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BIOSORPTION POTENTIAL OF THE MAIN FRACTIONS SEPARATED FROM PEAT (POIANA STAMPEI, ROMANIA)

BY

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Abstract. In this study it was investigated the separation possibility of the main organic fraction of peat (Poiana Stampei, Romania), consisting in humic substances and cellulosic waste, for its use as biosorbents in the removal process of Cu(II) ions from aqueous solution. In order to separate the two fractions, the peat was treated with sodium hydroxide solutions of different concentrations (0.1 – 4.0 N), at two different temperatures (20 and 50°C) for 3 h of mixing. In this way, only the solubilisation of humic substances from the peat composition takes place, which can be separated from cellulosic waste by filtration. After filtration, the humic substances were re-precipitated in strong acid media (pH < 1.0), and then both obtained fractions were washed and dried in air. The efficiency of separation process was evaluated in each case. All resulted fractions were used as biosorbents for the removal of Cu(II) ions from aqueous solution. The experimental results have shown that the fractions separated by the treatment of peat with 2N NaOH solution at 50°C exhibit the highest biosorption capacities.

Keywords: peat; humic substances; cellulosic waste; Cu(II) ions; biosorption.

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1. Introduction

The removal of heavy metal ions from industrial wastewater by biosorption has been proved to be a viable alternative to conventional methods (such as chemical precipitation, ion exchange, osmosis, coagulation, electrochemical techniques etc.) (Dabrowski *et al.*, 2004; Llanos *et al.*, 2010; Nguyen *et al.*, 2013). This is because the biosorption is considered an effective and low-cost method for environmental bioremediation, because it does not generate large amounts of secondary wastes (Febrianto *et al.*, 2009), and can be easily adapted for the large scale applications due to its viability. However, all these advantages of biosorption are important in practical applications, only if the biosorbent used in the removal processes of heavy metals is available in large quantities, its preparation is simple, involve only few steps and is not expensive (Hlihor and Gavrilescu, 2009).

Numerous studies from literature have been reported the utilization of various materials of biologic origin (natural materials, agricultural and industrial wastes), in the efficient removal of heavy metals ions from aqueous media in various experimental conditions (Kratochvil and Volesky, 1998; Wang and Chen, 2009; Wu *et al.*, 2016). The high removal efficiency of heavy metals on such biosorbents is mainly dictated by both the large number and variety of functional groups from their surface (Febrianto *et al.*, 2009; Montazer-Rahmati *et al.*, 2011), which can interact with metal ions from aqueous media, in well-defined experimental conditions.

Peat is considered an inexpensive and widely available material, which has proved to be an efficient biosorbent for a variety of heavy metals (Brown *et al.*, 2000). This is because peat is a porous material, which contains organic matter in various decomposition stages, and in which lignin, cellulose and humic substances are the major components (Brown *et al.*, 2000; Babel and Krniavan, 2003). These main components have in their structure numerous reactive functional groups, which can be involved in chemical bindings of metal ions from aqueous solution, being also responsible for the good cation-exchange properties of peat (Bulgariu *et al.*, 2011). Thus, numerous previous experimental studies have reported the efficacy of peat in the removal of Cd(II), Zn(II), Cu(II), Pb(II), Hg(II), Co(II), Ni(II) etc., (Brown *et al.*, 2000; Bulgariu *et al.*, 2007; Bulgariu *et al.*, 2009; Caramalau *et al.*, 2009) from aqueous solution by biosorption. Unfortunately, the efficiency of heavy metal removal on peat is substantial only at relatively low concentrations of metal ions in aqueous solutions. At higher heavy metal ions concentrations, the biosorption efficiency drastically decreases, and for ensuring efficient removal, two or more biosorption steps are required. This happens because the biosorption capacity of peat is mainly determined by the number and geometrical availability of –COOH and –OH groups from its surface (Bulgariu *et al.*, 2011). Therefore, the increasing of free hydroxyl and carboxyl superficial groups of peat should

increase its biosorption capacity, making it more efficient in heavy metals biosorption processes. This can be done by the separation of the main fractions of peat, through a simple procedure, and then the utilization of the separated fractions as biosorbents for the retention of heavy metal ions from aqueous solution.

In this study, we have examined the separation possibility of the main fraction of peat (humic substances and cellulosic waste), and their utilization as biosorbents for the removal of Cu(II) ions from solutions. The separation procedure of the main fractions from peat is based on the treatment of raw peat with NaOH solution, when the solubilisation of humic substances occurs, followed by their re-precipitation in strong acidic media. Both fractions were washed and dried, and then used for Cu(II) removal from aqueous solution. The optimal conditions required for the separation of the humic substances and cellulosic waste from peat were established considering both the amounts of peat fractions obtained after separation, and their efficiency in Cu(II) ions biosorption.

2. Experimental

2.1. Materials

Peat was collected from Poiana Stampei (Romania), at depths below 1.0 m. Before utilization, the peat sample was washed several times with distilled water, dried in air at 60°C for 10 h, grinded and sieved. The grain-size of obtained particles was lower than 1.0-1.5 mm.

NaOH solutions (0.1 - 4.0 N) used for the peat treatment were prepared by dissolving an adequate quantity of solid sodium hydroxide (purchased from Chemical Company) in distilled water, followed by the standardization of obtained solutions (Bejan *et al.*, 2006). A HNO₃ solution (63%) was used for the re-precipitation of humic substances separated from peat.

The stock solution of Cu(II) ions (635.22 mg·L⁻¹) was prepared from copper sulphate salt. The stock solution was then used to obtain the working solutions (12.71 mg Cu(II)·L⁻¹) by dilution with distilled water.

All the chemical reagents used in this study were of analytical grade and were used without further purifications.

2.2. Procedure for Separation of Peat Fractions

To separate the two main organic fractions from peat (humic substances and cellulosic waste), samples of 0.5 g of peat were treated with NaOH solution with different concentrations, between 0.1 and 4 N, at two different temperatures, 20 and 50°C respectively. After 3 h of mixing, the samples were filtered, and the two peat fractions: the cellulosic waste (solid) and humic

substances (liquid), were separated. The dissolved humic substances were re-precipitated with 63% HNO₃ solution, and filtered again. Both solid fractions, humic substances and cellulosic waste obtained from each peat sample were then washed for several times with distilled water, dried in air for 72 h at room temperature (20 ± 2°C) and mortared. Before their storage in desiccators for further uses, all fractions were weighed with an analytical balance (RAGWAG XA 60/120, precision ± 10⁻⁴ g), and their percents were calculated using Eq. (1),

$$\% \text{ separated fraction} = \frac{m_{fraction}}{m_{peat}^i} \cdot 100 \quad (1)$$

where: % separated fraction is the percent of fraction separated from peat, [%]; $m_{fraction}$ is the mass of fraction weighed after drying, [g] and m_{peat}^i is the mass of peat sample, [g].

2.3. Biosorption Experiments

The biosorption of Cu(II) ions on each fraction separated from peat samples was tested in batch system, at room temperature (20 ± 2°C). The experiments were performed by contacting 25 mL of Cu(II) solution (12.71 mg·L⁻¹) with 0.1 g of peat fractions, for 24 h, with intermittent stirring. After biosorption, all samples were filtered, and the Cu(II) ions concentration in solution was determined spectrophotometrically with rubeanic acid (Digital Spectrophotometer S 104 D, 1 cm glass cell, 390 nm, against blank solution) (Dean, 1995).

The biosorption capacity [q , mg·g⁻¹] and removal percent (R , %) of each peat fraction for Cu(II) ions was calculated from the experimental results, using the relations (2, 3),

$$q = \frac{(c_0 - c) \cdot (V / 1000)}{m} \quad (2)$$

$$R = \frac{c_0 - c}{c_0} \cdot 100 \quad (3)$$

where: c_0 is the initial Cu(II) ions concentration in solution, [mg·L⁻¹], c is the equilibrium concentration of Cu(II) ions in the solution, [mg·L⁻¹], V is volume of solution, [mL], and m is the mass of the peat fractions, [g].

3. Results and Discussion

One of the most used modality to separate the humic substances from natural materials is their treatment with NaOH solution (Technical Report, 2012) and this procedure was applied and in case of peat. At the treatment of natural materials with NaOH solution, most of humic compounds (acids, esters, anhydrides etc.) will react with NaOH solution, forming sodium salts. The formed sodium salts of humic compounds have higher solubility in aqueous media, due to the increase of their ionization degree. This will determine the solubilisation of humic substances, while the cellulosic compounds remains insoluble, making thus possible their separation. After filtration, the dissolved humic substances can be re-precipitated by changing the pH of aqueous solution from basic to acid ($\text{pH} < 1.0$). Starting from these considerations, the separation of humic substances and cellulosic waste from peat was done following the elementary steps illustrated in Fig. 1.

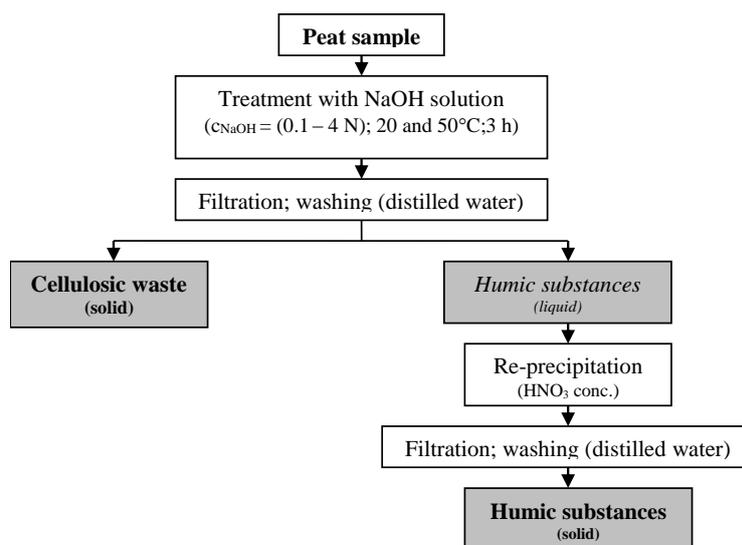


Fig. 1 – Separation scheme of humic substances and cellulosic waste from peat samples.

In order to establish the optimal concentration of NaOH solution which allows the separation of maximum quantity of humic substances from peat, five different concentrations of NaOH solution were used, at two different temperatures (20 and 50°C) and 3 h of mixing. The obtained results are summarized in Tables 1 and 2, with the mention that the losses generated by washing and filtration steps were not considered in the calculation of the percent of separated fractions.

As it can be observed from Tables 1 and 2, the percent of humic substances separated from peat increases with the increase of NaOH concentration and temperature. This is due to the fact that the increase of concentration and of temperature will facilitate the reaction between humic substances and NaOH, resulting higher quantities of soluble sodium salts, which are easy separated of cellulosic waste through filtration.

Table 1
The Percents of Peat Fractions Separated at 20°C

No.	C _{NaOH} , [equiv.·L ⁻¹]	Humic substances, [%]	Cellulosic waste, [%]
1.	0.1	1.74	64.42
2.	1.0	7.67	66.94
3.	2.0	11.61	61.67
4.	3.0	10.93	66.83
5.	4.0	17.44	67.82

Table 2
The Percents of Peat Fractions Separated at 50°C

No.	C _{NaOH} , [equiv.·L ⁻¹]	Humic substances, [%]	Cellulosic waste, [%]
1.	0.1	8.08	61.53
2.	1.0	13.52	48.29
3.	2.0	13.05	56.36
4.	3.0	17.96	48.89
5.	4.0	20.30	63.73

Thus, the highest percent of humic substances is obtained at the treatment of peat sample with 4 N NaOH solution at 50°C and, in these conditions the percent of cellulosic waste is also high. Therefore the treatment of peat samples with NaOH solution (4 N) at 50°C and 3 h of stirring was considered optimal for the separation of two main fractions (humic substances and cellulosic waste) from peat. However, besides establishing the separation procedure, it is required the evaluation of biosorption capacity of separated fractions for their use as biosorbents in the removal of metal ions.

In this study, the testing of biosorption potential of the separated main fraction of peat was done by mixing 25 mL of Cu(II) ions solution (12.71 mg·L⁻¹) with 0.1 g of separated fractions, at room temperature, in batch systems. The variation of the biosorption capacity and the removal efficiency, calculated from experimental results for each fraction, as a function on the concentration of NaOH solution used for their separation at the two considered temperatures, are presented in Figs. 2 and 3.

It can be observed from Figs. 2 and 3 that both in case of humic substances and in case of cellulosic waste the values of biosorption capacity for

Cu(II) ions highly depends on the concentration of NaOH solution used for their separation and on the working temperature. The maximum values of these parameters are attained at a NaOH concentration of 2 N and 50°C, indicating that under these experimental conditions, the separated fractions have the highest affinity for Cu(II) ions from aqueous media.

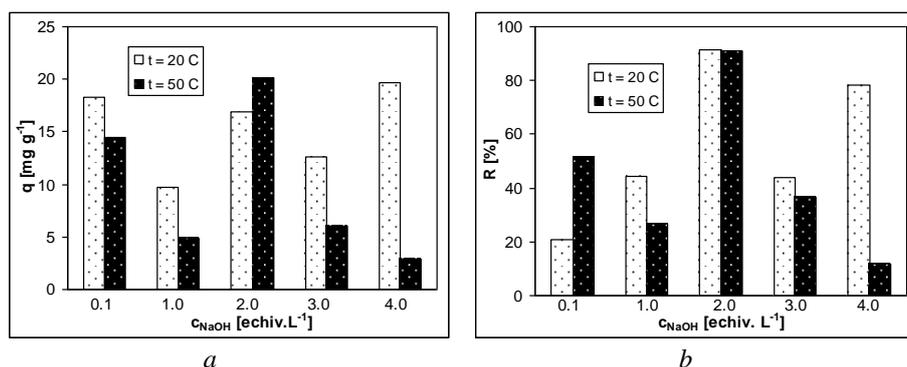


Fig. 2 – The values of biosorption capacity (a) and removal percent (b) obtained for Cu(II) ions in case of humic substance utilization as biosorbents.

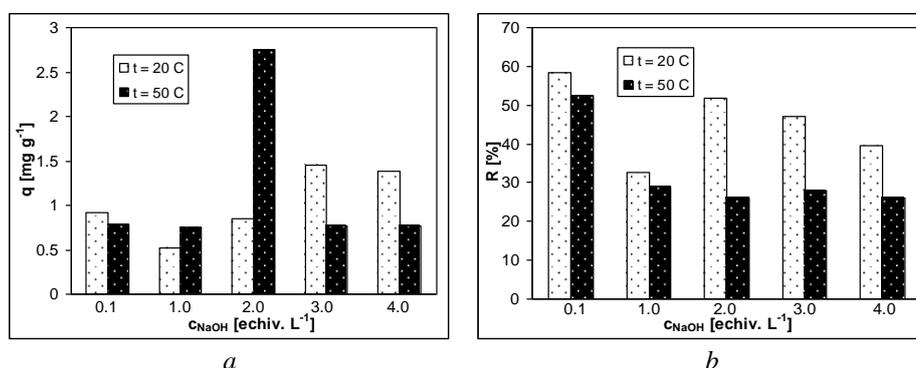


Fig. 3 – The values of biosorption capacity (a) and removal efficiency (b) for Cu(II) ions in the case of cellulosic waste utilization as biosorbents.

The increase of NaOH concentration over 2N does not improve the biosorption performances of separated fractions even if the quantities of separated fractions are higher (Tables 1 and 2). A possible explanation can be that at the utilization of NaOH solutions with concentration higher than 2 N, besides the solubilisation of humic substances, the lignin solubilisation process becomes also important. This determines that, after re-precipitation, the quantity of obtained solid material becomes higher, but it is represented by a mixture of humic substances and lignin. While the humic substances have numerous

reactive superficial functional groups (free carboxyl groups) which can easily interact with metal ions from aqueous solution, the reactivity of functional groups from lignin surface is much lower (most of them being hydroxyl groups, blocked from geometric considerations) (Guo *et al.*, 2008). In addition, because the re-precipitation of these two components is done from a mixture, it is possible that during re-precipitation, the lignin molecules are retained on the surface of humic substances. Under these conditions, the affinity of obtained solid material for Cu(II) ions from aqueous solution is lower, which can explain the experimental values of the biosorption capacity.

Therefore, considering all these experimental observations it can be noticed that the separation of the two main fractions from peat (humic substances and cellulosic waste) can be optimal done using a 2 N NaOH solution, at 50°C for 3 h contact time. These experimental conditions will ensure the separation of large enough quantities of the two fractions, which have high affinity for the metal ions (Cu(II) ions, in this case) from aqueous solutions.

3. Conclusions

In this study we examined the separation possibility of two main organic fractions from peat, namely humic substances and cellulosic waste, in order to use them as biosorbents for heavy metals removal. The separation of the peat fractions was done by treating the raw peat with NaOH solution with different concentrations (0.1 – 4.0 N), at two different temperatures (20 and 50°C) and 3 h of mixing. By this treatment, humic substances are solubilized and can be separated from cellulosic waste through filtration. In order to obtain solid humic substances, their re-precipitation is done in strong acidic media (pH < 1.0). The experimental results have shown that the highest quantities of these two fractions are obtained at the treatment of peat samples with 4 N NaOH solution and at 50°C. The use of the separated fractions as biosorbents in the heavy metals removal processes requires the evaluation of their biosorption capacity. In our study, the biosorption capacity of these two peat fractions was assessed for the removal of Cu(II) ions from aqueous solution. According with the experimental results, the maximum values of biosorption capacity is obtained from peat treated with 2 N NaOH solution and 50°C. The fractions separated under these conditions are obtained in large enough quantities and have the highest affinity for Cu(II) ions from aqueous media.

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POTENȚIALUL BIOSORBTIV A PRINCIPALELOR FRAȚIUNI SEPARATE DIN TURBĂ (POIANA STAMPEI, ROMÂNIA)

(Rezumat)

În acest studiu s-a investigat posibilitatea separării principalelor fracțiuni din turbă (Poiana Stampei, România), substanțe humice și deșeuri celulozice, pentru a fi utilizate ca biosorbenti, în procesul de îndepărtare a ionilor Cu(II) din soluții apoasă. Pentru separarea celor două fracțiuni, turba a fost tratată cu soluții de hidroxid de sodiu de diferite concentrații (0.1 – 4.0 N), la două temperaturi diferite (20 și 50°C) și amestecare timp de 3 ore. În urma acestui tratament are loc doar solubilizarea substanțelor humice din compoziția turbei, care poate fi separată de deșeurile celulozice prin filtrare. După filtrare, substanțele humice au fost re-precipitate în mediu puternic acid (pH <1.0). Ambele fracțiuni obținute au fost spălate și uscate în aer, iar eficiența procesului de separare a fost evaluată în fiecare caz. Toate fracțiunile obținute au fost utilizate ca biosorbenti pentru îndepărtarea ionilor de Cu(II) din soluție apoasă. Rezultatele experimentale au arătat că valorile cele mai mari ale capacității de biosorbție s-au obținut pentru fracțiunile separate prin tratarea turbei cu soluție de NaOH 2N, la 50°C.