**Buletinul Ştiinţific al Universităţii "Politehnica" din Timisoara, ROMÂNIA**
**Seria CHIMIE ŞI INGINERIA MEDIULUI**
***Chem. Bull. "POLITEHNICA" Univ. (Timişoara)*** ***Volume 54(68), 1, 2009***

# Cobalt (II) Removal from Aqueous Solutions by Adsorption on Modified Peat Moss

C. Caramalău, L. Bulgariu, M. Macoveanu

Technical University "Gheorghe Asachi" of Iaşi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, Bd. D. Mangeron, 71A, 700050, Iaşi, Romania
Phone: (0232) 271759, Fax: (0232) 271759, E-Mail: lbulg@ch.tuiasi.ro, http://www.ch.tuiasi.ro

**Abstract**: The adsorption behaviour of cobalt (II) from aqueous solutions on un-treated and treated peat moss was investigated. The treatments suppose the mixing of peat moss with 0.2 mol/L aqueous solution of $HNO_3$ and NaOH, respectively. The influence of initial solution pH, peat moss dose, initial cobalt (II) concentration and contact time, was studied in batch experiments. The optimum results were obtained at pH = 6.0 (acetate buffer), an adsorbent dose of 5 g/L and an initial concentration of 240 mg Co(II)/L. The experimental results have show that in case of peat moss treated with NaOH, the adsorption capacity increase with 15 % and the contact time necessary for to attain the equilibrium decrease until 15 min. In case of peat moss treated with $HNO_3$, the adsorption capacity slowly decrease and the contact time required for to attain the equilibrium has almost the same value as un-treated peat. The adsorption process of cobalt (II) on un-treated and treated peat moss was tested with Langmuir isotherm model and the isotherm constants were deduced from this.

**Keywords:** peat moss, cobalt (II) ions, adsorption, chemical treatments, isotherm

## 1. Introduction

Environmental contamination with metal ions represents a potential treat to human, animals and plants. The metal ions do not undergo biodegradation and many of them are soluble in aqueous solutions, therefore become more available for living systems and accumulate in the environment [1].

Cobalt (II) compounds are essential in many industries. Their applications in nuclear power plants, metallurgy, mining, pigments, paints and electronic are only few examples where the presence of cobalt in waste waters represents a major environmental problem [2, 3].

Conventional methods for removing dissolved metal ions fro aqueous media include chemical precipitation, chemical oxidation and reduction, ion exchange and activated carbon adsorption [3-5]. However, these processes have significant disadvantages, such as incomplete removal of metal ions, high quantities of toxic sludge, required additional reagents and have high operation cost.

In recent years, considerable attention has been received the utilization of adsorption technique, in which the adsorbents are natural material or industrial and agricultural wastes, to passively remove of metal ions from aqueous effluents. Thus, the utilization of peat [6-8], living and death biomass [9-11] or clay and related minerals [12-14] offers an efficient and cost-effective alternative compared to traditional chemical and physical remediation and decontamination techniques.

A large number of studies from literature related the performances of different such adsorbents for the removal of different metal ions under various experimental conditions. In most of these is showed that such natural or waste products can be good adsorbents for metal ions and some of them have excellent ion-exchange properties.

The adsorbent used in this study is peat moss (from Poiana Stampei, Romania). This a complex material, obtained by partial degradation of vegetables, and where the major constituents are cellulose, lignin and humic substances [15]. Due to these constituents, the peat moss has in its structure different polar groups (such as carboxylic, phenolic, alcoholic, etheric, etc.) which can chemical bind metal ions from aqueous solutions.

In ours previous studies [16, 17], it has that cobalt (II) can be successfully removed from aqueous solutions (> 97 %) when its initial concentration is lower than 100 mg/L. For a higher initial metal ion concentration the cobalt removal percents drastically decrease, and the adsorption process is not efficient any more.

In order to improve the adsorption capacity of peat moss for cobalt, simple chemical treatments were used. These treatments suppose the mixing of peat moss with 0.2 mol/L aqueous solutions of $HNO_3$ and NaOH, respectively. An increasing of adsorption capacity for cobalt (II) with less 15 % and a decreasing of contact time necessary for to attain the equilibrium until 15 min was obtained, when the peat moss was treated with NaOH solution. The main advantage of this procedure is that the increasing of adsorption capacity of peat moss is done without to be used additional expensive additives.

In this study, the batch experiments were conducted in order to investigate the adsorption of cobalt (II) ions from aqueous solutions on un-treated and treated peat moss.

The influence of initial solution pH, peat moss dose, initial cobalt (II) concentration and contact time, was studied in order to establish the optimum experimental conditions for adsorption process. The Langmuir isotherm model was used for the mathematical description of cobalt (II) adsorption on un-treated and treated peat moss, and the isotherm constants were deduced from this.

## 2. Experimental

*2. 1. Materials*

Experiments were carried out using peat moss sampled from Poiana Stampei, Romania. The material was dried in air (4 days) at room temperature, and the grounded and sieved the particles have the granulation less than 1-2 mm.

All chemical reagents were of analytical degree and were used without further purifications. The stock solution of cobalt, containing 600 mg Co(II)/L, was prepared by cobalt nitrate (from Aldrich) dissolving in twice distilled water. After preparation the solution was standardized [18], for to determine the exact concentration of metal ion. The working solutions were obtained by diluting the stock solution with twice distilled water. The initial solution pH values of work aqueous solutions were obtained using 2N $HNO_3$ solution or acetate buffer ($CH_3COOH/CH_3COONa$).

*2. 2. Methods*

The treatment of peat moss was done with $HNO_3$ and NaOH. Thus, 2.0 g of peat moss was mechanically shake, for 60 min, with 100 mL of 0.2 mol/L $HNO_3$ and 0.2 mol/L NaOH, respectively. After 24 hours, the peat moss samples were filtrated, washed with twice distilled water (10-12 times), dried for 5 hours at 80-85 °C and then mortared.

The adsorption experiments were performed by batch technique, mixing samples of cca. 0.125 g of un-treated and treated peat moss with volumes of 25 mL solution of known concentration of lead (24 – 240 mg Co(II)/L), in a 150 mL conical flasks. The initial pH of work solutions was obtained adding small volumes of 2N $HNO_3$ solution (for pH=2.0 and 3.0) and 5.0 mL of acetate buffer (for pH = 4.0 and 6.0), and was measured with a Radelkis OK-281 pH/ion-meter, equipped with a combined glass electrode. After a determined time (usually 24 hours) with intermittent stirring, the phases were separated by filtration and the cobalt (II) concentration in filtrate was analyzed spectrophotometrically with rubeanic acid (Digital Spectrophotometer S 104 D, $\lambda$ = 450 nm, 1 cm glass cell, against a blank solution [19]), using a prepared calibration graph.

The effect of peat moss dose on cobalt (II) adsorption was determined by mixing adsorbent samples between 3 and 30 g/L with 25 mL of cobalt (II) solution (50 mg/L) at pH = 6.0. For the contact time experiments, we use the same procedure as described above, with the difference that the samples were filtrated after a specific period of time.

The cobalt (II) adsorption on un-treated and treated peat moss was quantitatively evaluated using amount of metal ion adsorbed on weight unit of adsorbent (q, mg/g) and percent of cobalt removal (R, %), calculated according with their definition relations [20].

## 3. Results and discussion

Peat moss is usually described as a complex material, which contains organic matter in various decomposition stages [15], and which has as major constituent lignin, cellulose and humic substances. These constituents contain numerous functional groups, which can be involved in specific chemical interaction (ion-exchange or complexation) with metal ions, during of their adsorption from aqueous solutions. Thus, the efficiency of adsorption process will depend both on the affinity of metal ion for functional groups from adsorbent surface, and on the availability of these to interact with metal ions.

For a particular metal ion, the increasing of adsorption process efficiency can be done by increasing the availability of functional groups from adsorbent surface, using specific treatments. Thus, we select $HNO_3$ and NaOH for the treatments, because a mineral acid can remove the metal ions which are already complexed on superficial functional groups of adsorbent (and thus these become free), and a strong base for to increase the ionization degree of the functional groups of adsorbent, without to be affected the structure and the conformation of peat moss.

Under these conditions is expected that the amount of cobalt ion retained on peat moss to depend on the type of chemical treatment, as well as other experimental parameters, such as initial solution pH, adsorbent dose, initial metal ion concentration and contact time.

*3. 1. Effect of initial solution pH*

The initial solution pH is an important parameter in the adsorption process of metal ions from aqueous solutions, which affect both the dissociation degree of functional groups from adsorbent surface and the speciation and solubility of metal ions [21].

In this study, the initial solution pH was adjusted with 2N $HNO_3$ (for pH=2.0 and 3.0) and with acetate buffer (for pH = 4.0 and 6.0). The adsorption efficiency of cobalt (II) on un-treated and treated peat moss as a function of initial solution pH is presented in Figure 1.

As can be seen from Figure 1, the adsorption efficiency gradually increased with the increase of initial solution pH, and this effect is more pronounced in case of peat moss treated with NaOH, than in case of un-treated peat moss, or for the peat moss treated with $HNO_3$.

This behaviour is mainly determined by the ionic state of functional groups from adsorbent surface involved in adsorption process. Thus at pH = 2.0, most of functional groups are un-dissociated and the obtained values of removal percent are lower (< 15 %), in all cases. The increasing of initial solution pH determined the increasing of functional groups dissociation degree, and thus the cobalt (II) ions can be more easily bonded. In consequence, the adsorption efficiency increases.

Because the maximum efficiency of cobalt (II) removal is obtained at initial solution pH = 6.0 (acetate buffer), this was considered as optimum value, and was used in all further experiments.

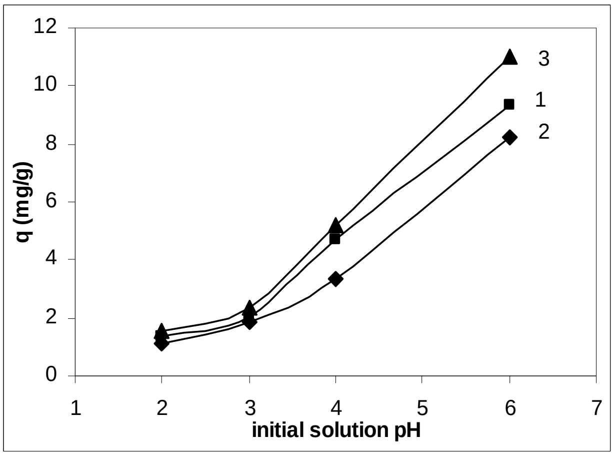


Figure 1. Effect of initial solution pH on cobalt (II) removal on (1) un-treated peat moss, (2) peat moss treated with $HNO_3$, (3) peat moss treated with NaOH (50 mg Co(II)/L, peat dose = 5 g/L; time = 24 h; t = 19.5 °C)

### *3. 2. Effect of peat moss dose*

Figure 2 presents the effect of adsorbent dose for cobalt (II) adsorption on un-treated and treated peat moss.

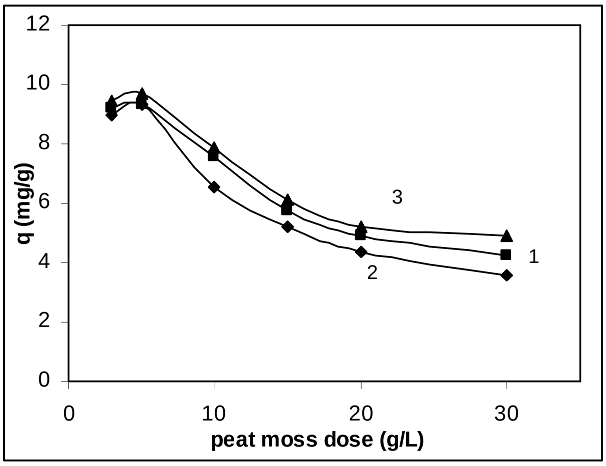


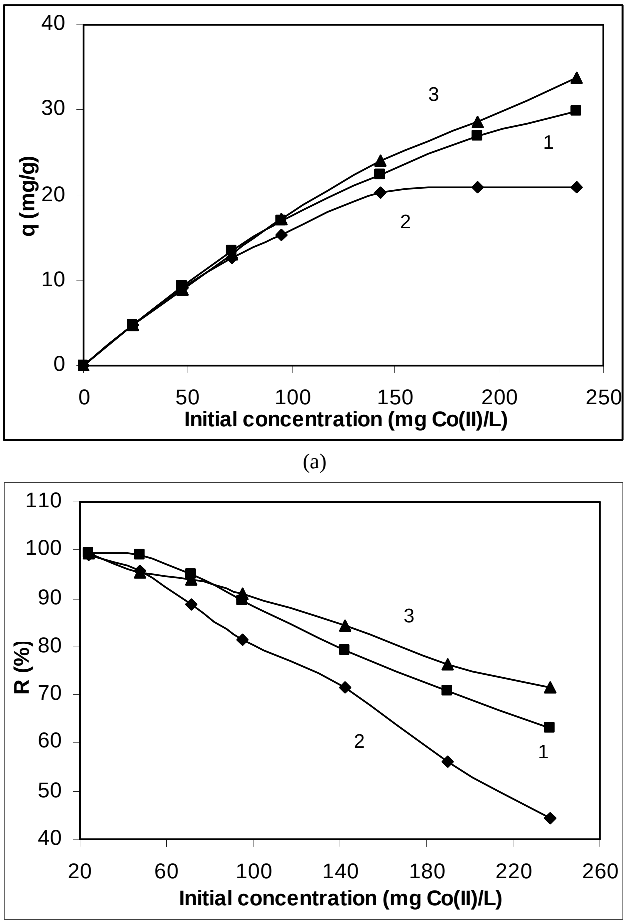
Figure 2. Effect of adsorbent dose for cobalt (II) removal on (1) un-treated peat moss, (2) peat moss treated with $HNO_3$, (3) peat moss treated with NaOH (50 mg Co(II)/L, pH = 6.0 (acetate buffer), time = 24 hours, t = 19.5 °C)

It can be observed that varying the adsorbent dose from 3 to 30 g/L, the q values decrease from 9.36 to 4.23 mg/g for un-treated peat moss, from 9.02 to 3.57 for peat moss treated with $HNO_3$, and from 9.68 to 4.88 for peat moss treated with NaOH, respectively. Therefore 5 g peat moss/L was considered sufficient for quantitative removal of cobalt (II) from aqueous solutions, and was selected as the optimum value for the adsorption experiments.

### *3.3. Effect of initial cobalt (II) concentration*

The cobalt (II) removal on un-treated and treated peat moss was studied as a function of its initial concentration under optimized conditions, initial solution pH and amount of adsorbent.

The amount of cobalt (II) retained on weight unit of adsorbent (q, mg/g) (Fig. 3a) increase with the increasing of initial metal ion concentration from aqueous solution. At the same time, the percent of cobalt (II) removal (R, %) (Fig. 3b) sharply decrease with the increasing of the initial concentration. This opposite trend is determined by the fact that at higher concentrations, the most superficial groups are already occupied and in consequence, the diffusion of cobalt (II) ions to the un-reacted functional groups is inhibited.



(a)

(b)

Figure 3. Effect of initial cobalt (II) concentration on the adsorption on (1) un-treated peat moss, (2) peat moss treated with $HNO_3$, (3) peat moss treated with NaOH (pH = 6.0 (acetate buffer), 5 g peat moss/L, time = 24 hours, t = 19.5 °C)

On the other hand, the efficiency of cobalt (II) removal follows the order: peat moss treated with NaOH (q = 34.20 mg/g) > un-treated peat moss (q = 29.75 mg/g) > peat moss treated with $HNO_3$ (q = 20.85 mg/g) for an initial cobalt (II) concentration of 240 mg/L. The experimental results indicate that in case of peat moss treated with NaOH, the adsorption capacity for cobalt (II) increase with 15 %, in comparison with un-treated peat moss.

A good retention of cobalt (II) take place at initial metal ion concentration lower than 95 mg/L in case of un-treated peat moss, 65 mg/L in case of peat moss treated with $HNO_3$, and 120 mg/L in case of peat moss treated with NaOH, when the residual concentration is lower than the permissible limit for cobalt discharge. The increasing of initial cobalt (II) concentration over these values, determined a decrease of adsorption efficiency, and in consequence for its removal are necessary two or more adsorption steps.

These experimental results suggest that the removal of cobalt (II) from aqueous solutions, by adsorption on un-treated and treated peat moss occurs predominantly by ion-exchange interactions, and the efficiency of adsorption process depends on the ionic state of superficial functional groups of adsorbent. Thus, in case of peat moss treated with $HNO_3$, most of functional groups are un-dissociated and the number of electrostatic interactions between these and the metal ion is low. When, the peat moss is treated with NaOH, the dissociation degree of functional groups increase drastically, and the ion-exchange interactions are facilitated.

### *3. 4. Effect of contact time*

The effect of contact time between adsorbent (un-treated and treated peat moss) and cobalt (II) aqueous solutions with an initial concentration of 50 mg/L and pH = 6.0 (acetate buffer) is illustrated in Fig. 4.

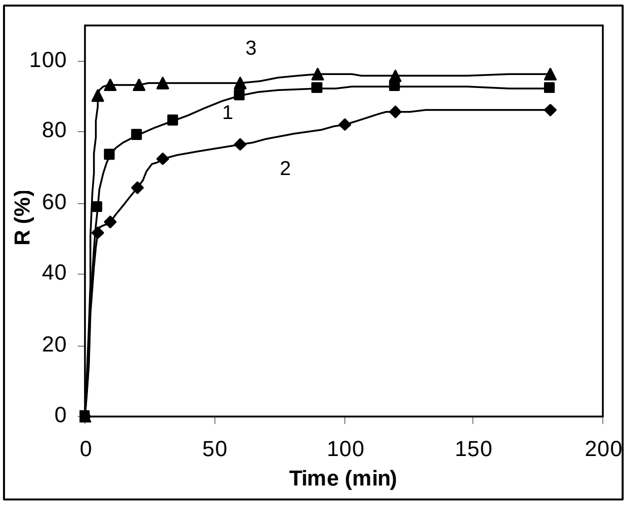


Figure 4. The effect of contact time on cobalt (II) removal on (1) un-treated peat moss, (2) peat moss treated with $HNO_3$, (3) peat moss treated with NaOH (5 g peat/L, t = 19.5 °C)

It can be seen that the cobalt (II) removal percent increase rapidly with the contact time up to 15 min for the peat moss treated with NaOH, up to 60 min for the un-treated peat moss, and up to 100 min in case of peat moss treated with $HNO_3$. After this fast initial step, the rate of adsorption process becomes slower and the maximum removal is attained.

The low values of contact time necessarily for to reach the equilibrium sustains the hypothesis that the cobalt (II) adsorption on un-treated and treated peat moss occurs predominantly by electrostatic interactions.

### *3.4. Adsorption isotherms*

The different values of cobalt removal percents obtained for its adsorption on un-treated and treated peat moss are in agreement with the values of quantitative parameters obtained from Langmuir isotherm model. This model gives the best fit of experimental results.

The Langmuir isotherm model can be used when the adsorbed coverage is limited to one molecular layer, and describes chemosorption as the formation of an ionic or covalent bond between adsorbent and metal ion [21]. The linear expression of Langmuir isotherm model is:

$$\frac{c}{q} = \frac{c}{q_{\max}} + \frac{1}{q_{\max} \cdot K_L} \qquad (1)$$

where: $q_{max}$ is the maximum adsorption capacity (mg/g), q is the equilibrium adsorption capacity (mg/g), c is the equilibrium solution concentration (mg/L) and $K_L$ is the Langmuir constant (L/mg) related to the free energy of adsorption.

The graphical representation of the linear form of Langmuir adsorption isotherm model for the cobalt (II) adorption on un-treated and treated peat moss is illustrated in Fig. 5, and the isotherm model parameters are summarized in Table 1.

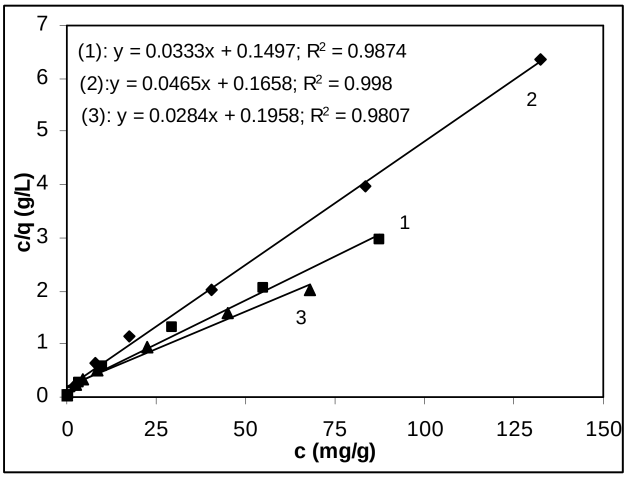


Fig. 5. Application of Langmuir model for cobalt (II) adsorption on (1) un-treated peat moss, (2) peat moss treated with $HNO_3$, (3) peat moss treated with NaOH (pH = 6.0 (acetate buffer), 5 g peat/L, time = 24 hours)

The high values of correlation coefficients ($R^2 > 0.98$) indicate a good agreement between parameters and confirm the monolayer adsorption of cobalt (II) on un-treated and treated peat moss. The maximum adsorption capacity ($q_{max}$), which is a measure of adsorption capacity to form a monolayer, is higher in case of cobalt (II) adsorption on peat moss treated with NaOH, than in case of cobalt (II) adsorption on un-treated peat moss, and both are higher than the value obtained in case of cobalt (II) adsorption on peat moss treated with $HNO_3$. In addition, the $K_L$ values decrease in the same order, and suggest that between functional groups of adsorbent and cobalt (II) ions from aqueous solution strong interactions occur.

*TABLE 1. Isotherm constants for cobalt adsorption on studied peat's moss*

| Parameter | Un-treated peat moss | Peat moss treated with $HNO_3$ | Peat moss treated with NaOH |
|---|---|---|---|
| $R^2$ | 0.9874 | 0.9980 | 0.9807 |
| $q_{max}$ (mg/g) | 30.03 | 21.51 | 35.21 |
| $K_L$ (L/mg) | 0.2220 | 0.2802 | 0.1451 |
| ΔG (kJ/mol) | -23.05 | -23.63 | -22.02 |

The change in the free energy (ΔG) was calculated from the Langmuir constant using eq (2):

$$\Delta G = -RT \ln K_L \qquad (2)$$

where: R is universal gas constant (8.314 J/mol K) and T is the absolute temperature. The negative values of ΔG (Table 1) indicate that the removal process of cobalt (II) by adsorption on un-treated and treated peat moss is feasible and spontaneous. In addition, the lower and negative value of ΔG obtained in case of cobalt (II) adsorption on peat moss treated with NaOH suggest that after the treatment, the availability of functional groups from adsorbent surface, increase.

## 4. Conclusions

In this study was investigated the adsorption behaviour of cobalt (II) from aqueous solutions on un-treated and treated peat moss. The treatments suppose the mixing of peat moss with 0.2 mol/L aqueous solutions of $HNO_3$ and NaOH, respectively. The adsorption experiments were carried out in batch systems, in order to evaluate the adsorption capacity of peat moss before and after treatments.

The efficiency of cobalt (II) adsorption on un-treated and treated peat moss was studied as a function of initial solution pH, adsorbent dose, initial cobalt (II) concentration and contact time. The optimum results were obtained at pH = 6.0 (acetate buffer) and adsorbent dose of 5 g/L and an initial concentration of 240 mg Co(II)/L, when the efficiency of cobalt (II) adsorption as a function of peat moss type follows the order: peat moss treated with NaOH (q = 34.20 mg/g) > un-treated peat moss (q = 29.75 mg/g) > peat moss treated with $HNO_3$ (q = 20.85 mg/g). The experimental results, also indicate that the removal percent of cobalt (II) increases with the initial solution and decrease with initial cobalt (II) concentration.

The Langmuir isotherm model was used for the mathematical description of cobalt (II) adsorption on un-treated and treated peat moss. The maximum adsorption capacity ($q_{max}$) is higher in case of cobalt (II) adsorption on peat moss treated with NaOH, than in case of cobalt (II) adsorption on un-treated peat moss, and both are higher than the value obtained in case of cobalt (II) adsorption on peat moss treated with $HNO_3$. In addition, the change in free energy (ΔG) calculated from Langmuir constant confirm the feasible and spontaneous adsorption of cobalt (II) on un-treated and treated peat moss.

## REFERENCES

1. Laws E.A., Aquatic Pollution an Introductory Text, third ed., John Wiley and Sons, New York, **2000**. pp 23-25.
2. Baun D.L. and Christensen T.H., Speciation of heavy metals in landfill leachate: a review. *Waste Manage. Res.* Vol. 22, **2004**, pp. 3–23.
3. Babel S. and Krniavan T.A., Low cost adsorbants for the heavy metals uptake from contaminated water: a review. *J. Hazard. Mater.* Vol. B 97, **2003**, pp. 219 – 243.
4. Sengupta, A.K., Zhu, Y. and Hauze, D., Metal (II) ion binding onto chelating exchange with nitrogen donor atoms: some new observations and related implications. *Environmental Science and Technology*, Vol. 25 (3), **1991**, pp. 481– 488.
5. Igwe J.C. and Abia A.A., A bioseparation process or removing heavy metals from water using biosorbents. *Afr. J. Biotech.* Vol. 5, **2006**, pp. 1167-1179.
6. Coupal B. and Spiff A.I., The treatment of waste waters with peat moss. *Wat. Res.* Vol. 33(2), **1999**, pp. 1071 – 1076.
7. Brown P.A., Gill S.A. and Allen S.J., Metal removal from waste waters using peat. *Wat. Res.* Vol. 34, **2000**, pp. 3907 – 3916.
8. Ho Y.S., John Wase D.A. and Forster C.F., Kinetic studies of competitive adsorption by sphagnum moss peat. *Environ. Tech*. Vol. 17, **1996**, pp. 71 – 77.
9. An H.K., Park B.Y. and Kim D.S., Crab shell for the removal of heavy metals from aqueous solutions. *Water Res.* Vol. 35, **2001**, pp. 3551–3556.
10. Volesky B. and Holan Z.R., Biosorption of heavy metals, *Biotechnol. Progress*, Vol. 11, 1995, pp. 235–250.
11. Rae I.B. and Gibb S.W., Removal of metals from aqueous solutions using natural chitinous materials, *Water Sci. Technol.* Vol. 47, **2003**, pp. 189–196.
12. Angove, M.J., Wells, J.D. and Johnson, B.B., The influence of temperature on the adsorption of cadmium (II) and cobalt (II) on goethite. *J. Colloid Interface Sci.* Vol. 211, **1999**, pp. 281–290.
13. Chen L. and Lu S.,Sorption and desorption of radio cobalt on montmorillonite - effects of pH, ionic strength and fulvicacid. *Appl.Radiat.Isot.* Vol. 66, **2008**, pp. 288–294.
14. Hayes K.F. and Leckie, J.O., Modeling ionic strength effects on cation adsorption at hydrous oxide/solution interfaces. *J. Colloid Interface Sci.* Vol. 15, **1987**, pp. 564–572.
15. Bailey S.E., Olin T.J., Bricka M.R. and Adrian D.D., A review of potentially low cost sorbents for heavy metals. *Wat. Res.* Vol. 33(11), **1999**, pp. 2469 – 2479.
16. Caramalau C., Bulgariu L. and Macobeanu M., Adsorption characteristics of cobalt (II) ions from aqueous solutions on Romanian peat moss. *Envr. Eng. Manag. J.* **2009**, in press.
17. Caramalau C., Bulgariu L. and Macobeanu M., Kinetic study of cobalt adsorption on peat activated by simple chemical treatments. *Envr. Eng. Manag. J.* **2009**, in press.
18. Dean J.A., Analytical Chemistry Handbook. 3rd ed. McGrow-Hill Inc. New York. **1995**. pp 3.105 – 3.109.
19. Flaska A.H. and Barnard A.J., Chelates in Analytical Chemistry. Marcel Dekker Inc. New York. **1976**. pp 16 – 28.
20. Allen S.J., McKay G. and Porter J.F., Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems, *J. Coll. Interf. Sci.* Vol. 280, **2004**, pp. 322–333.
21. Ma W. and Tobin J.M., Determination and modelling of effects of pH on peat biosorption of chromium, copper and cadmium. *Biochem. Eng. J.* Vol. 18, **2004**, pp. 33–40.