

## MODIFIED RAW MATERIALS: SYNTHESIS, CHARACTERIZATION AND APPLICATION FOR Cd<sup>2+</sup> IONS REMOVAL

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**ABSTRACT.** The adsorption behavior of some lowcost adsorbents such as bentonite, meal thistle and carbonized walnut husk with respect to Cd<sup>2+</sup> ions in aqueous solutions has been studied. The several process parameters (contact time, initial metal concentration, sorption capacity, extraction degree, rate constants, sorption rates and sorption energy) were found. For the Cd<sup>2+</sup> ions adsorption the equilibrium time onto bentonite, meal thistle and carbonized walnut husk were found to be 2 h, 25 and 10 min, respectively. Adsorption parameters were determined using both Langmuir and Freundlich isotherms. Sorption isotherms of cadmium ions onto MBT (modified bentonite) and MTM (modified thistle meal) were the best of all described by the equation of Freundlich sorption (correlation coefficients are closest to unit). In contrast the sorption of Cd<sup>2+</sup> ions onto MCWH (modified carbonized walnut husk) was described by the Langmuir isothermic model where the adsorption occurs on homogeneous surface by monolayer sorption without interaction between sorbed ions. The obtained results demonstrate that bentonite, meal thistle and carbonized walnut husk can remove Cd<sup>2+</sup> ions from aqueous solutions. It means that cheap and available raw materials can be efficient adsorbents and capable to remove cationic heavy metal species from waste water. The ion-exchange mechanism of adsorption of cadmium ions by the MBT, MTM, MCWH was proposed.

**Keywords:** sorption, Cd, bentonite, meal thistle, carbonized walnut husk, kinetics.

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## INTRODUCTION

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless products. The presence of heavy metal ions is of major concern due to their toxicity to many life forms. Cadmium also exposes human health to severe risks, as it can provoke cancer, kidney damage, mucous membrane destruction, vomiting, bone damage as well as affect the production of progesterone and testosterone [1, 2]. That is why one of modern priority tasks in the field of environment protection is search of effective and environmental friendly technologies of sewage treatment.

Nowadays for removing of dissolved heavy metals the numerous processes, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis and electrodialysis exist [3]. Among them, ion exchange techniques using solid adsorbents is a promising method for treating wastewater, owing to its advantages such as operational simplicity, low cost, availability in large amount and ability to treat pollutants in a sufficiently large scale operation [3, 4]. The use of sorbents based on natural, synthetic and modified aluminosilicates can serve as a base for new technology development of heavy metal adsorption. The aluminosilicates of two-dimensional structure clay minerals (montmorillonite, vermiculite, bentonite) and three-dimensional structure of natural and synthetic zeolites as sorbents are already widely used [5, 6].

East Kazakhstan has rich deposits of bentonite clays which are suitable for sorption of heavy metal ions. Because of their availability and rather low cost the production of sorbents is economically profitable [7]. It was shown [8, 9] that the sorption processes performed by montmorillonite occurs according to the following three mechanisms:

a) substitution by cations of the exchange cationic complex locating as an between the elementary layers, and on the basal surface of mineral particles;

b) usage of hydrogen bonds of the external hydroxyl groups;

c) usage of valence "disrupted" bonds at the edges and corners, on the shifted stages of montmorillonite crystal growth.

Vegetable materials accumulating in significant quantities as various waste products in pulp and paper industry, agriculture, confectionery have of practical interest as a raw material for sorbents preparation. They can be used for solving some environmental problems such as purification of waste water, gas emissions and soil [10].

Sorbents on the basis of waste from vegetable raw materials can become even more available and cheap alternative. For the elimination of heavy metals from waste water the low cost agricultural rest by-products such as rice husk [11], nutshell [12], coconut husk [13] have been investigated by various research groups. To increase the adsorptive capacity of sorbents during processing raw plant material the various methods such as mechanical, physical, chemical methods, including thermal treatment of raw materials are used [14-18]. The effect of heat treatment of the rice husk on the adsorbent capacity of sorbents towards to Fe(III), Cu(II), Cd(II), Pb(II) ions in solution have been studied [19]. Cost is an important parameter for comparing the sorbent materials [20]. Improved sorption capacity may compensate the cost of additional processing. There is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored. Their feasibility for the removal of heavy metals should be studied in detail.

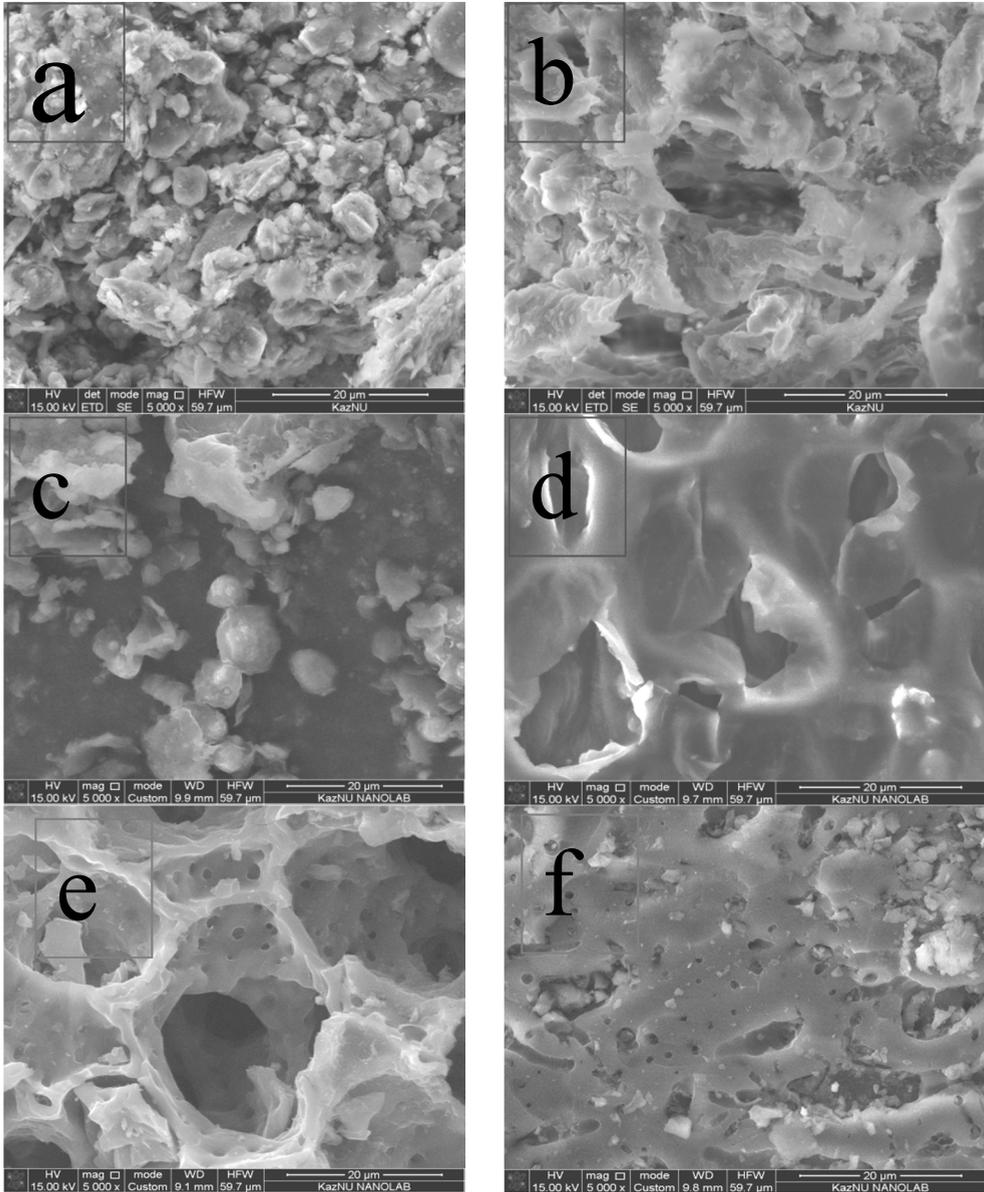
In this paper, a novel non-modified (bentonite (BT), thistle meal (TM), carbonized walnut husk (CWH)) and modified (MBT, MTM and MCWH) sorbents were developed and used to remove Cd(II) from aqueous solution. The choice of metal ion is explained that Cd(II) ions are the most widespread and dangerous on toxicity degree as pollutant. Also, the possibility of usage of low-cost adsorbents for removal of heavy metals from aqueous solution was found. The chemical composition of TM and CWH was determined using the X-ray phase analysis. The morphology of BT, MBT, TM, MTM and MCWH was characterized by scanning electron microscopy (SEM). The adsorption performance of Cd(II) onto MBT, MTM and MCWH was investigated. The adsorption conditions pH value, adsorption time and initial concentration were investigated in detail. The adsorption isotherms and adsorption kinetics were discussed.

## RESULTS AND DISCUSSION

### Characterization of sorbents

Figure 1 presents the typical SEM images of non-modified BT, TM, WHC and modified sorbents MBT, MTM and MCWH. Non-modified BT, TM, (Fig. 1 a, c, e) had a substantially uniform texture provided predominantly by micropores with diameter in the range of 1-4  $\mu\text{m}$ . From the SEM images, the modified sorbent has a developed microporous structure, an increase of pores size in comparison with the non-modified sorbents. As a result of acid-base modification, the surface structure of TM is changed, possibly due to the formation of Na-O groups. The surface morphology indicates that the BT and TM are easily modified after the acid-base treatment, washing and drying

procedures. The surface of MCHW particles underwent to profound changes (Fig. 1 e, f) after carbonization and mechanical activation to comparison with CHW, which had the ordered macroporous structure.

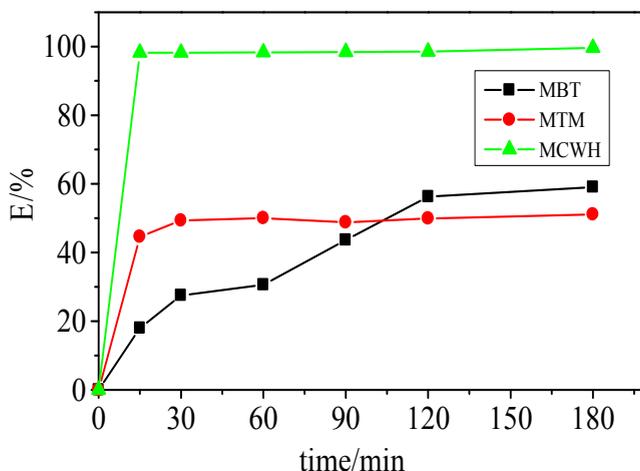


**Figure 1.** SEM images of non-modified and modified sorbents: (a) BT, (b) MBT, (c) TM, (d) MTM (e) CWH and (f) MCWH.

## Adsorption of Cd ions by modified sorbents

### *Effect of total contact time*

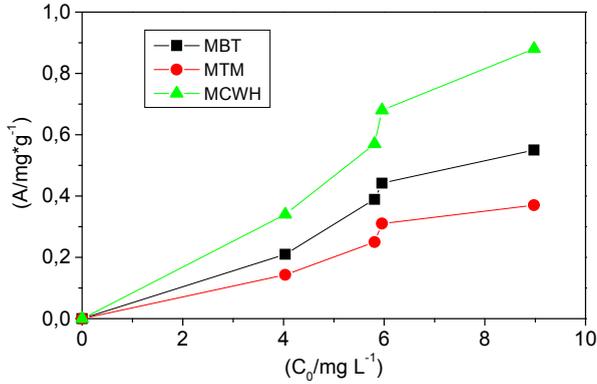
The effect of total contact time on the adsorption of Cd(II) ions by MB, MTM, MCWH was investigated at 25°C in the time range 15-180 min and the results were presented in Fig. 2. It can be seen that the capacity of MB, MTM and MCWH for Cd<sup>2+</sup> ions was depended from contact time. The adsorption of MB, MTM, MCWH for Cd(II) ions increased sharply during the first 15 min and then tended to be equilibrium. It can be seen from Fig. 2, that the values of adsorption capacity of Cd(II) were 61, 50, 95%, respectively. So, the sorption equilibrium of MB, MTM, MCWH was set at 120, 25 and 10 min, respectively.



**Figure 2.** Effect of total contact time on the adsorption of Cd(II) by MBT, MTM, MCWH at 25°C.

### *Effect of initial concentration of Cd(II) ions*

The effect of the initial concentration of Cd(II) ions on the adsorption can be established on the basis of the sorption isotherms. The adsorption of Cd(II) by MB, MTM, MCWH was studied at 25°C in the concentration range 4-9 mg/L while keeping all other parameters constant. The results were presented in Figure 3. The adsorption of MB, MTM, MCWH for Cd(II) ions increased sharply and then gradually tended to be equilibrium. This is in accordance with the observations reported for natural adsorbents, that the adsorption increases with rising initial concentration of heavy metal ions [21, 22].



**Figure 3.** Effect of initial concentration of Cd(II) on the adsorption by MBT, MTM, MCWH at 25°C.

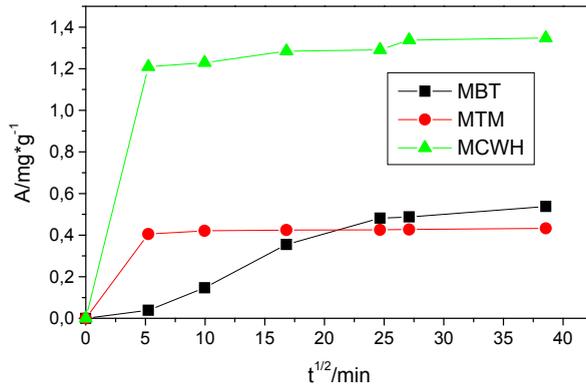
In the case of microporous sorbents, the sorption of metal ions consists of the following stages:

1. Rapid transportation of Cd(II) ions onto the surface of MB, MTM, MCWH;
2. Intraparticle diffusion as the rate-limiting step;
3. Final equilibrium step due to the lower concentration of metal ions in aqueous solution [23].

One of these stages is a limiting factor. To obtain of the rate determining step applies the equation proposed by Weber and Morris [24], which is follows:

$$A = K_p * t^{1/2} \quad (1)$$

where, A is the amount of the metal absorbed (mg/g) at time t and  $K_p$  is the interparticle diffusion rate constant.



**Figure 4.** Plots for intra particle diffusion for Cd (II) adsorption by MBT, MTM, MCWH at 25°C.

The plots of A versus  $t^{1/2}$  (Fig.4) are not linear over the entire time range, indicating that more than one process is affecting the adsorption. This type of non-linearity has been reported previously by various authors [25, 26] and has been interpreted as showing that both boundary layer diffusion (the initial curved portion) and intra-particle diffusion (the final linear portion) are occurring.

### Adsorption kinetics

The kinetics of metal ions sorption by modified sorbents MBT, MTM, MCWH was studied for its possible importance in treatment of metal-bearing industrial effluents. In the present study, pseudo-first-order and pseudo-second-order kinetic models were employed to test the experimental data [27, 28]. The pseudo-first-order and pseudo-second-order models are respectively described by the following equations:

$$\ln(C_0 - C_x) = \ln C_0 - k_1 t \quad (2)$$

$$\ln \frac{C_x^a}{C_x^b} = -\ln \frac{C_0^b}{C_0^a} + k_2 (C_0^a - C_0^b) t \quad (3)$$

where  $C_0$  and  $C_x$  are the quantities of adsorbate adsorbed on the adsorbents at the beginning and time  $t$  (mg/g), respectively;  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{L mg}^{-1} \text{min}^{-1}$ ) are the rate constants of pseudo-first-order and pseudo-second-order models, respectively.

The kinetic data were linearized using the pseudo-first-order and pseudo-second-order models, and plotted between  $\ln(C_0 - C_x)$  versus  $t$  and  $\ln \frac{C_x^a}{C_x^b}$  versus  $t$ , respectively.

For definition of kinetic characteristics, such as energy of activation and rate constant, the sorption was carried out at 25 and 35°C for definition of temperature influence. The obtained results are presented in Table 1. As the sorption is exothermic process, the increase in temperature leads to shifting of equilibrium towards the desorption. Data in Table 1 shows that rise of temperature has negative impact on the sorption of Cd(II) ions.

As the adsorption process is exothermic [29], so that with increasing temperature the equilibrium shifts towards reagents, i.e. amplifies desorption process, which is likely to lead a reduction the rate of the direct reaction - sorption of metal ions.

The results given in Table 1 show that, for all sorbents the correlation coefficients values for pseudo-second-order model were much lower than those obtained using the pseudo-first-order model. Thus, it means that the pseudo-first-order model explains the kinetic process better. As seen from the Table 1, the highest rate of sorption is inherent to MTM.

**Table 1.** Kinetic parameters for the adsorption of Cd(II).

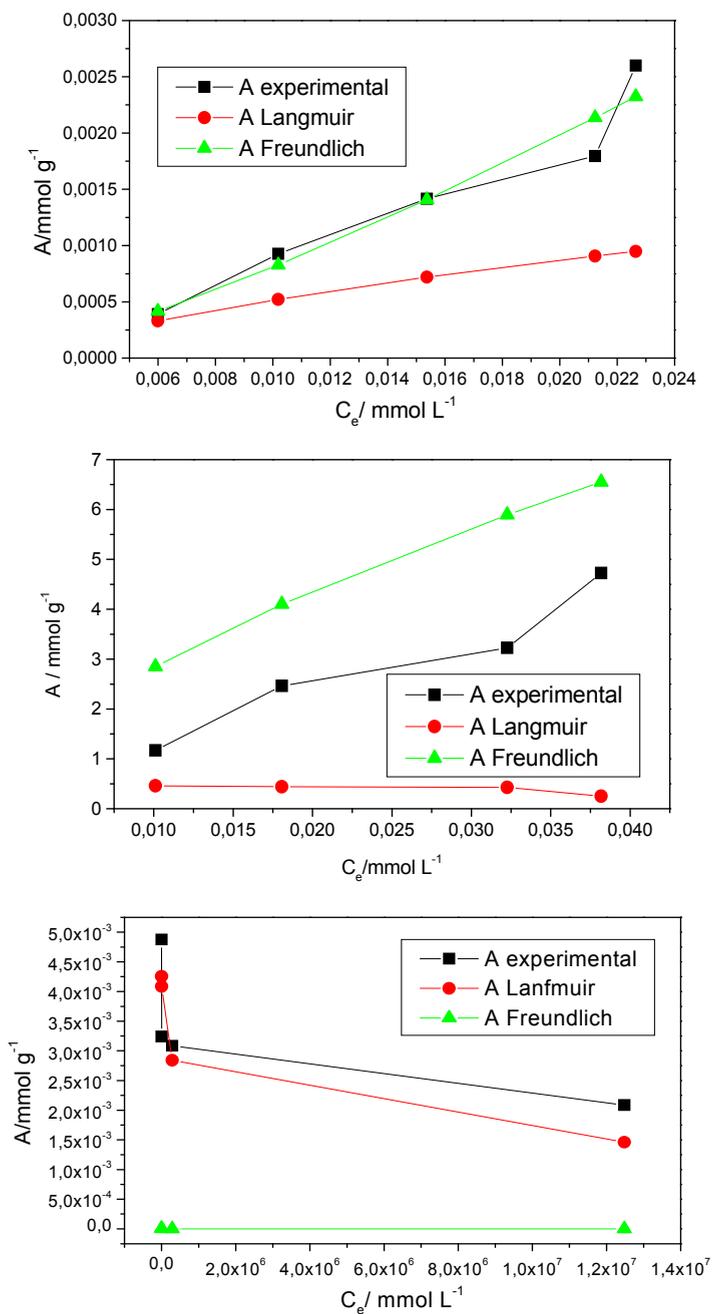
Sorbent	t (°C)	c <sub>0</sub> (mg L <sup>-1</sup> )	Pseudo-first order model		Pseudo-second order model		E <sub>a</sub> (kJ mol <sup>-1</sup> )
			k <sub>1</sub> (min <sup>-1</sup> )	R <sup>2</sup>	k <sub>2</sub> (L mg <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>	
MBT	25	10	0.004	0.913	5.35735·10 <sup>-7</sup>	0.847	-21.95
	35	10	0.003	0.987	2.42080·10 <sup>-7</sup>	0.545	
MTM	25	10	0.013	0.963	1.26761·10 <sup>-6</sup>	0.708	-28.06
	35	10	0.009	0.953	1.27255·10 <sup>-6</sup>	0.895	
MCWH	25	14	0.004	0.998	5.54012·10 <sup>-6</sup>	0.931	-52.89
	35	14	0.002	0.915	6.05081·10 <sup>-6</sup>	0.767	

From Table 1, all the values of E<sub>a</sub> were between -21.95 and -52.89 KJ mol<sup>-1</sup> for the Cd(II) ions adsorption of MBT, MTM, MCWH, which revealed that both chemisorption and physisorption coexisted during the adsorption processes. The negative sorption energy indicates on decreasing of process rate with temperature increase. This is probably due to the shift of the chemical equilibrium towards the initial components. Consequently, the desorption process is dominated by the metal ions with the surface of the sorbents.

### Adsorption isotherms

Adsorption isotherm has a great importance at the description of sorption process. It demonstrates the adsorption as a function of the equilibrium concentration of the adsorbates in solution. Figure 5 shows the adsorption isotherms of Cd(II) onto MBT (a), MTM (b) and MCWH (c) at adsorbent dose 1.0g/100 ml, contact time 180 min, pH 6 and at 25°C. As seen from Fig. 5, the isotherm results indicated a good adsorption capacity of MBT, MTM and MCWH for Cd(II) ions. In additional, the capacity of MBT, MTM and MCWH for Cd(II) ions followed the sequence of MCWH > MBT > MTM. The Langmuir and Freundlich isotherms were used to normalize the adsorption.

The parameters of the Langmuir and Freundlich isotherms were shown in Table 2. The correlation coefficients values (R<sup>2</sup>) indicated that the adsorption of Cd(II) ions onto MBT and MTM was fitted better by the Freundlich isotherm equation (R<sup>2</sup> = 0.964–0.974) than the Langmuir isotherm equation (R<sup>2</sup> = 0.901). Therefore, the adsorption of MBT and MTM of Cd(II) ions can be mainly considered as monolayer adsorption. But the adsorption of Cd(II) ions onto MCWH was fitted better by the Langmuir isotherm equation (R<sup>2</sup> = 0.964–0.974) than the Freundlich isotherm equation (R<sup>2</sup> = 0.823).



**Figure 5.** Adsorption isotherms of Cd(II) onto MBT (a), MTM (b) and MCWH (c) at adsorbent dose 1.0g/100 ml, contact time 180 min, pH 6 and at 25°C.

The low correlation coefficients values ( $R^2$ ) indicate that the surface of adsorbent is non-uniform, between the adsorbed particles interaction takes place, and the active centers are not completely independent from each other.

**Table 2.** Parameters of adsorption isotherms of  $\text{Cd}^{2+}$  ions.

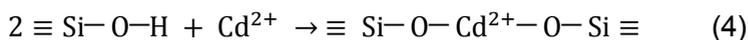
Sorbent	Langmuir isotherm			Freundlich isotherm		
	$K \times 10^3$ (L mmol <sup>-1</sup> )	$A_{\infty} \times 10^3$ (mmol g <sup>-1</sup> )	$R^2$	$K \times 10^{-3}$ (L mmol <sup>-1</sup> )	1/n	$R^2$
MBT	0.001	142850.00	0.651	0.196	1.037	0.974
MTM	0.026	5.35	0.822	0.051	0.626	0.964
MCWH	8.170	4.71	0.901	407.380	3.649	0.823

## Adsorption mechanism

### *Sorption by the MBT*

It is known that the bentonite clays (BC) are the cheap sorbents for extraction of heavy metals ions [30] and the main mineral, being their part is montmorillonite. The structure of montmorillonite represents layers of silicon-oxygen tetrahedrons between which the aluminium-oxygen octahedrons are concluded. Replacement of  $\text{Al}^{3+}$  ions by  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions leads to emergence of a structural negative charge which is compensated by interlayered (exchange) cations ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ). Montmorillonite has a 2:1 alumino silicate semi-basic unit layer, where 2:1, ratio refers to two tetrahedral sheets sandwiching an octahedral sheet in between. The composition of montmorillonite is presented by the following formula:  $(\text{OH})_4\text{Si}_8(\text{Al}_{3.34}\text{Mg}_{0.66})\text{O}_{20}$  [31].

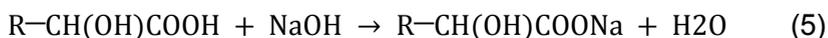
Acid activation of layered silicates is a widespread way of modifying which is necessary for increasing of material porosity [32]. The mechanism of acid processing is reduced to dissolution and washing away of alkaline and the alkaline-earth metals cations ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ) from a mineral framework. Adsorption of cadmium ions the modified bentonite clay of the Dinovavrovoe field (East Kazakhstan) is caused by interaction the silanolic groups with metal ions. Adsorption proceeds on the ion-exchange mechanism which is presented as follows:



### ***Sorption by the MTM***

It is known that a component of a thistle meal is cellulose. Cellulose – polysaccharide which molecules are presented in the form of long chains with spatially correct structure, consisting of β-D-glucose (β-D-glucopirane) links connected by glucosidic bonds [33].

Extreme adsorptive capacity of adsorbent is characterized by concentration of carboxyl groups. Carboxyl groups can be present at cellulose, generally because of oxidation of alcohols and carbonyl groups in positions 1,2,3 and 6 of a polysaccharidic chain as a result of isolation and purification of cellulose. The cellulose modified by alkali is characterized by higher reactionary ability in comparison with initial object:



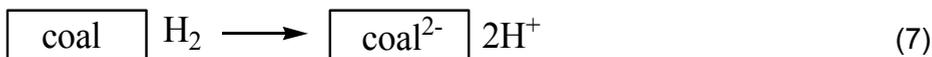
It is agreed with literature data for the cellulose-containing polymeric materials [34]. The obtained sorbent can be classified as cation exchanger. The sorption mechanism of cadmium ions by the modified thistle meal also is ion-exchange with formation of the chelate complexes:



### ***Sorption by the MCWH***

Among of the porous carbon materials one of perspective sorbents is the walnut shell. This type of vegetable cellulose is characterized by the high content of carbon, existence by primary transport porous structure and the low maintenance of mineral part. The commercial analogs obtained on the basis of a walnut shell are valuable active coals let out industrially. The most important purpose of application of carbonization process is increase of carbon specific content, removal of easily volatile compounds from composition of initial vegetable cellulose, creation of porous material with the big porosity which is evenly distributed on all material volume. Heat treatment of a walnut shell is resulted by increase available and formation of new pores, merge of two or several pores in one, increase in a surface and volume of pores due to burning out of carbon part.

The chemical nature of a coal surface in many respects defines the extraction extent of heavy metals ions from solutions. Experience shows that coal not only is capable to selective adsorption of metals ions, but also the phenomena of exchange adsorption can proceed on it. It is explained by the electrochemical theory [35]. The surface of coal can absorb hydrogen which is formed during coal production and its activation. At the same time coal behaves as acid adsorbent:



## CONCLUSIONS

In summary, MBT, MTM, MCWH were prepared successfully from bentonite of the Dinovavrovoe field, thistle meal and carbonized walnut husk and used as adsorbents for removing Cd(II) from aqueous solutions. Adsorption kinetic and isotherm processes for adsorption of Cd(II) ions onto MBT and MTM were found to correlate with pseudo-first-order model and Freundlich isotherm equation, respectively. Comparison of the regression coefficients  $R^2$  shows that the Freundlich model better describes the experimental data of the adsorption on MBT and MTM. This indicates that the adsorption of Cd(II) occurs on a heterogeneous surface and that the majority of active sites have different quantities of energy. But the adsorption of Cd(II) ions onto MCWH was fitted better by the Langmuir isotherm equation than the Freundlich isotherm equation. This can indicate the applicability of monolayer coverage of Cd ions on the surface of adsorbent. In addition, the capacity of MBT, MTM and MCWH for Cd(II) ions followed the sequence of MCWH > MBT > MTM. Furthermore, energy changes were  $-21.95$ ,  $-28.06$  and  $-52.89$  kJ/mol for the Cd(II) ions adsorption of MBT, MTM, MCWH at  $25^\circ\text{C}$ , which revealed that the adsorption processes including chemisorption and physisorption were complicated. Negative values of the activation energy are probably associated with the shift of the chemical equilibrium towards the initial components. Consequently, the desorption process is dominated by the metal ions with the surface of the sorbents. Adsorption of cadmium ions by the MBT, MTM, MCWH is characterized by the ion-exchange mechanism. In conclusion, these low cost natural adsorbents show efficiency and selectivity for the removal of Cd(II) ions from aqueous solutions.

## EXPERIMENTAL SECTION

### Materials and methods

All used chemicals and solvents were of analytical grade quality. Cadmium chloride, ( $\text{CdCl}_2 \cdot 6\text{H}_2\text{O}$ ) was used as source for Cd(II).

Concentration of cadmium ions before and after sorption was monitored by nuclear-absorbing spectrophotometer Shimadzu 6200. Definition of structure changes and morphology of particles surface of a natural sorbents after modification was carried out on a Quanta 200i 3D by the SEM (scanning electronic microscopy). The X-ray phase analysis was performed using computerized diffractometer DRON-2 with the modernized collimation on the filtered CuK $\alpha$ -radiation.

### Natural sorbents preparation

Natural sorbents preparation consists of mechanical cleaning of initial raw material and modification of the obtained product.

### Preparation of MBT

Bentonite from Dinozavrovoe field (East Kazakhstan) was used, the main characteristics of which are listed in Table 3. As seen from Table 3, BT practically represents monomineral raw material which contains 95% of montmorillonite.

**Table 3.** Characteristics of BT from Dinozavrovoe field

Physical characteristics	Fraction (mm)	Montmorillonite (%)	Moisture content (%)	Sand (%)	Swelling number (on 2 g)
Value	0,07	90-95	12	1-2	24

In a 500 mL beaker was added 40 g of crude wood sawdust and 200 mL of 4,5-5,5% phosphoric acid. The obtained mixture was kept for 23-25 h at ambient temperature and washed by distilled water until the pH was neutral. Then, the wood sawdust, BT and water were mixed in ratio 2:1:2 and then stirred until the uniform structure suspension was not formed. The final mixture was dried at 80-85°C for 3,5-4 h, then crushed to form a particles of 3-15 mm in size. Obtained MBT was dried in a oven at 90-95°C for 0,75-1 h.

### Preparation of MTM

The chemical composition of TM was determined using the X-ray phase analysis, which is listed in Table 4.

**Table 4.** The chemical composition of TM.

Content, %									
C	O	Mg	Al	Si	P	S	K	Ca	Fe
42,20	53,94	0,44	0,12	0,38	0,38	0,09	1,42	0,75	0,11

The obtained data indicate that TM contains organic substances 42.20% and oxygen 53.94%.

In a 1 L beaker was added 10 g of TM and 500 mL of sodium hydroxide water solution (1 g of NaOH was dissolved). The pH 8 was used. Then, the mixture was heated at 100°C for 30 min and cooled at ambient temperature. The desired pH 5 was adjusted by using aqueous solution of diluted HCl. The obtained product was filtered, washed by distilled water and dried.

### Preparation of MCWH

The chemical composition of CWH was determined using the X-ray phase analysis, which is listed in Table 5.

**Table 5.** Technical and elemental analysis of the CWH.

Technical analysis, %				Elemental analysis, %			
moisture	ash	volatile	C	H	S	N	O
7,2	0,3	76,1	56,4	6,5	0,2	0,3	36,6

As seen from the data listed in Table 5, CWH have a relatively high content of carbon. This indicates that CWH can be a promising porous carbon material as TM.

For preparation of MCWH a walnut husk was used, which is withdrawal of food confectionery production [10]. As the walnut husk had the big sizes therefore at the initial stage before treatment it was crushed. This procedure allows obtain sorbent with high sorption ability and increase its specific surface. In a 200 mL beaker was added 20 g of walnut husk and 100 ml of 10% sulfuric acid. The treatment by sulfuric acid activates a surface and increases the size of a husk pores. The obtained walnut husk was washed by the distilled water. Then, the drying of walnut husk in a oven at 400±5°C for 30 min gives MCWH.

### Sorption experiment

For the adsorption kinetics study, 1 g of adsorbent was weighed into the flasks with 100 mL solution of metal ion at the concentrations of 2-14 mg L<sup>-1</sup>. The temperature was maintained at 25°C. The process was carried out statically without agitation. The equilibration was defined according to the curves of the adsorption capacity changes on the interaction time of the sorbent with a solution.

The equilibrium adsorption capacity  $A$  (mg g<sup>-1</sup>) was calculated using the following equation.

$$A = \frac{c_0 - c_e}{m} * V, \quad (9)$$

where  $c_0$  and  $c_e$  are the initial and equilibrium concentrations of metal ions in the liquid phase (mg L<sup>-1</sup>), respectively,  $A$  is the adsorption capacity of metal ions (mg/g),  $V$  is the volume of the solution (L), and  $m$  is the mass of the adsorbent used in adsorption experiments (g).

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