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Purification of Sewage from Cationic Dyes Modified by Bentonites

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Abstract:
In the present work the results of the research of natural bentonite which was modified with organo-amine of Dash-Salahly deposit of Azerbaijan were given. Its physical-chemical characteristics were presented. The increase of interplanar space which allows us to use it as a sorbent of some cationic dyes from sewage was established using X-ray structural and IR-spectroscopic analysis. Adsorption of cationic dyes – thionine, methylene violet, brilliant green on bentonite which was modified with organo amine is two times higher than on cation-substituted forms of bentonite. And it shows modified bentonite is more economical and useful for adsorption of cationic dyes.

Keywords: *cationicdyes, modified bentonite, adsorption, X-raydiagram, IR-spectra.*

1. Introduction

Many industries give rise to dye-bearing effluents in their production processes. Textile industries, particularly, are major consumers of water and release a fair amount of color in their effluents[i].With growth of industry, basically, chemical and light industry the amount of sewage which contains large amount of hazardous inorganic and organic compounds, rises and complete treatment of them is practically impossible. [ii]

Presence of heavy metals in human environment is of a major concern due to their tendency to accumulate in living organisms, and by that find their way into the human body causing various diseases and disorders [iii].

Natural reservoirs are contaminated more frequently with waste waters which contain ions of heavy metals like Cu^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, as well as organic pollution. The prominent cations and anions found on clay surface are Ca^{2+}, Mg^2+, $H^{+,}$ K^+, NH_4^+, Na^+, and SO_4^{2-}, Cl^-, PO_4^{3-}, NO_3^-.These ions can be exchanged with other ions relatively easily without affecting the clay mineral structure [iv].

Dyeing wastewaters is one of the most difficult industry wastewaters being treated.

Dyes are coloured compounds appropriate for colouring textiles, wool, leather, paper and fibres. Natural dyes for example, indigo have been being used for more than 5000 years. Today, there are more than 10,000 dyes with various chemical structures available. high solubility of dyes present in water causes wide dissemination into the environment, thus causing detrimental to crops, aquatic life and human health [v].

There are three methods for removing dyes: biological treatment, chemical and physical methods. Biological treatment is an economical method but is restricted cause of its technical constraints. This method requires a large land and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Chemical methods are so expensive and maybe make a secondary pollution in the water because of excessive chemical use. Different physical methods are also widely used, such as membrane-filtration processes (nanofiltration, reverse osmosis, electro dialysis, . . .) and adsorption techniques. In the first technique membranes have a limited lifetime and they maybe their life time before completing the process will be finished [vi].

Numerous studies have been devoted to dye adsorption kinetics, equilibrium modeling, and mechanisms as well as to the factors that affect adsorption. The examined adsorbents include activated carbon, mesoporous molecular sieves, some natural adsorbents (such as clays and clay minerals, cellulosic materials, chitin, and chitosan, certain waste materials, and some agricultural byproducts [vii].Adsorption is an alternative technology for metal separation from aqueous solutions. With the selection of a proper adsorbent, the adsorption process can be a promising technique for the removal of certain types of contaminants. Adsorption is used as a tertiary treatment process in a number of wastewater treatment plants to fulfill the requirements of effluent regulations.

This contamination is an integral part of an industrial production like metallurgical, mining, electron, textile and other industries. No matter how they are purified waste waters of these productions contain these contaminants. That's why adsorption method which is a method of advanced treatment is more expedient. Naturally, a need arises for searching an effective and cheap natural sorbent. Azerbaijan has a large supply of clayish minerals, for example, Dash-Salahly deposit of bentonite. We have conducted major works on using the properties of these minerals and by their further activation [viii].

Clay minerals, such as bentonite and zeolite, are some of the potential alternatives, as they have large specific surface areas with a net negative charge, which can be electrically compensated for by inorganic and organic cations from the environment. Their sorption capabilities come from their high surface areas and exchange capacities (Babel and Kurniawan, 2003). It is a highly effective natural clay mineral, especially in granular form, used for the purification of wastewater and sludge dewatering. A part from that, bentonite is a natural material that contains essential compounds such as aluminium, iron and clay materials which are useful for the treatment of wastewater. Moreover, bentonite is cheaper than chemicals and it fulfils the economic benefits of the operators as well as environmental concerns [ix,x].

We took clay samples from various areas of Dash-Salahly deposit, they were thoroughly washed off from coarse-grained inclusions and the most effective samples which contain up to 75-80% montmorillonite were detected using X-ray diagram.

The unique feature of montmorillonite is that water molecules and other polar molecules may penetrate between structural layers and cause lattice expansion towards axis of «C». Under normal conditions montmorillonite of Dash-Salahly deposit (DSM) contains ions of Na^+ and Ca^{2+} as exchange ions it has interplanar spacing which equals to ~12,5 Å, that allows including organic components into its structure[xi].

One of the most important colloidal and chemical characteristics of complex silicates is their cation-exchange ability. This property underlies chemical modification of a surface of sorbents by exchange reactions with organic and inorganic cations. Considering high hydrophilic ability of bentonite clay there was a need for preliminary processing of it with inorganic or organic salts which provides chemical, mactrostructural modification, i.e. its enrichment, as well as leads to the change of the sizes of interplanar spacing of a mineral which depends on the position of organic cations between silicate layers [xii,xiii].

1.1. Experimental Part

We studied pore-structure characteristics of the clay and sorbents which are given in the Table 1.

Octadecylamineacetate salt (ODA) was used as surfactants [xiv].

№	Sorbents	Am, mol/g	$S_{specific}$, cm^2/g	V_s, $cm^3/г$	$\tau_{effective}$, cm
1	DM	0,20	48,0	0,805	0,006
2	DM, modif.	0,37	89,12	0,0927	0,007
3	Al-form DM	0,31	64,20	0,087	0,0063
4	Fe-form DM	0,30	60,84	0,086	0,0065

Table 1: Pore-structure indicators of primary and modified forms of bentonite

where Am – monolayer capacity; $S_{specific.}$– specific surface value of adsorbent, V_s – total pore volume of adsorbent; $\tau_{eff.}$ – effective pore radius of adsorbent.

X-ray patterns and IR-spectra of natural bentonite and modified forms were taken.

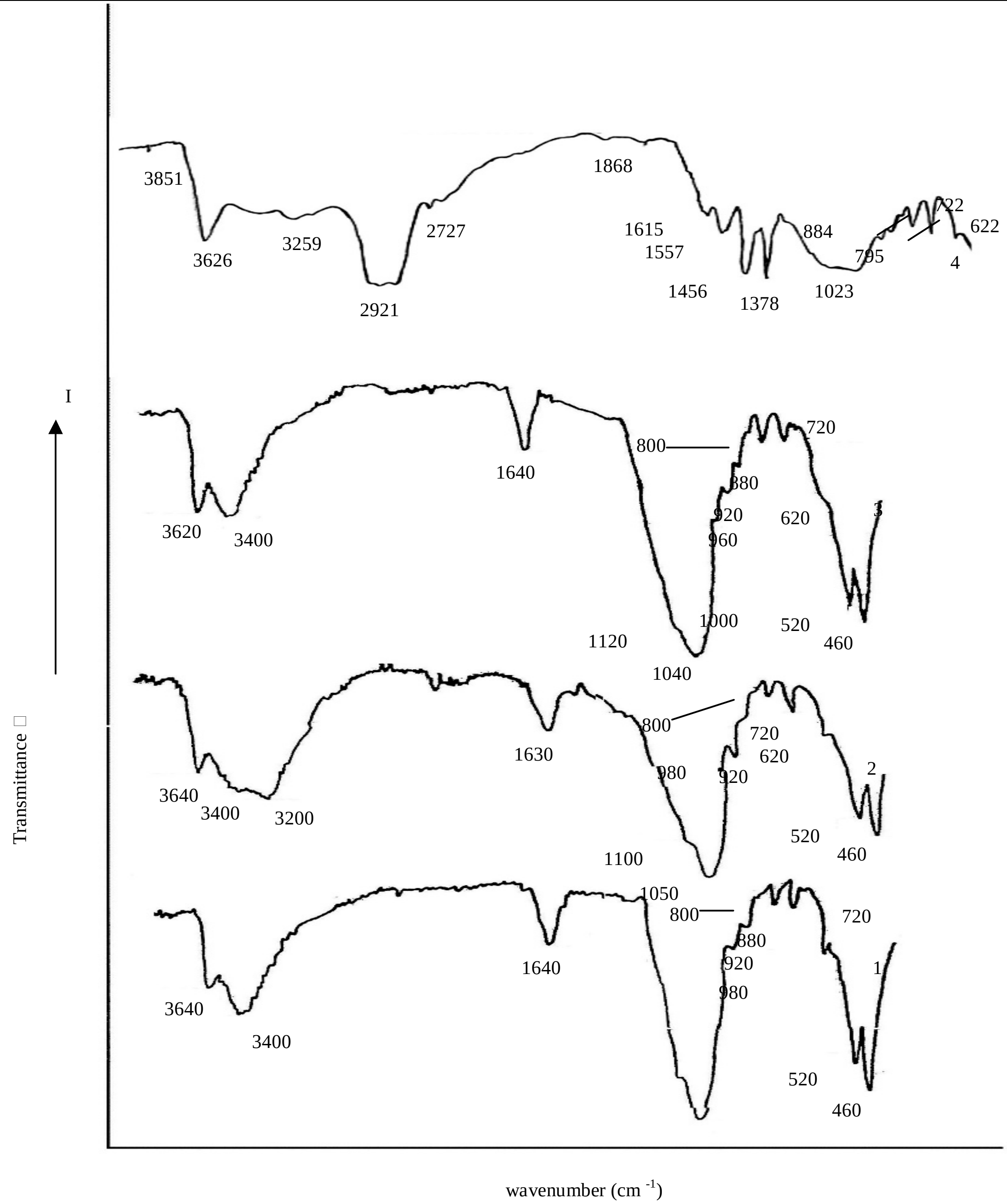

Figure 1: IR-spectra of natural bentonite (1), cation substituted Al^{3+}(2) and Fe^{3+}(3) and modified ODAA bentonite (4)

Fig. 1 shows IR-spectra of natural, cation substituted forms of bentonite (Al^{+3}- and Fe^{+3}- forms) and organobentonite (ODAB). New adsorption bands appear on modified forms of bentonite. In case of monocation forms adsorption bands are more intensive than in initial bentonite. In organobentonite adsorption bands appear in the range of 3200-3330 cm^{-1}, 2800-3000 cm^{-1}, 1400-1500 cm^{-1}. Adsorption bands in 3200-3300 cm^{-1} and 1540 cm^{-1} are related to antisymmetric valence and deformation vibrations of amine groups which form coordination bond with aprotonic centers of a surface of sorbents. Adsorption bands in the region of 2800-3000 cm^{-1} belong to antisymmetric and symmetric valence vibrations of CH_2-groups of adsorbed surfactants. Intensiveness of adsorption bands in 3420 cm^{-1}, which belong to natural montmorillonite increases due to overlapping of spectrum on it, which corresponds to NH_2 – amine group [xv] (Fig. 1).

On X-ray diagrams of modified bentonite we observed the increase of inter packet space up to 20 Å, which confirms penetration of hydrocarbon chain of amine in the structure of clay parallel to packet, overlap is observed even in over-equivalent sorption. On IR-spectra it was detected that new adsorption bonds which conform to hydrocarbon radical appear due to surfactants [xvi].

Sorption capacity of hydrophobizated ODA bentonite of octadecylaminebentonite (ODAB) is nearly two times higher than in Al- and Fe(II)-forms, that's why it was selected for further researches. Surfactants form organophilic layers between particles of montmorillonite, which reduce surface energy on phase boundary, increase the distance between layers of bentonite and simplify penetration of dye molecules into interplanar spacing of a clayish mineral.

Thus, hydrophobization of bentonite with organic substances puts obstacles for close approach of particles when it is dried and due to this number of contacts between separate particles of aggregates is reduced. In one word, for swelling and microporous disperse materials we should speak about and hydrophobic behavior of active centers of adsorption

Theanine (T), brilliant green (BG), methylene violet (MV) were used as organic compounds for adsorption.

Adsorption of dyes was conducted under static conditions from model solutions.

Interaction between molecules of cation dyes and clayish minerals is related to the type of specific molecular interactions between functional groups of adsorbents and bentonite. In this case all molecules of dyes adsorbed with bentonite are under strong interaction of electrostatic field of hydrated exchange cations of bentonite.

In view of this we selected ODAB as the most effective sorbent and further researches were conducted by using it.

Obtained sorbents were studied as sorbents of organic substances of abovementioned dyes. Fig. 2 shows diffraction patterns of initial sorbents and after adsorption of dyes. It is seen that intensity of basal reflections characterizing bentonite in all samples changes from 11.55 to 17.61; from 4.40 to 4.58 and from 3.79 to 4.26, that is explained by expansion of interplanar spacing and penetration of molecules of organic dyes into them, i.e. the change of reflexes is related to the adsorption of dyes.

Under optimum conditions (pH–7, t^0C–20^0, τ_r–1 hour) we studied their adsorption [xvii].

Table 2 shows the results of adsorption of dyes on obtained samples.

Samples	T	BG	MV	T	BG	MV	T	BG	MV	T	BG	MV
	Smg/g			Smg/g			Smg/g			Smg/g		
	$C_{primary.}$ 250 mg/l			$C_{primary.}$ 500 mg/l			$C_{primary}$ 750 mg/l			$C_{primary}$ 1000 mg/l		
Natural DM	4,0	3,4	3,7	18,0	15,0	17,0	49,0	34,0	39,1	60,9	48,5	59.9
Al–DM	12,1	10,2	10,3	25,7	24,5	24,6	56,2	40,3	47,2	78,3	64.5	75.3
Fe–DM	12,2	10,8	10,6	25,0	25,1	25,4	57,4	45,0	49,5	84,0	80,1	85,6
ODA+DM	12,5	11,8	12	33,8	34,0	35,0	64,2	60.1	59,2	150,2	146,1	140.4

Table 2: Sorption of T, BG, MV on natural bentonite, its cation substituted and hydrophobizated forms

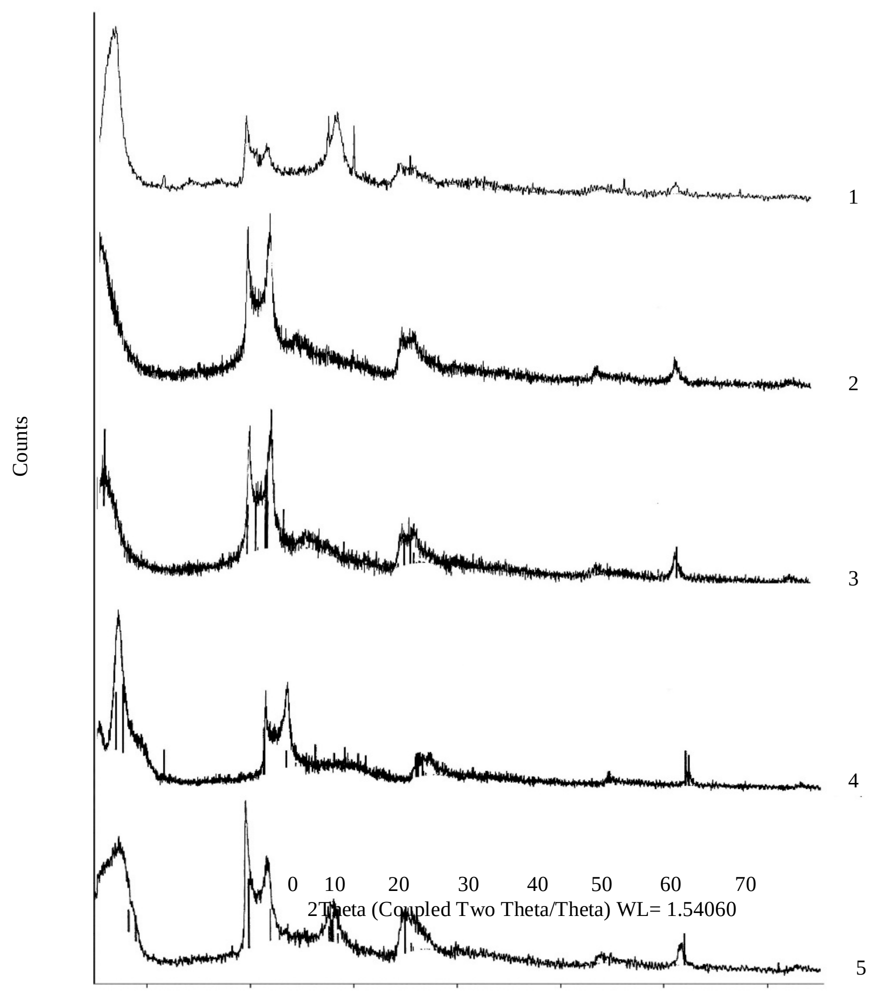

Figure 2: X-ray diagram of natural (1), modified ODAA (2), after adsorption of thionine (3), brilliant green (4) and methylene violet (5)

2. Results and Discussion

At the first we should know that Knowledge of surface properties, is very important and fundamental for the determination of the characteristics of the surface functional groups and their interactions with ions from aqueous solutions.

The purpose of this research was reaching to a maximum adsorption of dyes on bentonite with a low-cost method. So we compared the adsorption method with several combinations. Concentration of dyes was selected from 125–1000 mg/l. Sorption capacity of bentonite and its modified forms in relation to T, BG, MV is increased with the growth of concentration of the modified bentonite. So we could understand sorption with modified sorbents proceeds more intensively than with polycationic natural DM.

Bentonite modified with octadecylamineacetate as a surfactant which can be recommended as an effective sorbent of dyes, showed the best result in this research.

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