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The Using Natural Organic Matter for the Removal Heavy Metals from Contaminated Soil by Electro Kinetic Processes

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Abstract

This work presents the results of removal Pb, Cd, Cu, Zn from mixed soil with natural organic absorbent as gumat and cow manure by electrokinetic processes. By electrokinetic experiment it has been observed that the total contents of Pb, Cd, Cu, Zn in the experimental soils samples were increased depending on electrodes and organic matter mix. The molecular absorption spectrums of hydroxyl, carbonil, carboxyl and phenolic groups arising, shifting and disappear in contaminated soil, soil: gumat, soil: manure mixed samples by treated EK processes.

Keywords: organic matter in soil, soil electro kinetic remedation, heavy metals in soil, cow manure

1. Introduction

Soil is dynamic living system of mixture of minerals, organic matter, gases, liquids, and micro organisms. Soil contamination leads to changing the structure of these components, the interactions and dynamic patterns lost. As for lead, then half of the total amount of the toxicant transferred to the environment from the combustion of leaded petrol car in the city and a motorcycle on pasture field of livestock in rural areas. Heavy metals, into the soil or contained in it, exposed various transformations. The main processes in soil with heavy metals are sorption, migration, transformation, plant uptake, removal of ground water and inclusion in the biogeochemical cycles. Soils have a natural ability to translate part of the heavy metals in the slow-moving state is mainly due to the humus content. As a result of the accumulation intensity of humic substances zinc, copper, lead and cadmium in contaminated soil often exceeds their content background. According to the intensity of accumulation of heavy metals in humus are located in the following order of Cu > Cd > Pb = Co > Ni > Zn > Mn and macroelements (N, P, S, Mg, Fe, K) does not accumulate. Determined that effect of humic substances on the Cu, Pb, Cr (III) leads to the chelating and reduce the toxicity of these heavy metals. Humic substances are formed by the decomposition of plant and animal residues under the action of micro-organisms and abiotic environmental factors are macro-components of organic matter of soil and aquatic ecosystems, as well as solid fuels. Have determined by synchrotron X-Ray analytical techniques that lead a strong connection with a stable gumat and fulvic acid forms more than other heavy metals (*G. M. Varshal 1999*). Most of the literature indicates that with the increase in pH increases the bond strength of heavy metals with organic and mineral components of soil (*B. Gorbатов, 1983, B. Gorbатов, Zyrin NG, 1988, Obukhov, AI et al., 1990*). In particular, xenobiotic as mercury, cadmium, and lead are toxic when not connected to a structures of biomolecules. They are connected to a strong end of the biogroup protein. Humic acid and heavy metals in soil are formed in a stable polymer. Lead metals have slow oxidation and are created carbonate and clay minerals, Fe, Mn and Al oxide to join and connect organic matter. If lead concentration is high, it precipitated in forms of hydroxide, phosphate, carbonate. Soil organic matter has spectral peaks due to alkyl –CH₂ at 2930–2850 cm⁻¹, bands for protein amide OC-NH around 1680 and 1530 cm⁻¹, carboxylate anion –COO- at 1600 and 1400 cm⁻¹, and carboxylic acid COOH around 1720 cm⁻¹ (*Janik et al., 1998*). This makes it easier to formation a lead organic group in complex compounds (*Kabata-Pyendias, Pyendias, 1989, V. Chirita 1994*) and (*E. Chrenekova 1982*) have studied the connection of metals ions to gumus acids of carboxy (SOON), phenol (OH), alcohol (OH), ketones (C = O), amino group (-NH₂), and amido (= NH). At this time, various saturation organic mineral compounds are formed. Have studied the connection to acid and metal ions gumus, carboxy (SOON), phenol

(OH), alcohol (OH), ketones (C = O), amino group (-NH₂) and connect groups amido (= NH)(V.Chirita 1994, Ye.Chrenekova 1982).Organic material input could help to retain cationic nutrients and buffer pH value decline in soils(YuGe ZHANG et al.,2015).

Manure is a valuable material that can be used as a source of organic matter.The chemical characteristics of Mongolian livestock’s manure primarily depend upon the chemical composition of the pastureplants, water, air and climate condition. Manure is an excellent natural fertilizer containing nitrogen, phosphorus, potassium and other nutrients. It also adds organic matter to the soil which may improve soil structure, aeration, soil moisture-holding capacity, and water infiltration.The use of manure helps to maintain the organic matter content of the soil which can improve soil structure and water infiltration. However, manure is quickly decomposed under warm, moist soil conditions. With the manure rates used for most crops, organic matter content in soil is only temporarily increased.

In recent years, there has been increasing interest in finding innovative solutions for the efficient removal of contaminants from soils pollution. The **electrokinetic method** used for remediation of soil contaminated with heavy metals is a new developing technique for cleaning soil from heavy metals (N.Utchimuthuet.al., 2012, Zhongming Li et.al., 1996, Ts.Ochirkhuu 2015).

This work have studied a heavy metal detoxification in contaminated soil samples by using cow manure are common.Activated the processes foran interaction to organic matter(gumat, manure) and heavy metals in contaminated soil by electrokineticmethod in experimental condition and determined the total concentration of Pb, Cd, Cu, Zn near electrodes. And have observed that the differences of morphological structure of experimental soils treated by electrokinetic processes. The infra-red absorption spectrums of hydroxyl, carbonil, carboxyl and phenolic groups arising, shifting and disappear when organic matters interacting to heavy metals in contaminated soil by treating EK processes.

2. Materials and methods

2.1 SAMPLE PREPERATION

- Soil samples have been collected from the region UB city. The soil contaminated by TM.
- Have prepared the soil sample for XRF and FTIR analysis by instruction method.
- Sample preparation for SEM measurement:Sample were dried in vacuum desiccator for hour and coated with gold using sputtering technique

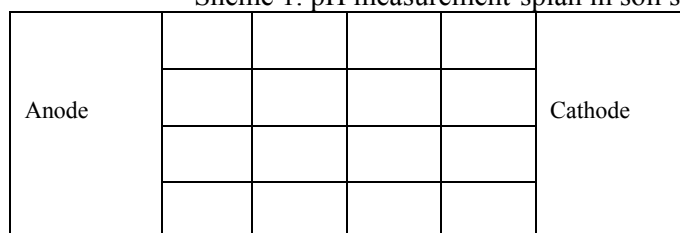
2.2 ELECTROKINETIC SET UP

Electrokinetic experiments were conducted in 50x50x20cm³organicglass box with 4 section.There are comtaminated soil: dist water, soil: gumat: distwater (3:1:3),soil: manure: distwater (3:1:3) samples. Each section has anode and cathode titanium electrode. On both sides of electrodes, each two titan plate electrodes (cm³) were used to apply the electro field. Were keeping the ratio of soil, organic matter and distilled water during the EK processes.

2.3 EXPERIMENTAL CONDITIONS

U,v	I, mA	J, mA/cm ²	T, min	S, cm ²
24-30	240	48	480	5

Scheme 1. pH measurement’splan in soil samples



Have measured the pH value of experimental soil samples at the nodal 9 points of a square (Scheme1).

Table 1. The average value of pH for soil samples during EK processes

Contaminated soil sample			Soil:gumat sample			Soil:manure sample		
Anode	center	cathode	Anode	center	cathode	Anode	center	cathode
5.0	5.2	6.0	4.5	4.8	6.5	5.0	5.1	4.0
5.2	5.5	6.5	5.0	4.5	6.0	5.0	5.1	4.3
5.3	5.5	6.0	5.0	4.4	6.0	5.0	5.1	4.0

Have observed that the soil: manure mixed sample has relatively low value of pH near the cathode. This effect supported a mobility of heavy metals.

2.4 Analytical procedure

o Removal efficiency of metal ions by electrokinetic is defined as following equation:

Removal efficiency (%) = $(C_i - C_f / C_i) * 100$ where, C_i is initial metals concentration (ppm) of soil and C_f is the final concentration of metals after electrokinetic treatment in soil.

o Soil pH tester HANNA The contents of heavy metals in these soils samples have been determined by the energy dispersive X-ray fluorescence spectrometer EDXRF-S2 Ranger.

o The soil samples were analyzed by FT-IR spectrometer (Shimadzu FT-IR IR-Prestige-21). The FT-IR spectra of the samples were recorded in the spectral region of 4000-400 cm^{-1} with 2 cm^{-1} resolution.

o Structural changing of soils samples have studied by TEM "SEMTRAC mini" (x500).

3. Results and discussion

3.1 The heavy metal contents for experimental soil samples and their content after EK processes

Table 1. Heavy metal contents for experimental samples

Element, ppm	Contaminated soil №1	Contaminated soil №2	Gumat	Manure
Pb	1537.7	234.0	24.3	50.5
Cr	231.5	65.0	38.0	12.9
Zn	335.3	71.0	40.5	34.2
Cu	205.9 26.0	227.8 37.0	15.8	27.0
Organic matter, %	4.9	4.3	15.7	8.6

Table 2. Heavy metal contents for soil samples after EK processes

Element, ppm	Total content, ppm						
	Contaminated soil samples №1 №2	Near anode	Near cathode	Soil: gumat /anode	Soil: gumat /cathode	Soil: manure /anode	Soil: manure /cathode
Pb	1537.7	1107.6	1255.7	2385.3	2453.4	2053.3	2195.7
	234.0	244.0	342.0	112.0	156.0	123.0	345.0
Cr	231.5	7960.7	315.0	6434.1	221.0	6341.3	70.2
	65.0	42.0	127.0	2319.0	54.0	316.0	56.0
Zn	335.3	166.2	281.8	285.7	453.8	284.4	400.3
	71.0	76.0	88.3	35.0	80.3	54.0	97.0
Cu	205.9	227.8	159.1	355.6	268.8	302.3	204.6
	26.0	37.0	15.0	48.5	23.5	22.8	20.4

According to the presented data in the tables 1 and 2 the Pb, Cr, Cu total contents in soil: gumat and soil:manure samples after EK are increasing more than in soil samples no mixed such the organic matters. And it is observed that the Pb, Cr, Zn total contents in soil: gumat and soil: manure samples after EK are increasing more than in soil samples no mixed such the organic matters. In general, addition of organic matter in soil samples have increased the removal of Pb, Cr, Zn, Cu differently.

3.2 Removal heavy metals from samples of contaminated soil by using natural organics and EK processes

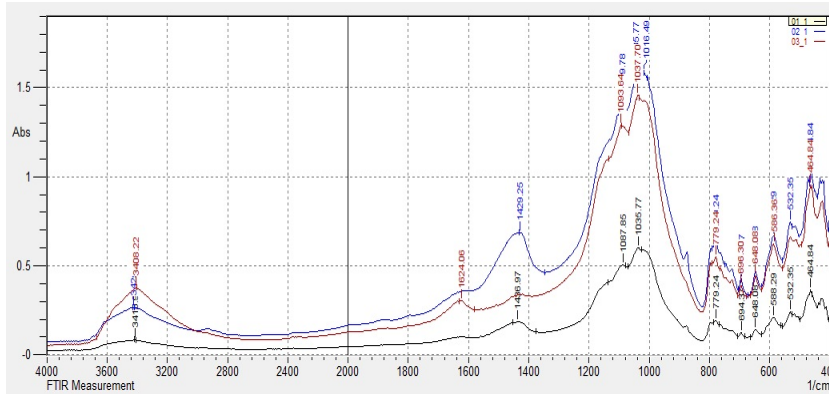
Table 3. Removal heavy metals from samples of contaminated soil by using natural organics and EK processes

Heavy metals	Removal heavy metals, %						
	Contaminated soil samples №1 №2	Near anode	Near cathode	Soil: gumat /anode	Soil: gumat /cathode	Soil: manure /anode	Soil: manure /cathode
Pb	1537.7	29	18	55.4	59.5	33.6	34.6
	234.0	4.2	46.1	52.1	33.3	47.4	47.7
Cr	231.5	3338	36	2679	4.5	2681	69.6
	65.0	35.3	95.3	3558	16.9	386	13.8

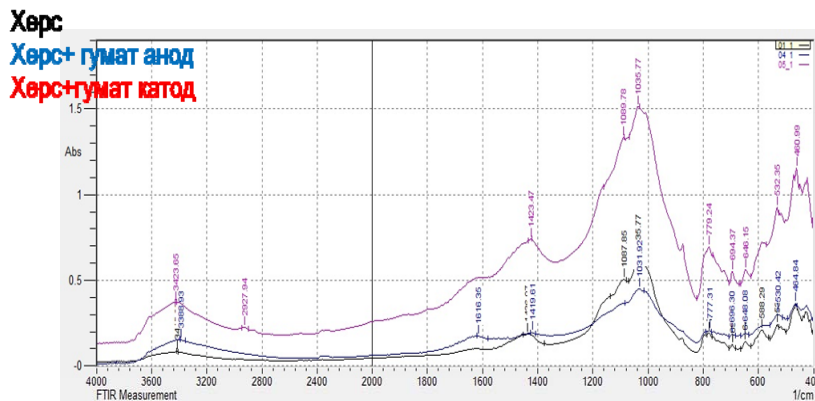
Zn	335.3	50.4	15.9	14.7	35.3	15.1	42.8
	71.0	7.0	24.6	50.7	13.0	23.9	36.6
Cu	1537.7	10.6	22.7	72.7	30.5	46.8	0.6
	26.0	42.3	42.3	86.5	9.6	12.3	21.5

According to the presented data in the table 3, the removal percent Pb, Cr is relatively high in the sample-near electrodes of soil: gumat and soil: manure treated by EK processes.

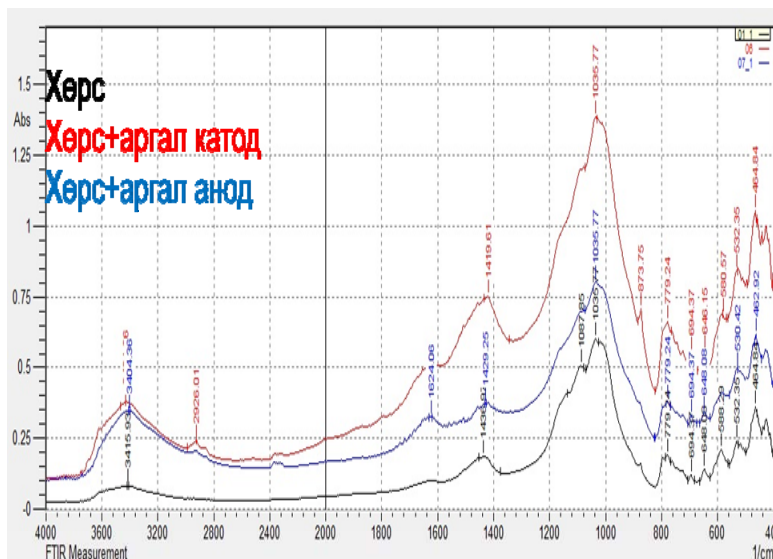
3.3 Complex formation of metal and organic matter in IR spectrum



Picture 1. IR absorption spectrum for contaminated soil by treated EK processes (most below spectrum corresponds to contaminated soil №1, middle spectrum-for soil samples near anode, upper spectrum-near cathode)



Picture 2. IR absorption spectrum for soil:gumat (1:2) samples by treated EK processes (most below spectrum corresponds to contaminated soil №1, middle spectrum-for soil:gumat samples near anode, upper spectrum-for soil:gumat samples near cathode)



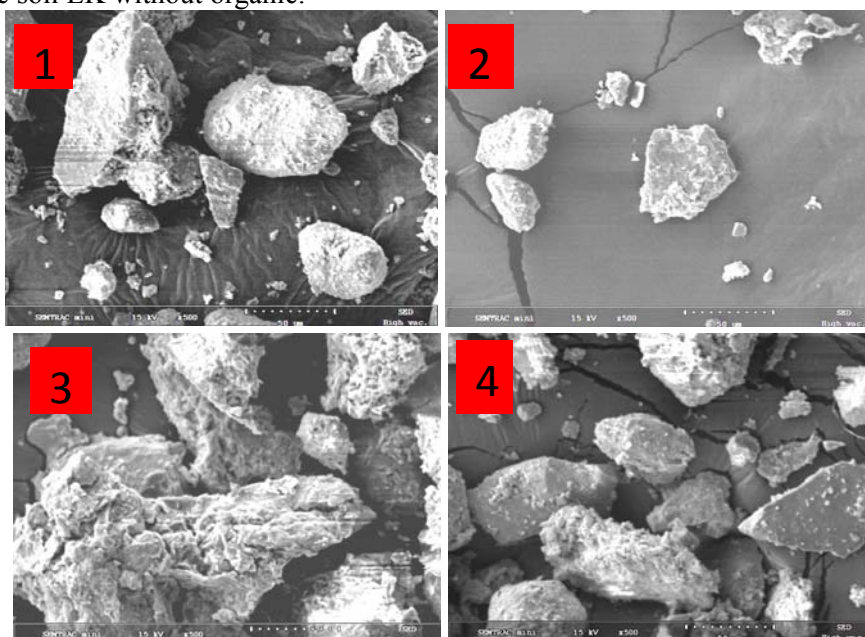
Picture 3. IR absorption spectrum for soil:manure (1:2) samples by treated EK processes (most below spectrum corresponds to contaminated soil №1, middle spectrum-for soil:manure samples near anode, upper spectrum-for soil:manure samples near cathode)

In the infra-red absorption spectrum show the contaminated soil sample (Pic.1), the soil:gumat sample (Pic.2), the soil:manure sample (Pic.3) by treated EK processes. There are an infra-red absorption spectrums of hydroxyl, carbonil, carboxyl and phenolic groups arising, shifting and disappear when organic matters

interacting to heavy metals in contaminated soil by treating EK processes. For example, the absorption spectrum 1624.06 cm^{-1} (C=C aromatic and carbonil) arised in the contaminated soil-near anode, in the soil:gumat sample-near anode, in the soil:manure sample-near anode by treated EK processes. It's connected to the cations of organic matters in the contaminated soil, in the soil:gumat, in the soil:manure samples. The spectrum not disappeared in the in the contaminated soil sample no treated EK. The intensity of this spectrum of all samples -near anode more than near cathode-in the comtaninated soil, soil:gumat, soil:manure. The spectrum 2927.94 cm^{-1} (-CH₃ and =CH₂), 1089.78 cm^{-1} (polysaccharide)- in the contaminated soil- near cathode; 1616.35 cm^{-1} in the soil:gumat sample-near anode, 2920 cm^{-1} -CH₂ - near cathode; 2926.01 cm^{-1} (CH₂, CH₃ shift), 1624.06 cm^{-1} -near cathode; 1420.92 cm^{-1} (-) - in the contaminated soil sample after treated EK shifted to 1429.26 cm^{-1} (-COO-) -near anode, 1419.61 cm^{-1} (-COO-)-near cathode, 1436.26 cm^{-1} -near anode in the soil:manure sample and 1420.92 cm^{-1} (-COO-) disappeared near anode-in the soil:gumat sample.

3.4 Morphological structures of soil and soil mixed with organic matters after EK processes.

Picture 4 shows that the morphological structures of contaminated soil and soil: gumat, soil: manure samples are differently. Particularly, structures of the soil EK treatment with organic matter are different from the soil EK without organic.



Picture 4. Soil samples: 1) before EK processes 2) after EK processes 3) soil:gumat mixed sample treated by EK 4) soil:manure mixed sample treated by EK (x500).

4. Conclusion

The pH values of experimental samples ranged from 4.0 to 6.5 during EK processes. There are molecular absorption spectrums of hydroxyl, carbonil, carboxyl and phenolic groups arising, shifting and disappear when organic matters interacting to heavy metals in contaminated soil by treating EK processes. Morphology structures for contaminated soil sample and soil: gumat, soil: manure mixture samples by treated electro kinetic processes of the experimental conditions are differently as show by photo TEM "SEMTRAC mini" (x500). The contaminated soil by heavy metals such as pollutant Pb, Cr, Zn, Cu is considered to be detox by electrokinetic processes and using the natural organic sorbent as gumat, cow manure. In a further study of the natural organic substances such as livestock's manure and it's complexation with heavy metals of interest in solving analytical and environmental problems.

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Study of Pani Nanofibers Supported Pt Catalysts for Fuel Cell

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Abstract In this study, the preparation and characterization of polyaniline nanofibers supported platinum (Pt) as novel cathode catalyst for Proton exchange membrane fuel cells (PEMFCs) are presented. This paper aims to study the production of polyaniline nanofibers (PANI-NFs) at different aniline/oxidant ratios via interfacial polymerization method. PANI-NFs supported Pt catalysts (Pt/PANI-NFs) were synthesized by an ethylene glycol reduction method. The synthesized PANI support material and Pt/PANI catalyst are analyzed using several methods on Scanning Electron Microscopy with LXRf system (SEM), X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR).

Keywords: Proton exchange membrane fuel cell; Alternative support material; Platinum; Polyaniline nanofiber; interfacial method

Исследование полианилиновых нано-волокон, поддерживающих платиновые катализаторы для топливных элементов

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Аннотация В этой работе рассмотрены вопросы изготовления и характеристики полианилиновых нано-волокон, поддерживаемых платиной (Pt), как новый вид катода катализатора для протон-обменных мембранных топливных элементов. Целью данной работы является изучение изготовления полианилиновых нано-волокон (ПАНИ-НВ) по методу межфазовой полимеризации при различных соотношениях анилина /окислителя.

ПАНИ-НВ поддерживающие платину (Pt) катализаторы (Pt/ПАНИ-НВ) синтезированы методом выделения этиленгликоля. Синтезированный ПАНИ- поддерживаемый материал и катализаторы Pt/ПАНИ изучены с помощью различных методов, таких как растровая электронная микроскопия, рентгеновская дифракция и инфракрасная спектроскопия с фурье преобразованием.

Ключевые слова: Протон-обменные мембранные топливные элементы; полианилиновые нано-волокна; межфазовый метод

I. Introduction

Proton exchange membrane fuel cells (PEMFCs) are highly attractive power sources for a variety of applications, due to their high energy efficiency and low emission. Despite these advantages, however, there are two problems with continued use of present low temperature fuel cell electrodes. The first problem is that mostly carbon supports used that suffer corrosion and the second problem is that high Pt loading needed due to low Pt utilization in the electrode. Therefore, a lot of research has been focused on new support materials that conductive polymers and oxides [1-3].

Conductive polymers have been investigated as carbon-substitute support materials for fuel cell catalysts, due to their high accessible surface area, low electrical resistance and good environmental stability. Within conductive polymers, PANI is one of the most studied materials because of its easy to synthesize in aqueous solutions, commercially available at low cost, and good redox properties and unique physico-chemical