VALORIZATION OF LOW-COST NATURAL MATERIALS IN DEPOLLUTION PROCESSES OF WASTEWATER

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Abstract. The adsorption on non-conventional and low-cost materials for removal of toxic heavy metals and oil products from aqueous media has become important in the last years, because is an efficient and cost-effective alternative compared to traditional chemical and physical remediation, and also other decontamination techniques. The good efficiency, minimization of secondary (chemical or biological) wastes and low cost of adsorbent materials, are only few main advantages of adsorption that can be used for the removal of such pollutants in high volumes of aqueous solutions, being thus more adequate for large scale applications. In this paper, are presented the adsorptive characteristics of a low-cost material that are abundant in our region, namely: Romanian peat moss from Poiana Stampei (Romania), for the removal of different toxic heavy metal ions (Pb(II), Hg(II), Co(II) and Ni(II)) and oil products from aqueous media. The experiments have concerned the influence of several experimental parameters (initial solution pH, adsorbent dose, initial heavy metals concentration, contact time, and temperature) on the heavy metals and oil products removal efficiency. The most important conditions for desorption of heavy metal ions from loaded-materials, required for their regeneration are also presented.

Keywords: heavy metals, oils products, low-cost natural materials, peat moss, wastewater treatment.

Introduction

The industrial effluents usually contain significant amounts of pollutants, such as heavy metals or oil products, which increase the environmental pollution problems and causing the deterioration of aquatic ecosystems. These pollutants are discharged from various industries, such as textile, pigments, storage batteries, plastics, mining, electroplating, metallurgical processes, combustible transportation and storage, etc. [1, 2], and are considered persistent environmental contaminants, because cannot be destroyed and degraded, or these processes occurs in a very long period of time [3]. In addition, due to their toxic effect and accumulation tendency throughout the food chain, the heavy metals and oil pollution represents an important problem with serious ecological and human health consequences. Thus, it is desirable to eliminate these compounds from industrial wastewaters, and this could be also important from economical considerations.

Various kinds of methods are currently used for the treatment of polluted aqueous effluents. In case of heavy metals the most important removal methods are chemical precipitation, flocculation, electrochemical treatment, ion exchange and adsorption [4-6]. In case of oil pollution, the dispersants, booms and skimmers can be used as cleanup methods to destroy or remove the oil slicks from water surface [7-9]. Unfortunately, many of these methods are not economically feasible even for small-scale industries, because require additional reagents or generate secondary wastes that required also a supplementary treatment.

In regards with its simplicity, the retention of pollutants on solid adsorbents is an effective method which can be used for the removal of heavy metals and oil products from wastewaters, in special when the utilized adsorbent is not very expensive [10]. From this perspective, natural materials which are available in large quantities or certain waste products from industrial or agricultural activities may have potential as inexpensive adsorbents. The peat moss is one example of such low-const adsorbents which can be utilized for the removal of heavy metals and oil products from aqueous effluents [11, 12]. The major reasons that promote the use of peat moss and adsorbent material are: biodegradability, use of renewable resources, waste recycling of life cycle extension, lower cost per unit, lower impact on ecosystem if released or lost during clean-up operations, and public perception that the products are environmental friendly.

In general, peat moss is considered a complex solid material with organic matter in various stages of decomposition, which contains lignin, cellulose and humic substances as major constituents [13, 14]. These constituents, especially lignin, have numerous polar functional groups (ex. alcoholic, phenolic, carboxylic, aldehydic, ketonic, etheric, etc.) which can be involved in the chemical interactions with metal ions. Due to these properties, peat moss tends to have a high cation exchange capacity and is an effective adsorbent for various heavy metals [15-17]. On the other hand, due to these major components with long hydrocarbon chains, the peat moss has an accentuated hydrophobic character, compatible with the structure of oil products, and can be used for the removal of such compounds from aqueous solutions.

In this study, we have investigated the effectiveness of peat moss as adsorbent for the removal of several heavy metals (Pb(II), Hg(II), Co(II), Ni(II)) and oil products from aqueous media. The influence of various experimental parameters (initial solution pH, peat dose, contact time, temperature, viscosity, initial concentration, etc.) was considered. The experiments have been followed: (***i***) the influence of several experimental parameters on the efficiency of adsorption process, and (***ii***) conditions for desorption of heavy metal ions from loaded-materials, required for their regeneration. The studied adsorbent showed high efficiency and good selectivity for studied heavy metals and oil products and should be considered for the removal of these pollutants from wastewaters samples.

Experimental

The peat moss used for the adsorption experiments was drawing at 0.5 m depth from Poiana Stampei, Romania. It is of low decomposition degree, with the following characteristics: pH = 4.96 (in water), ash = 5.32 %, total organic carbon = 33.68 %, total oxygen = 14.14 %, total nitrogen = 0.75 %, total phosphorus = 2.34 %. The peat moss samples was dried in air for 6 hours at 70 ± 2 °C, grounded and sieved until the particle dimension was less than 1-2 mm, and then stored in desiccators for the further use.

Stock solutions of heavy metal ions (Pb(II), Hg(II), Co(II) and Ni(II)), containing 10^{-2} mol M(II) L^{-1} were prepared by dissolving metal nitrate salts in double distilled water. The working solutions were obtained by diluting the stock solutions with double distilled water. Fresh dilutions were prepared and used for each experiment. The initial pH of working solutions was adjusted to required value with 0.1 mol L^{-1} HNO_3 or NaOH solution, before mixing the adsorbent.

The adsorption experiments were performed for a single component by batch technique, mixing a constant amount of low-cost material (0.125-0.200 g peat moss) with volume of 25 mL of known heavy metals concentration, in 150 mL conical flasks, with intermittent stirring for a required time (usually, 24 hours). The effect of initial solution pH was investigated at room temperature, and constant initial concentration of heavy metal ions, adjusting the pH values between 2.0 and 6.0. This pH interval was chosen for all studied metal ions to remain free M^{2+} species in solution. A series of such conical flasks were intermittently shaken in water bath at three different temperatures, for 3-4 hours, in order to study the effect of temperature on the sorption process efficiency. For kinetic experiments, a constant amount of adsorbent (0.125-0.200 g) was mixed with 25 mL of known heavy metals initial concentration, at various time intervals between 5 and 180 min.

At the end of sorption procedure, the adsorbent was separated through filtration, and the heavy metals concentration in filtrate was determined spectrophotometrically (Digital Spectrophotometer S 104 D, 1 cm glass cell), using a specific method for each heavy metal ion [18].

The adsorption capacity of considered low-cost materials was quantitatively evaluated using the amount of heavy metal retained on weight unit of adsorbent (*q*, mmol/g) and the percent of heavy metal removed (*R*, %), calculated with the following equations:

$$q = \frac{(c_0 - c)\cdot(V/1000)}{m} \tag{1}$$

$$R,\% = \frac{(c_0 - c)}{c_0}\cdot 100 \tag{2}$$

where: c_0 is the initial concentration of heavy metals solution (mmol/L), c is the equilibrium concentration of heavy metals solution (mmol/L), V is volume of solution (mL), and m is the adsorbent mass (g).

The petroleum-based liquid employed in the sorption tests was Light Fuel Oil (LFO) of regional production provided by PETROM Company (Romania). Three runs of the measurements were made at room temperature of 22 ± 2 °C. The test deals with determination of initial sorption capacity of sorbent as the pick-up ratio. It is expressed as the ratio between amount of oil (g) retained per unit mass of sorbent (g). The initial sorption capacity *S* (g oil /g sorbent) has been determined by gravimetric method of analysis using a digital balance with resolution of 0.001g and may be written as follows [23]:

$$S = \frac{W_{SO} - W_S}{W_S} = \frac{W_O}{W_S} \tag{3}$$

where: W_S means the weight of fresh adsorbent sample (g), W_{SO} denotes the weight of adsorbent saturated with oil product (g) and W_O is the weight of oil product retained into adsorbent matrix (g). Note that, under normal conditions, an adsorbent will not be exposed to sufficient oil layer thickness to become completely saturated. Therefore, this test gives the maximum possible sorption capacity data without the competing presence of water.

Results and discussion

Utilization of peat moss as low-cost material for the removal of heavy metals

Generally, the removal of metal ions from aqueous solution by adsorption takes places with maximum efficiency only in well-defined experimental conditions. From this reason, it is important to study the influence of several experimental parameters (such as initial solution pH, adsorbent dose, contact time or temperature) on the adsorption capacity of a given adsorbent.

One of the most important experimental parameter that should be establish is the initial solution pH, because many studies from literature have shown that low-cost materials act as a good adsorbent in a rather narrow pH range [19]. This is because the initial solution pH not only influenced the speciation and solubility of heavy metal ions, but also the dissociation degree of functional groups from adsorbent surface (ex: hydroxyl, carboxyl, carbonyl, amino, etc.), considered as adsorption sites.

In order to explain the influence of this parameter on the adsorption efficiency using peat moss as adsorbent, we must considering the following:

(i) at low pH values (acid media) – most of heavy metals are present as free positively charged cations (M^{n+}), that could interact with negatively charged functional groups from adsorbent surface. But, at low pH values most of functional groups from peat moss surface are un-dissociated or positively charged and cannot interact with metal ions from aqueous solution.

(ii) when pH is increased – the dissociation degree of functional groups from peat moss also increases, these become negatively charged, and will start to binds the positively charged metal ions from aqueous solution. Unfortunately, the increasing of pH determined the increasing of HO^- ions concentration from aqueous solution, and thus the speciation of metal ions can be changed. Experimental studies have been showed that if the pH value of aqueous solution is higher than 8, the hydrolysis of most metal ions occurs, accompanied by the formation of some insoluble aqua-complexes, and this is not desirable during of adsorption process.

In consequence, the increasing of initial solution pH will be done gradually, and the optimum value will correspond to the maximum of adsorption efficiency (Figure 1). For most studied adsorption systems, the maximum adsorption efficiency is obtained at an initial solution pH value of 6.0, and this was considered as optimum value and was used in all further experiments (Table 1).

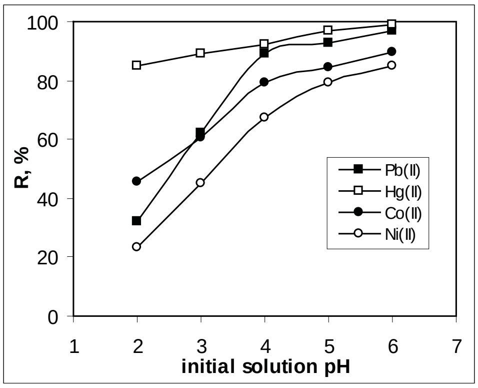

Figure 1. Influence of initial solution pH on the heavy metals adsorption onto peat moss.

Table 1

Optimum experimental conditions for the adsorption of heavy metals onto peat moss [20].

Heavy metal	pH	adsorbent dose (g/L)	Contact time (min)	Temperature (°C)
Pb(II)	6.0	5.0	50	22
Hg(II)	6.0	5.0	50	24
Co(II)	6.0	5.0	55	25
Ni(II)	6.0	5.0	60	25

The adsorbent dose is another important experimental parameter which has a great influence on the sorption process, and determines the potential of adsorbent through the binding sites available to remove heavy metal ions at a specific concentration [21]. By analyzing the dependences obtained in these experiments, it can be established that an adsorbent dose of 5.0 g/L, can be considered sufficient for the quantitative removal of heavy metal ions from aqueous solutions (Table 1).

The contact time between the two phases required to reach the equilibrium state is also a parameter that should be optimized in adsorption processes of metal ions from aqueous solutions. Unsatisfactory value of this parameter drastically limits the practical use of a given sorption process, even if its efficiency in the heavy metal ions removal is high.

The effect of contact time between solid phase – adsorbent material and aqueous phase – heavy metal ions solution has been investigated at room temperature in considered optimum experimental conditions (initial solution pH, adsorbent dose), for a given value of initial concentration of metal ions. The adsorbents were kept in contact with metal-bearing solution for different period of time (between 5 and 180 min) and the experimental dependences obtained for the adsorption of several heavy metal ions on peat moss are illustrated in Figure 2.

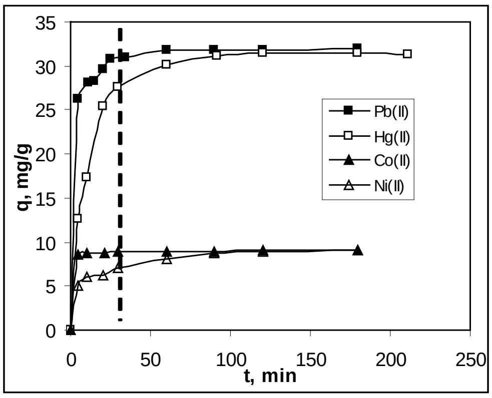

Figure 2. Influence of contact time on the adsorption of heavy metals onto peat moss.

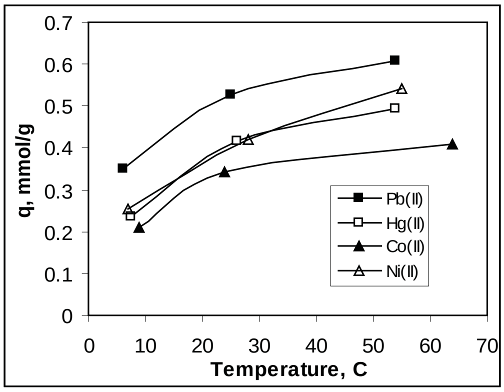

Figure 3. Influence of temperature on the adsorption of heavy metals onto peat moss.

The experimental data presented in Figure 2 indicate that the amount of heavy metal ions retained increase with the increasing of contact time and the sorption process reaches the equilibrium state after approximately 3 hours. The amount of heavy metal ions adsorbed increases sharply during the first 15 – 30 min of the process, when more than 85 % of metal ions were retained. After this initial step the rate of adsorption process becomes slower near to the equilibrium, which is practically obtained after 50-60 min (Table 1). No further significant adsorption is noted beyond 3 hours.

Temperature is also important for the retention of heavy metal ions, because this parameter dealing with the thermodynamics of the sorption process. It is known that temperature is directly related to the kinetic energy of the metal ions and it can account for the diffusion processes [22]. In order to study the effect of temperature, the adsorption experiments have been carried out at 6 – 65 °C, at optimum pH value and adsorbent dose of 5 g/L of peat moss. The equilibrium contact time was maintained between 3 and 4 hours, and the obtained experimental results related to the influence of these parameters are presented in Figure 3.

The results presented in Figure 3, show that the amount of heavy metal retained (q, mmol/g) increases with rise of temperature, during of the equilibrium time; and this effect is even more pronounced as the initial concentration of metal ions from aqueous solutions is higher. These results indicated the endothermic nature of heavy metals sorption on considered adsorbent, and may be due to the strengthening of adsorptive forces between superficial functional groups from peat moss and metal ions from aqueous solution. On the basis of these results, it was recommended that at large scale the removal of heavy metal ions from aqueous solutions by adsorption on peat moss to be performed at ambient temperature, and this is dictated especially from economical considerations.

In order to make the adsorption process more economical, it is necessary to regenerate the loaded-adsorbents. Different concentrations of aqueous solutions of mineral acids were tested in batch conditions for to desorb the heavy metals from loaded-peat moss. The obtained results (Table 2) have indicates that the most of heavy metal ions can be readily eluted with 0.1 mol/L HCl solution, and that a volume of 10 mL acid solution is enough to treat 1 g of loaded-adsorbent.

The adsorbent samples (washed with double distilled water and dried) were reuse in three sorption / desorption cycles, and the loss in the sorption capacity (see Table 2) was less than 8 % for studied heavy metal ions. This means that, peat moss could be repeatedly used in heavy metals retention without detectable losses in their initial sorption capacity. These studies further confirm that the adsorption of heavy metal ions on considered low-cost materials is mostly by chemical nature, and that the interactions are stronger. The greatest part of the binding is reversible, so an ion exchange mechanism could explain the obtained results and share of other interaction forces is lower.

Table 2

Percent of heavy metals eluted from loaded-adsorbent by using 10^{-1}mol/L HCl solution [20].

Heavy metal	% eluted	% loss
Pb(II)	96.53	5.08
Co(II)	92.81	7.01
Ni(II)	91.24	7.53

Utilization of peat moss as low-cost material for the removal of oil products

The water contaminated with trace of oil products cannot be used as drinking water and in many cases this is not suitable as industrial water or irrigation water. As a consequence of several hazardous accidental oil spills in the previous decades, the interest for investigation of cleanup methods becomes one of the priorities among the directions of the environmental research. The sorption capacities of peat moss for LFO was determined in triplicate according to *test,* and the results are summarized in Table 3, together with average value and standard deviation data.

Table 3

Initial sorption capacity of peat for LFO, T = 22 ± 2 ºC [23].

	Run no.1	Run no.2	Run no.3	Average	Standard deviation
S (g/g)	7.387	7.472	7.878	7.579	0.214

The initial sorption capacity of 7.579 ± 0.214 g/g is given by the properties of sorbent such as porosity and capillaries as well as by the properties of oil product as viscosity, density and surface tension. The adsorption capacity of 7.579 g/g is relatively high suggesting that the retention of liquid phase into adsorbent matrix occurs due to adsorption and capillary phenomena.

The removal of oil products from water surface by sorption was investigated in our previous papers using the design of experiments (DoE) and response surface methodological (RSM) approach [23, 24]. The experimental design used for the modeling of adsorption process was carried out choosing three main factors (design variables), namely: the dosage of adsorbent, drainage time and the initial thickness of oil products on water surface. Since the cleanup process occurs on the top surface of water column it is appropriate to express the adsorbent dosage as amount of adsorbent per unit of surface area. Thus, in this application the adsorbent dosage was expressed as adsorbent amount in (g) per unit of polluted given in (dm^2), M (g/dm^2). The drainage time is given in seconds, t (s).

The application of peat as floating adsorbent for oil products (LFO) removal from water surface was investigated using the design of experiments and response surface methodology. The response surface plots indicate that the removal efficiency is influenced considerably by the adsorbent dosage and the initial thickness of oil slick on water. The optimal solution determined for adsorption process over the region of experimentation is as follows: adsorbent dosage of 4.89 g/dm^2, drainage time of 12 s and the initial thickness of oil products of 3.9 mm. In such conditions a maximal removal efficiency of 98.74% was obtained experimentally.

Conclusions

Adsorption of heavy metal ions and oil products from aqueous solutions on the low-cost adsorbent materials is a relative simple method that gained credibility in the last years, because it has good efficiency, minimize the obtaining of secondary (chemical or biological) wastes and low cost of these materials. In comparison with other methods, the adsorption on low-cost materials can be used for the removal of heavy metal ions and oil products in much higher volumes of aqueous solutions.

The experimental studies performed in this area have concerned the use of peat moss that is abundant in our region. This adsorbent was tested for the removal of some heavy metal ions (Pb(II), Hg(II), Co(II) and Ni(II)) and oil products, from aqueous media. The experimental results obtained in these studies have shown that: (***i***) the efficiency of adsorption processes are influenced by several experimental parameters, such as initial solution pH, adsorbent dose, contact time and temperature, and from this reason their study is important in order to found the optimum experimental conditions for to obtain a maximum removal yield; (***ii***) the heavy metal ions from loaded-adsorbent materials can be easily eluted by using a diluted mineral acids solutions (such as 0.1 mol/L HCl solution), after that the regenerated materials can be used in other few adsorption / desorption cycles; (***iii***) in case of oil products the optimal solution determined for adsorption process is: adsorbent dosage of 4.89 g/dm^2, drainage time of 12 s and the initial thickness of oil products of 3.9 mm. The main practical drawback of the adsorption method for the removal of heavy metal ions and oil products from aqueous media is that such low-cost adsorbent materials can be used only in batch systems, which has a reduced applicability at industrial scale. The industrial utilization of the adsorption method requires the use of continuous systems. The solving of this problem remains in attention for the further research studies, in order to found some advantageous practical solutions.

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