

PAPER • OPEN ACCESS

Cadmium Removal from Aqueous Solutions Using Nano-Iron Doped Lignite

To cite this article: Despina Pentari and Despina Vamvouka 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **221** 012135

View the [article online](#) for updates and enhancements.

Cadmium Removal from Aqueous Solutions Using Nano-Iron Doped Lignite

Despina Pentari ¹, Despina Vamvouka ²

¹School of Mineral Resources Engineering, Technical University of Crete, 73100 Chania, Crete, Greece

²School of Mineral Resources Engineering, Technical University of Crete, 73100 Chania, Crete, Greece

pentari@mred.tuc.gr

Abstract. In the present study the removal of Cadmium (Cd) from spiked aqueous solutions using low quality lignite (LG) was studied. A comparison between the adsorption capacity of activated carbon (AC) and lignite is presented, while the enhancement of the adsorption capacity, by adding Nano-scale zero valent iron (nZVI) onto AC and LG was investigated. To study the enhancement of adsorption capacity, two materials were synthesized (LGFe, ACFe). The sorbents were characterized by Scanning Electron Microscopy (SEM-EDX), while their sorption efficiency, for Cd removal, was investigated with kinetic and equilibrium studies performed in batch conditions. With the proposed procedure nZVI was successfully “loaded” onto lignite and Cd removal from solutions reached 90%. The addition of iron nanoparticles in organic materials significantly increased adsorptive capacity, which was more drastic in the case of lignite. The experiments showed that sorption equilibrium was achieved within 12 h for all materials and that maximum adsorption capacity of LG, AC, LGFe, and ACFe was 25.5mg/g, 30mg/g, 34.7mg/g, and 36.5mg/g, respectively. The results of the equilibrium experiments proved to fit better to the Freundlich equation.

1. Introduction

Environmental pollution by heavy metals is a hazard of prime interest and increasing significance. Heavy metal ions are released into the environment in a number of different ways and because of their accumulation in living organisms form a serious and complex problem that has been a focus of attention all over the world.

As far as surface and groundwater are concerned, heavy metals can be considered among the chief pollutants. The concentrations of these toxic elements have to be reduced to meet strict legislative standards. The conventional techniques for the removal of heavy metals include ion exchange, filtration, electrolytic or liquid extraction, chemical precipitation, reverse osmosis, and membrane techniques, [1-7]. In several cases the above mentioned techniques are either economically unfavourable or technically complicated making the arena ripe for new methods for treatment of metals contaminated water. Among new methods, the utilization of lignite, for the treatment of wastewater containing heavy metals, is gaining more attention as a simple, effective and economical means of pollution remediation. The mechanism by which metal ions are sorbed onto low rank coal is a matter of considerable debate. Various studies have reached to different conclusions, and theories related to the matter include ion-exchange, surface adsorption, complexation, chemisorption, and adsorption-complexation. Among these theories, ion exchange appears to be the most prevalent



mechanism [8]. Although the adsorption capacity of low rank coals is lower in comparison to that of other materials, the fact that they are plentiful and inexpensive makes them an attractive and inexpensive option for the removal of metals.

In Greece, there are several lignite deposits of various sizes, with low calorific value that cannot be utilized for power generation. Such lignites are rich in mineral matter and therefore possess low calorific value. Several studies [9-16] have been undertaken on the non-electric uses of lignite, with waste water treatment to be among the promising of them.

Cadmium is a heavy metal of significant environmental concern. It has been classified as carcinogen and teratogen that can impact different human organs. It can be released to the environment through different processes including fossil fuels combustion, metal production, electroplating, fertilizers application and batteries and pigments manufacturing. There is, therefore, a considerable interest in developing techniques to remove cadmium from contaminated water. Among the techniques proposed adsorption onto nanoscale zero valent iron is a particularly attractive and promising technique [10-12]. Nanoscale zero valent iron has been reported to possess high sorption capacities for different metals while its maximum adsorption capacity iron for Cd^{2+} was found to be up to 770mg/g at room temperature [10].

The aim of the present work is to investigate the possibility of using a greek lignite, rich in mineral matter, with low calorific value, for the removal of Cd ions from waste water. For comparison reasons the adsorption capacity of activated carbon (AC) is also investigated. To study the enhancement of adsorption capacity by adding nZVI onto the lignite, two materials, nano-iron doped lignite (LGFe) and nano-iron doped activated carbon (ACFe) were synthesized. The sorption efficiency, for Cd removal, was investigated with kinetic and equilibrium studies performed in batch conditions. Experimental data, produced by sorption isotherm studies, were fitted to the Langmuir and the Freundlich equations in order to decide which model describes better the sorption process.

2. Experimental

2.1. Sorbent characterization

The lignite sample LG was obtained from Drama, northern Greece, from a lignite deposit that cannot be exploited for power generation. For comparison purposes the sorption capacity of an activated carbon (05105 Sigma Aldrich) sample (AC) was also studied.

The lignite sample was crushed ($\text{Ø} < 1\text{mm}$), dried at 45°C for 24h and subsequently pulverized to pass through the 0,250 mm sieve. The proximate and ultimate analysis were conducted according ASTM D 3173-87 and ASTM D 3176-89 standards respectively, and calorific value was measured using an automatic calorimeter (Leco, model A300). The specific surface area of the samples was determined with the Nova 2200 apparatus (QuantChrom) according the BET method. Mineralogical components were determined by X-ray diffraction (XRD) using a Siemens D500 XRD instrument. The data were obtained at 35 kV and 35 mA, with a graphite monochromator, using CuK α radiation. The qualitative evaluation of the data was done with the Software Diffrac Plus from SOCABIM. The quantitative analysis was carried out by the Rietveld Method [20]. Morphology, texture, and composition of the samples were studied by scanning electron microscopy (SEM - EDX,) (Jeol 5400) equipped with an energy dispersive X-ray analyzer (INCA energy 300). High vacuum evaporation (JEE-4X, Jeol) was applied to form a thin carbon film to make the surface of the specimens electrically conductive.

2.2. Synthesis of Nano-iron doped sorbents

In order to investigate the enhancement of the adsorption capacity of the lignite sample, two sorbents doped with Nano-scale zero valent iron, namely Nano-iron doped lignite (LGFe) and Nano-iron doped activated carbon (ACFe), were synthesized. Nano-scale zero valent iron (nZVI) was "loaded" onto AC and LG by iron reductive precipitation with sodium borohydride. The reducing agent was added dropwise to the iron containing solution (1.0MFeCl_3) under continuous stirring. A black, rapidly settling down precipitate, was immediately formed. After 30min of stirring, the iron-carbon

composites were separated by vacuum filtration, washed with acetone three times and dried at 60 °C. Both slurry and reducing solution were kept at 2-3 °C (for decreasing the dissolved O₂). All reagents used were of analytical degree. Iron concentration was determined in the remaining solution in order to estimate the iron precipitation yield of the procedure.

The specific surface area and morphology, texture, and composition of the iron doped samples were studied as described above for the lignite sample.

2.3. Sorption experiments

The sorption efficiency for Cd removal, of the studied sorbents, was investigated with kinetic and equilibrium studies performed in batch conditions. All experiments were carried out in duplicate, with spiked aqueous solutions as sorbate. The Cd containing solutions were prepared using analytical grade nitrate salt (Cd(NO₃)₂ · 4H₂O). To analyze the experimental equilibrium data the Langmuir and Freundlich models have been tested.

Initial pH and pH throughout the experiments were determined using a pH meter (model InolabLevel1, by WTW).

2.3.1. Kinetic experiments. Batch experiments were conducted, at room temperature, in 400 mL plastic beakers, under continuous stirring. In each case 1 g of air dried sorbent and 100 mL of metal solution were used. Kinetic experiments were carried out with solutions of initial concentration of 500 mg/L Cd. After different periods of contact time (0.25h, 0.50h, 0.75h, 1h, 2h, 5h, 12h, 36h) the aqueous phase was withdrawn and filtered to determine the residual metal concentration. Cd analysis in solutions that were produced after treatment of the lignite sample with deionized water showed that there was no leaching from the sorbents. The residual concentration of the elements in the aqueous phase was analyzed by Flame Atomic Absorption Spectroscopy. The spectrometer used was the “Analyst 100” model by Perkin Elmer.

Table 1. Proximate and ultimate analysis, calorific value and main mineralogical components of LG

Ash (%)	42.2
Vol. Mat. (%)	67.9
Fixed C (%)	32.1
C (%)	61.58
H (%)	5.35
O (%)	25.69
N (%)	2.25
S (%)	5.13
Cal. Value (MJ/kg)	23560
MINERALS %	
Kaolinite	24
Bassanite	10
Anhydrite	7
Quartz	16
Muscovite/Illite	33

2.3.2. Equilibrium experiments. Sorption isotherm studies were conducted by varying the initial concentration of the elements from 10 to 1000 mg/L (10, 50, 100, 300, 500, 700, and 1000mg/L). The sorption conditions were kept the same as in sorption kinetics and 12 h was chosen as contact time. This time was chosen because in previous kinetic experiments it was proved to be sufficient to reach equilibrium. The residual concentration of Cadmium in the aqueous phase was determined by Flame Atomic Absorption Spectroscopy.

3. Results and discussions

3.1. Sorbents characterization

Table 1 illustrates the results of proximate and ultimate analysis, as well as the measurement of calorific value, and the main mineralogical components for the lignite sample under investigation. The results of the specific surface area of the four sorbents are presented on Table 2 while their morphology, texture, and composition are illustrated in Figure 1.

Table 2. The specific surface area of the sorbents

Sample	Surface area (m ² /g)
LG	154
AC	927
LGFe	109
ACFe	154

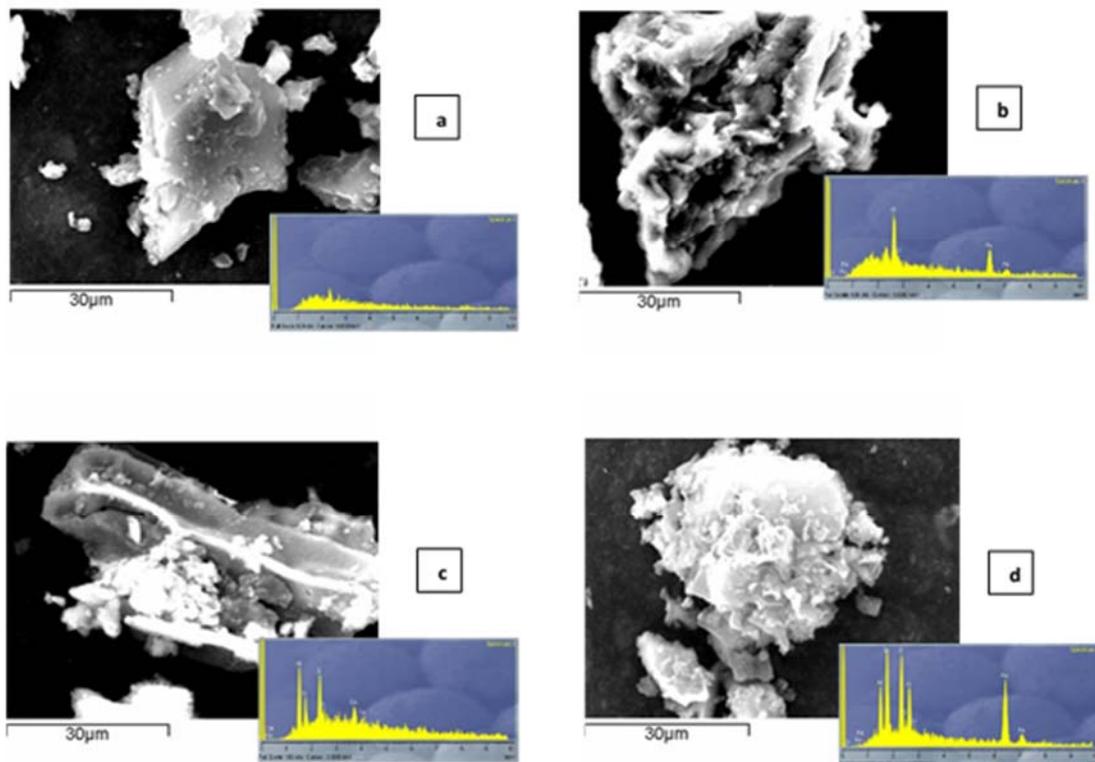


Figure 1. SEM secondary image of AC (a), ACFe (b), LG (c) and LGFe (d) with corresponding EDS spectrum

3.2 Sorption experiments

3.2.1. *Kinetic experiments.* The Cadmium removal, by the sorbents, as a function of contact time is presented in Figure 2. The kinetic experiments showed that sorption capacity (mg Cd/g sorbent) increased rapidly with increasing contact time, while the equilibrium was achieved within 12h for all the experiments.

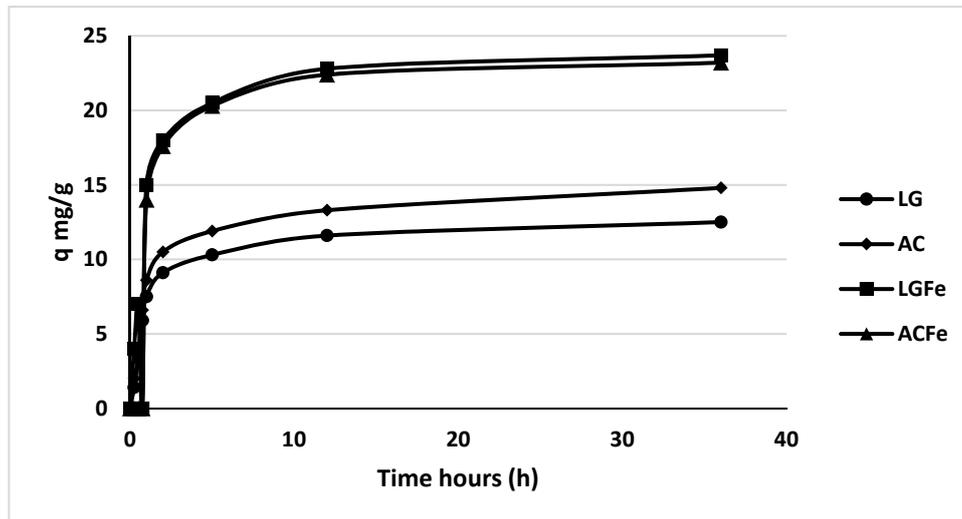


Figure 2. Sorption kinetics for the four sorbents. Experimental conditions: sorbent dosage 10g/L, pH 4.5, temperature 25°C, Cd initial concentration 500mg/L

3.2.2. *Equilibrium experiments.* The results of the equilibrium experiments are illustrated in Figure 3. The sorption isotherms may be considered of H or L type according to the classification of Giles et al., 1974 [24], indicating that the sorbents studied show high affinity for Cd. The amount of Cd, adsorbed on the sorbent samples increased with the increase of initial concentration up to 100 ppm. After this concentration no increment is observed, suggesting saturation for the active points on the lignite sample. When the initial concentration reaches 1000 ppm less than 50% of the metal added is adsorbed (Figure 4).

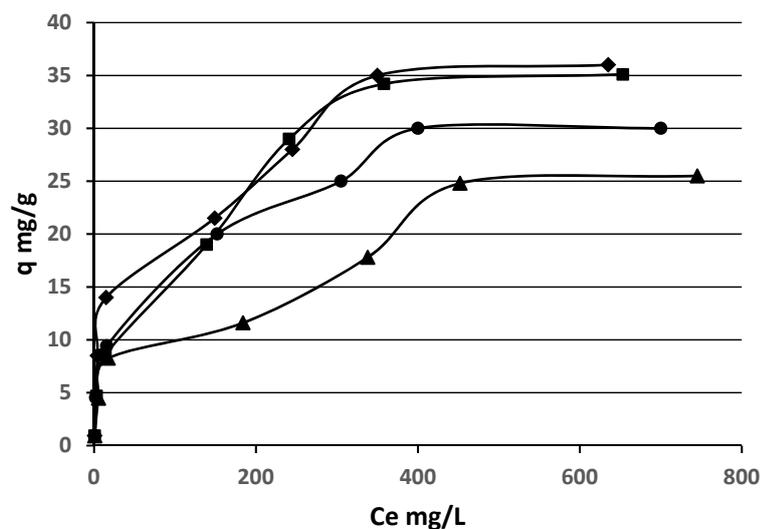


Figure 3. Sorption isotherms for the four sorbents. Experimental conditions: sorbent dosage 10g/L, pH 4.5, temperature 25°C, contact time 12h

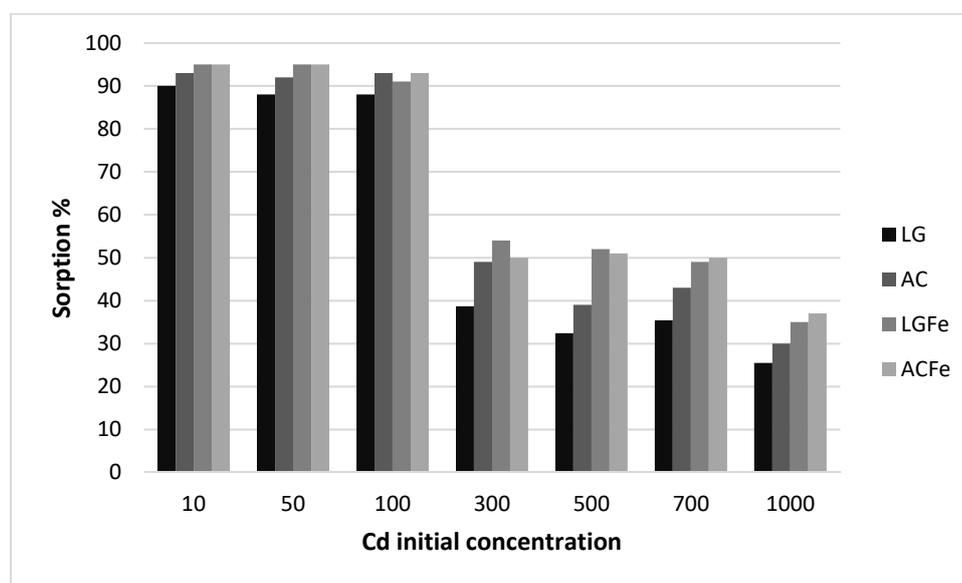


Figure 4. % sorption of Cd ions, on the sorbents for different initial metal concentration.

Experimental conditions: sorbent dosage 10g/L, pH 4.5, temperature 25oC, contact time 12h. To analyze the experimental equilibrium data and to obtain the maximum adsorption capacity of the lignite sample, the Langmuir [25] and Freundlich [26] models have been tested.

The equations used were:

- $q = q_{max}bCe/(1+bCe)$ (Langmuir),
- $q = KCe^{1/n}$ (Freundlich),

where q is the amount of metal ion adsorbed per unit mass of sorbent, C_e is the cation concentration at equilibrium, q_{max} is the maximum adsorption capacity; K is related to the adsorption capacity and b , n are constants related to adsorption intensity. For a nonlinear regression, MATLAB software was used. Experimental data of the present work were better fitted to the Freundlich equation than the Langmuir one, since the correlation coefficient (r^2) calculated for the Freundlich equation was higher than that for the Langmuir equation (Table 3). The maximum sorption capacities for the sorbents LG, AC, LGFe, and ACFe was 25.5 mg/g, 30 mg/g, 34.7mg/g, and 36.5mg/g, respectively. These sorption capacities for Cd, are equal or higher than those reported elsewhere [3, 6, 7, 9, 11, 27, 28].

Table 3. Langmuir and Freundlich constants 25°C, for the studied sorbents

	Langmuir			Freundlich		
	Q_{max} $mg\ g^{-1}$	b $L\ mg^{-1}$	r^2	K	n	r^2
LG	25.5	86.9	0.897	1.46	2.26	0.917
AC	30.0	74.3	0.927	1.56	2.12	0.939
LGFe	34.7	64.3	0.944	1.82	2.08	0.952
ACFe	36.5	84.3	0.901	1.59	1.98	0.956

4. Conclusions

With the proposed procedure nZVI was successfully “loaded” onto lignite and activated carbon. Cd removal from solutions reached 90%. The addition of iron nanoparticles in organic materials significantly increased adsorptive capacity, which was more drastic in the case of lignite. The experiments showed that sorption equilibrium was achieved within 12 h for all materials and that maximum adsorption capacity of LG, AC, LGFe, and ACFe was 25.5 mg/g, 30 mg/g, 34.7mg/g, and 36.5mg/g, respectively. The experimental data of the present work were better fitted to the Freundlich equation than the Langmuir one. The lignite sample studied is a raw material of low cost, plentiful in Greece, with high Cd uptake levels. This combination and the fact that no pH adjustment is required to improve its performance as sorbent, make it a promising material for metal contaminated wastewater treatment.

Additional work is required to identify the mechanism of the sorption process, to study the sorption of Cd in other forms, then nitrates, and to optimize the whole process. Desorption experiments should also be performed to check whether Cd can be easily desorbed in order to recycle the sorbent.

References

- [1] F. Gode, E. Pehlivan, “Adsorption of Cr(III) ions by Turkish brown coals”*Fuel Processing Technology* 86 pp 875-844 2005.
- [2] H.A. Qdais, H Moussa, “Removal of heavy metals from waste water by membrane processes: a comparative study”*Desalination* 164 (2) pp105-110 2004.
- [3] M. Jochova, M. Puncochar, J. Horacek, K. Stamberg, D. Vopalka, “Removal of heavy metals from water by lignite-based sorbents”*Fuel* 83 pp1197-12032004.
- [4] M. Dakiky, M. Khamis, A. Manassra, M. Mer’eb, “Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents”*Advances in Environmental Research* 6 pp 533-540 2002.
- [5] S. Lacour, J.C., Bollinger, B. Serpaud, P. Chantron, R. Arcos, “Removal of heavy metals in industrial wastewaters by ion-exchanger grafted textiles”*Analytica Chimica Acta* 428 pp121-132 2001
- [6] S. Karabulut, A. Karabakan, A. Denizli, Y. Yurum, “Batch removal of copper(II) and zink(II) from aqueous solutions with low rank Turkish coals”*Seperation and Purification Technology*. 18 pp 177-184 2000.
- [7] E. Pehlivan, G. Arslan, “Removal of metal ions using lignite in aqueous solution - Low cost biosorbents”*Fuel Processing Technology* 88 pp 99-106 2007.
- [8] P.A. Brown, S.A. Gill, S.J. Allen, “Metal removal from waste water using peat”*Water Research* 34 pp3907-3916 2000.
- [9] D.Pentari , V. Perdikatsis, D. Katsimicha, A. Kanaki “Sorption properties of low calorific value Greek lignites: Removal of lead, cadmium, zinc and copper ions from aqueous solutions”*Journal of Hazardous Materials* 2009.
- [10] Hardijeet K. Borai, Meera Joseph, Denis M. O’Caroll “Kinetics and Thermodynamics of Cadium ion removal by adsorption onto nano zerovalent iron particles”*Journal of Hazardous Materials* Vol.186 2011.
- [11] L.B Hoch, E.J Mack, B.W. Hydutsky, J.M Skluzacek, T.E Mallouk, “Carbothermal synthesis of carbon-supported nanoscale zero-valent iron particles for the remediation of hexavalent chromium”*Environmental Science and Technology*, Vol.42 2008.
- [12] Elliot D. and W.Zhang, “Field assessment of nanoparticles for groundwater treatment”*Enviromental Science and Technology*, Vol.35 2001.
- [13] C. Papanicolaou, T. Kotis, A. Foscolos, F. Goodarzi“Coals of Greece: a review of properties, uses and future perspectives”*International Journal of Coal Geology* 58 pp 147-169 2004.
- [14] G. Skodras, Th. Orfanoudaki, E. Kakaras, G. P. Sakellaropoulos “Production of special activated carbon from lignite for environmental purposes”*Fuel Processing Technology*pp77-

- 78 2002.
- [15] V. Kelesidis, C. Tsamantaki, A. Michalakis, G. Christidis, P. Makri, K. Papanikolaou, A. Foscolos, "Greek lignites as additives for the controlling filtration properties of water-bentonite suspensions at high temperatures" *Fuel* 86 pp1112-1121 2007.
- [16] V. Kelesidis, G. Christidis, P. Makri, V. Hadjistamou, C. Tsamantaki, A. Mihalakis, C. Papanikolaou, A. Foscolos, "Gelation of water-bentonite suspensions at high temperatures and rheological control with lignite addition" *Applied Clay Science* 36 pp 221-231 2007.
- [17] D. L Bish, S. A Howard, "Quantitative phase analysis using the Rietveld method" *Journal of Applied Crystallography* 21 pp 86-91 1988.
- [18] R. Pardo-Botello, C. Fernández-González, E. Pinilla-Gil, E. M. Cuerda-Correa, V. Gómez-Serrano, "Adsorption kinetics of zinc in multicomponent ionic systems" *Journal of Colloid and Interface Sciences* 227 pp292-298 2004.
- [19] G. Mckay, J. Porter, "Equilibrium Parameters for the Sorption of copper, cadmium and zinc ions onto peat" *Journal of Chemical Technology and Biotechnology* 69 309-320 20.
- [20] S. J. Allen, P. A. Brown, Isotherm analyses for single component and multi-component metal sorption onto lignite, *Journal of Chemical Technology and Biotechnology* 62 (1995) 17-24.
- [21] Y. S. Ho, G. Mackay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Research*. 34 (2000) 735-742.
- [22] C. Arpa, E. Basyilmaz, S. Bektas, O. Genc, Y. Yurum, Cation exchange properties of low-rank Turkish coals: removal of Hg, Cd and Pb from wastewater, *Fuel Processing Technology* 68 (2000) 111-120.
- [23] C. Lao, Z. Zeledon, X. Gamisans, M. Sole, Sorption of Cd(II) and Pb(II) from aqueous solutions by a low-rank coal (leonardite), *Separation and Purification. Technology* 45 pp 79-85 2005.
- [24] C. H. Giles, D. Smith, A. Huitson, "A general treatment and classification of the solute adsorption isotherm" *Journal of Colloid Interface Science* 47 pp755-766 1974.
- [25] I. Langmuir, "The adsorption of gases on plane surfaces of glass, mica and platinum", *Journal of American Chemical Society* 40 pp 1361-1403 1918.
- [26] H. Freundlich, *Colloid and Capillary Chemistry*, Methuen and Co. Ltd., London 1926.
- [27] T. K. Budinova, K. M. Gergova, N. V Petrov, V. N. Minkova, "Removal of metal ions from aqueous solution by activated carbons obtained from different raw materials", *Journal of Chemical Technology Biotechnology* 60 pp177-182 2004.
- [28] C. J. Lafferty, M. Hobday, "The use of low rank brown coal as an ion exchange material 1. Basic parameters and the ion exchange mechanism," *Fuel* 69 pp78-83 1990.