium (mg/dm^3).

According with the intra-particle model, if the diffusion process is the rate controlling step, the graphical representation of qt vs. $t^{1/2}$ should yield a straight line, passing through the origin. The experimental results have show that in case of Ni(II) adsorption on untreated histosol and modified histosol, the plots q_t vs. $t^{1/2}$ (Figure 5) does not go through the origin and two separated regions exists in all cases.

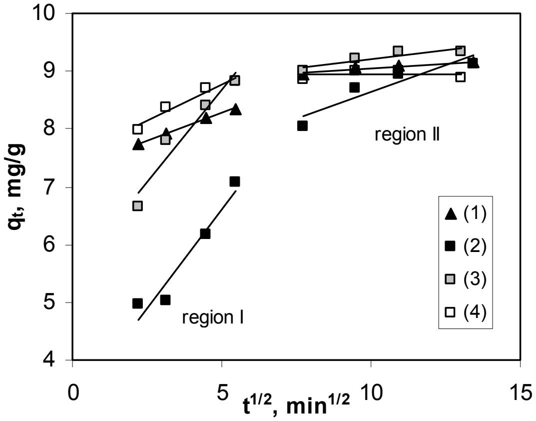

Figure 5. The plots of intra-particle diffusion model for the adsorption of Ni(II) onto: (1) untreated histosol; (2) histosol treated with HNO_3; (3) histosol treated with NaCl; (4) histosol treated with NaOH (pH = 6.0 (acetate buffer); 5 g adsorbent/dm^3).

The parameters of intra-particle diffusion model (k_{diff} and c), calculated for each region from the slopes and intercepts of the linear portions of the plots, are summarized in Table 3.

The deviation of the straight line from the origin indicate that the intra-particle diffusion process is not the rate controlling step [29], and the boundary layer diffusion controls the adsorption to some degree, in al cases. In addition, the higher values of the rate constants obtained from this model sustain the hypothesis that the intra-particle diffusion does not limit the rate of adsorption process of Ni(II) on untreated histosol and modified histosol. The first region (region I from Figure 5) is attributed to mass transfer of Ni(II) from the bulk solution to adsorbent surface, while the second region (region II from Figure 5) indicated the intra-particle diffusion.

The significant differences between these two regions is given by the slope, thus in all cases the first region has a pronounced slope, while the slope of second region is much lower. This indicate that the binging sites are located on adsorbent surface of the at external intra-layer surface, and are readily accessible from Ni(II) ions from aqueous solution.

The obtained experimental data have show a limited contribution of mass transfer and boundary layer diffusion in the adsorption process of Ni(II) on untreated histosol and histosol modified by considered chemical treatments, and that the intra-particle diffusion influenced the adsorption process in a certain degree.

Table 3. Intra-particle model parameters for the adsorption of Ni(II) on untreated histosol and modified histosol

Region I			
Adsorbent	R^2	c, mg/dm^3	k_{diff}^{I}, mg/g·min$^{1/2}$
Untreated histosol	0.9980	7.3215	0.1903
Histosol treated with HNO_3	0.9037	3.8499	0.5751
Histosol treated with NaCl	0.8281	4.1943	0.9049
Histosol treated with NaOH	0.9572	7.4981	0.2531
Region II			
Adsorbent	R^2	c, mg/dm^3	k_{diff}^{II}, mg/g·min$^{1/2}$
Untreated histosol	0.8633	8.7269	0.0322
Histosol treated with HNO_3	0.8682	6.7886	0.1844
Histosol treated with NaCl	0.7706	8.5965	0.0608
Histosol treated with NaOH	0.9006	8.9278	0.0181

CONCLUSIONS

In this study, the adsorptive characteristics of histosol modified by several simple chemical treatments have been investigated for the removal of Ni(II) ions from aqueous media, in comparison with untreated histosol. The chemical treatments imply the mixing of histosol with 0.2 mol/dm^3 aqueous solution of common chemical reagents (HNO_3, NaCl and NaOH, respectively), without the addition of supplementary additives, and thus the cost of adsorbent preparation remains low.

In order to estimate the adsorptive characteristics of modified histosol in the adsorption process of Ni(II) ions from aqueous solution, the influence of initial metal ion concentration and equilibrium contact time were studied, in optimum experimental conditions (pH = 6.0 (acetate buffer), 5 g adsorbent/dm^3), in comparison with untreated histosol. The experimental results have show that in case of treatments with NaCl and NaOH respectively, an increase of the adsorption capacity of histosol with 15.58 % and 24.19 % was obtained, while in case of treatment with HNO_3, the adsorption capacity decrease with 14.21 %, towards untreated histosol. Another important advantage of using modified is that the required time for Ni(II) ions adsorption is shorter.

The experimental data were best correlated with the Langmuir isotherm model. The maximum adsorption capacity was higher with 15.59 % in case of histosol treated with NaCl, with 43.96 % in case of histosol treated with NaOH, while in case of histosol treated with HNO_3 a decrease of this parameter with 13.62 % was obtained, in comparison with untreated histosol. The pseudo-second order model best describe the adsorption process of Ni(II) on untreated histosol and modified histosol. This model is based on the assumption that the rate controlling step is the chemical interaction between metal ions from aqueous solution and functional groups from adsorbent surface. The calculated values of model parameters indicate that the rate of adsorption process is limited by the availability of superficial functional groups to interact. Thus, when the availability of superficial functional groups is higher (in case of histosol treated with NaCl and NaOH, respectively), the rate of adsorption is also higher.

The results of this study show that the chemically modified histosol can have better adsorptive characteristics than untreated histosol, and could be employed as an efficient adsorbent for the removal of Ni(II) ions from aqueous media.

EXPERIMENTAL SECTION

Materials

In this study, histosol samples from Poiana Stampei (Romania) at depth below 0.5 m was used as adsorbent. Before use, the raw material was dried in air for 24 hours at room temperature (25 ± 0.5 °C), and then grounded and sieved until the particles had the granulation less than 1-2 mm. The chemical composition and some physical-chemical characteristics of this adsorbent have been presented in a previous study [30].

The chemical treatments were done by mixing histosol samples with aqueous solution of chemical reagents. Thus, 2.0 g of histosol was mechanically shaken with 100 cm^3 of 0.2 mol/dm^3 solution of HNO_3, NaCl and NaOH respectively, for 30 min. After 24 hours of stand-by the modified histosol samples were filtrated, washed with distilled water until a neutral pH, dried in air and then mortared.

Reagents

All chemical reagents (HNO_3, NaCl and NaOH) were of analytical degree and were used without further purifications. In all experiments, distilled water obtained from a commercial distillation system, was utilized for the preparation of solution. The stock solution of nickel, containing 611.29 mg Ni(II)/dm^3, was prepared by dissolving nickel nitrate (purchased from Reactivul Bucharest) in distilled water. Fresh dilution were prepared and used for each experiment. The initial pH value of working solutions was obtained using acetate buffer (CH_3COOH / CH_3COONa) with pH = 6.0.

Adsorption experiments

The adsorption experiments were performed by batch technique, at room temperature (25 ± 0.5 °C), mixing 0.125 g sample of untreated histosol and modified histosol with volume of 25 cm^3 solution of known concentration

(24.45 – 244.51 mg/dm^3), in 150 cm^3 conical flasks, with intermittent stirring. All experiments were run in optimum experimental conditions (pH = 6.0 (acetate buffer), adsorbent dose = 5 g/dm^3) previously established [22]. In case of kinetics experiments, a constant amount of untreated histosol and histosol modified by considered chemical treatments (5 g/dm^3) was mixed with 25 cm^3 of 48.90 mg/dm^3 Ni(II) solution, at various time intervals between 5 and 180 min. At the end of adsorption procedure, the phases were separated by filtration and the Ni(II) concentration in filtrate was determined using the spectrophotometric method (Digital Spectrophotometer S 104 D, rubeanic acid, λ = 600 nm, 1 cm glass cell) [31], using a prepared calibration graph.

Data evaluation

The adsorption efficiency of Ni(II) on untreated histosol and histosol modified by considered chemical treatments was quantitatively evaluated from experimental results using amount of Ni(II) retained on mass unit of adsorbent (*q*, mg/g), calculated from the mass balance expression:

$$q = \frac{(c_0 - c)\cdot(V/1000)}{m} \qquad (3)$$

where: c_0 is the initial Ni(II) concentration (mg/dm^3), c is the equilibrium concentration (mg/dm^3), V is the volume of solution (cm^3) and m is the adsorbent mass (g).

The difference between adsorption capacity of untreated histosol and histosol modified by considered chemical treatments was calculated according to the relation:

$$\Delta q = \frac{q_{\mathrm{mod}ified} - q_{untreated}}{q_{untreated}}\cdot 100 \qquad (4)$$

where: $q_{modified}$, $q_{untreated}$ are the amounts of Ni(II) retained on mass unit of modified histosol and untreated histosol, respectively (mg/g).

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