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REVIEW

Efficiency of Different Organic Surfactants on Nitrate Adsorption in Water

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Organoclays are modified clays in which the natural inorganic interlayer cations are replaced by organic cations. The net amount of organic cations adsorbed to the clay can exceed the cation exchange capacity of the clay, thus providing binding sites for exchangeable anions. Therefore, organic surfactants are efficient in the treatment of contaminated water. Here a review has been carried out to understand the efficiency of various organic surfactants, *viz.* hexadecyl trimethylammonium, hexadecyl pyridinium and benzethonium on nitrate reduction in drinking water. This study revealed that hexadecyl pyridinium are more efficient to remove nitrate in drinking water than other organic surfactants.

Keywords: Organic surfactant, Modified clay, Nitrate adsorption, Cation exchange capacity.

INTRODUCTION

Silicate layers stacked on one another are the main structure of clay minerals[1]. High cation exchange capacity (CEC), swelling capacity, high specific surface area and consequentially strong adsorption capacity are the most important characteristics of clay minerals which are widely used in different applications[1-4]. One of the major applications of clay minerals in water resources is contaminants adsorption in aqueous solution. Clay minerals have tendency to adsorb organic molecules, change to organoclay and create new materials[1,5]. Adsorbents of organic pollutants in soil, water and air, paints, cosmetics, refractory varnish, *etc.* are some applications of organoclay[6-8]. Organoclays are modified clays in which the natural inorganic interlayer cations are replaced by organic cations. The net amount of organic cations adsorbed to the clay can exceed the cation exchange capacity of the clay and provide binding sites for exchangeable anions[9]. High anion exchange capacity has made the organoclays being researched as adsorbents for anionic contaminants in environmental applications[10-12]. A number of research reported the modified clay minerals or organoclays are the most significant pollutants adsorption[11,13,14-17].

Due to easy availability and comparatively less cost the clay minerals and their modified forms have received wide attention in recent years as adsorbents of pollutant from aqueous medium. A short review has been carried out in this article on different organic surfactants to assess their efficiency in removal of nitrate in aqueous media. For this purpose, performance of various organics modifier such as hexadecyl pyridinium (HDPy), hexadecyl trimethylammonium (HDTMA) and benzethonium (BE) in particular, are reviewed. It is expected that the study will give a clear view on recent development of organic surfactants and their efficiency in removal of nitrate in water.

Modified clay as absorbents: Various clay minerals *viz.* sodium-montmorillonite, bentonite, kaolinite, halloysite and zinc-smectite are reviewed in this article as nitrate absorbant. Montmorillonite, bentonite and smectite belong to montmorillonite group. It has a 2:1 layer structure as shown in Fig. 1a, composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The tetrahedral and octahedral sheets combine in such a way that the tips of the tetrahedral of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. These are the clay minerals with substantial isomorphic substitution. The exchangeable cations in layers of montmorillonite balance the negative charges generated by the isomorphic substitution[18]. Kaolinite is a 1:1 layer mineral (Fig. 1b) which a product of advanced weathering processes. One layer of the mineral consists of an alumina octahedral sheet and a silica tetrahedral sheet that share a common plane of oxygen atoms and repeating layers of the mineral are hydrogen bonded together[19]. Halloysite is a 1:1 aluminosilicate clay mineral with a structure similar to kaolinite. Its main constituents are aluminium (20.90 %), silicon (21.76 %) and hydrogen (1.56 %). Halloysite typically forms by hydrothermal alteration of alumino-silicate minerals[20].

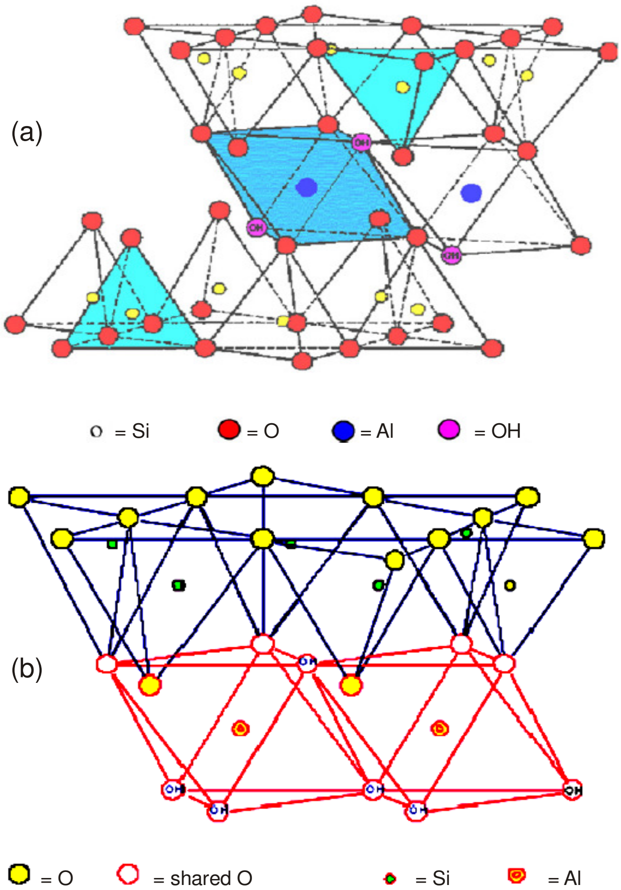

Fig. 1. Structure of the (a) montmorillonite (b) kaolinite

Different surfactants are usually used to modify the clay minerals. Most commonly used organic surfactants are hexadecyl pyridinium bromide ($C_{21}H_{38}NBr$), hexadecyl trimethylammonium bromide ($C_{19}H_{42}NBr$), hexadecyl pyridinium chloride ($C_{21}H_{38}NCl$), hexadecyl trimethylammonium chloride ($C_{19}H_{42}NCl$) and benzethonium chloride. Various methods *viz.* adsorption, ion exchange with inorganic cations and organic cations, binding of inorganic and organic anions, grafting of organic compounds, reaction with acids, pillaring by different types of poly cations, dehydroxylation and calcination, delamination and reaggregation of smectites and lyophilisation, ultrasound and plasma are used to modify clay minerals[21].

Efficiency of various organic surfactants: Performance of organic clay in removal of nitrate from aqueous media depends on the type of clay and the organic surfactants used to modify the clay. Number of researches have been carried out to improve the efficiency of modified clay prepared by using different surfactants and clay minerals[14-16]. A short review of the previous works with different surfactants and clay minerals is presented here.

Hexadecyl pyridinium surfactant: Hexadecyl pyridinium surfactant has recent been used by previous workers[14,15] to modify the clay minerals to improve its efficiency in nitrate remove from aqueous media[15]. Investigated the performance of three different organoclays prepared by modifying zinc-smectite, sodium-smectite and calcium-smectite using hexadecyl pyridinium surfactant. The results showed nitrate removal using organic modified zinc-smectite was more significant than sodium-smectite and calcium-smectite. Maximum nitrate adsorption into zinc-smectite was 18.11 mg/g at equilibrium for Zn-HDP. Fig. 2 shows maximum nitrate removal for different hexadecyl pyridinium dosages.

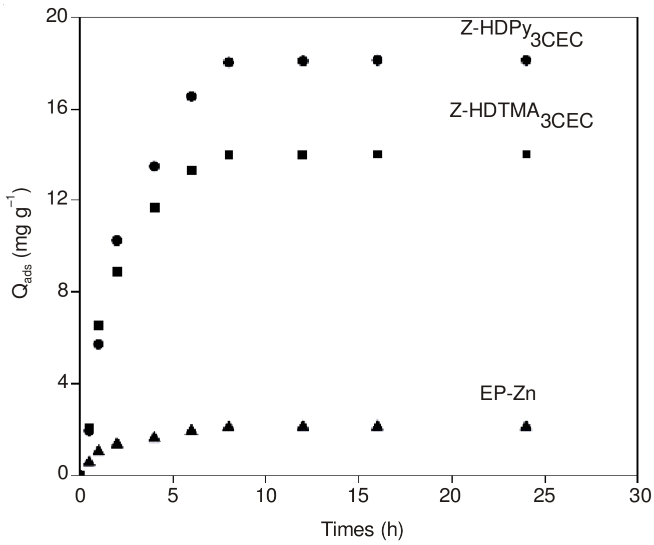

Fig. 2. Maximum removal of nitrate for different surfactant dosages into zinc-smectite [Ref. 15]

Nitrate and four different ions reduction into organic bentonite have been evaluated by Behnsen and Riebe[14]. Relative adsorbption of nitrate into hexadecyl pyridinium bentonite was 93 % which followed two other ions. Relative adsorption for all ions into hexadecyl pyridinium bentonite is depicted in Fig. 3.

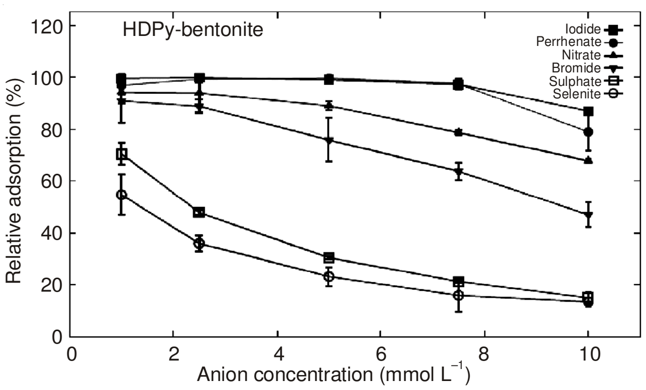

Fig. 3. Relative adsorption *vs.* initial anion concentration into hexadecyl pyridinium bentonite [Ref. 14]

Hexadecyl trimethylammonium surfactant: Hexadecyl trimethylammonium surfactant has also been used by Gammoudi *et al.*[15] to modify the clay minerals to improve its efficiency in remove of nitrate from aqueous media. The maximum amount of nitrate reduction into hexadecyl trimethylammonium zinc-smectite was 14.08 mg/g which related to $HDTMA_{3CEC}$. Fig. 4 showed maximum nitrate removal for various hexadecyl trimethylammonium dosages.

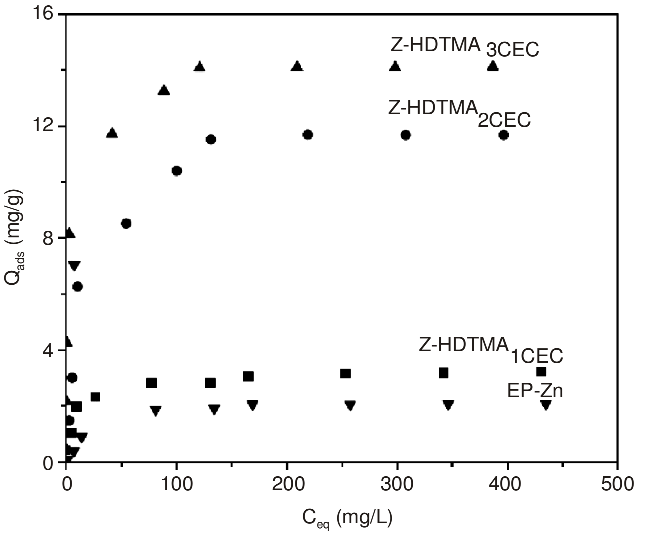

Fig. 4. Adsorption of nitrate ions into hexadecyl trimethylammonium zinc-smectite [Ref. 15]

Relative adsorption of 5 ions was investigated into organic hexadecyl trimethylammonium bentonite[14]. Relative adsorption of nitrate into hexadecyl trimethylammonium bentonite was 72 % which was follow two other ions. Fig. 5 shows relative adsorption for all ions into hexadecyl trimethylammonium bentonite.

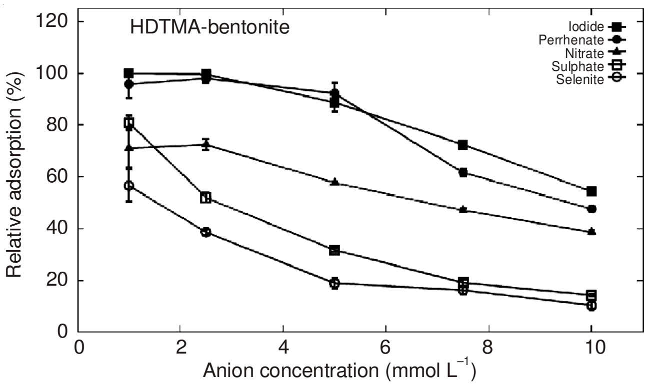

Fig. 5. Relative nitrate reduction into hexadecyl trimethylammonium bentonite (Ref. 14)

The behavior of three natural and organic clays *viz.*, bentonite, kaolinite and halloysite, have been studied by Xi *et al.*[16] to nitrate removal from aqueous solution with two different dosages ofhexadecyltrimethylammonium. Results showed the maximum nitrate adsorption for unmodified bentonite, kaolinite and halloysite were nil, 0.17 and 0.54 mg/g, respectively. Moreover, nitrate adsorption by modified clay minerals were 12.83 and 14.76 mg/g for two various dosages into bentonite, 1.54 and 4.87 mg/g for two various dosages into kaolinite and 1.78 and 1.93 mg/g for two various dosages into halloysite, respectively. Fig. 6 shows nitrate removal from all nine samples.

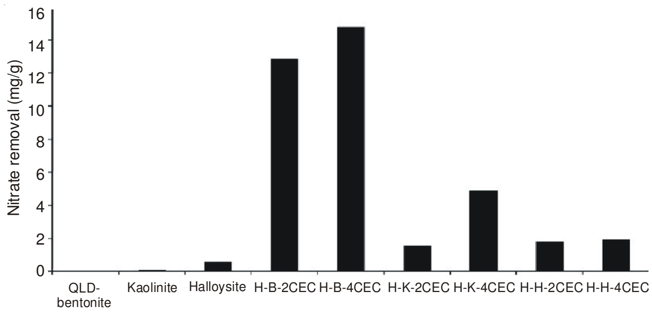

Fig. 6. Nitrate adsorption in unmodified and modified clay minerals into hexadecyl trimethylammonium [Ref. 16]

Benzethonium surfactant: Benzethonium surfactanthas been used by Behnsen and Riebe[14] to modify the clay minerals to improve its efficiency in removal of nitrate from aqueous media. Relative nitrate adsorption into organic benzethonium bentonite, 84 %, was less than relative nitrate adsorption into hexadecyl pyridinium bentonite and greater than hexadecyl trimethyl-ammonium bentonite. Furthermore, the maximum adsorption of the monovalent anions to benzethonium bentonite is less than on hexadecyl pyridinium bentonite for higher nitrate concentrations[14]. Relative adsorption is shown in Fig. 7.

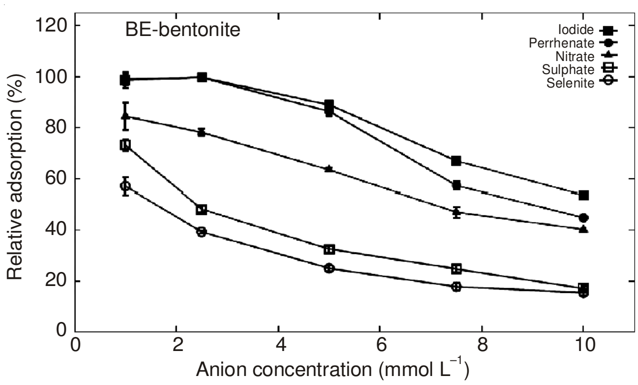

Fig. 7. Relative nitrate reduction into benzethonium bentonite [Ref. 14]

Results of the experiments carried out by various researchers discussed above are summarized in Table-1. From the review and the summary of experiments given in Table-1, following can be remarked.

(1) Organic surfactants can improve the efficiency of clay minerals as nitrate adsorbents. For instance, nitrate removal efficiency of zinc-smectite using hexadecyl pyridinium as surfactant can be improved from 3.6 to 36 %. Nitrate reduction capability of bentonite can be improved from zero to 73.5 % using hexadecyl trimethylammonium.

(2) The effects of organic surfactants on nitrate removal into different clay mineral are different. For example, nitrate removal into bentonite using benzethonium and hexadecyl trimethylammonium as organic surfactant are 96 and 84 %, respectively.

(3) The concentration of organic surfactant and nitrate reduction has direct relationship. In other words, increasing surfactant in clay minerals can improve the capacity of nitrate adsorption. For example, modification of zinc-smectite with hexadecyl trimethylammonium one time and three times can improve its efficiency from 11.7 to 28 %.

TABLE-1
SUMMARY OF THE RESULTS OF EXPERIMENTS BY VARIOUS RESEARCHERS

Adsorbent	CEC meq/100 g	Amount of adsorbent (g)	Volume of solution (mL)	Concentration (mg/L)	pH	Surfactant	Nitrate uptake (mg/g)	Nitrate uptake (%)	Reference
Zn-smectite	80	0.1	50	100	5.6	-	1.8	3.6	
Zn-smectite	80	0.1	50	100	5.6	HDPy$_{1\text{-}CEC}$	7.79	15.6	
Zn-smectite	80	0.1	50	100	5.6	HDTMA$_{1\text{-}CEC}$	5.89	11.7	15
Zn-smectite	80	0.1	50	100	5.6	HDPy$_{3\text{-}CEC}$	18.1	36	
Zn-smectite	80	0.1	50	100	5.6	HDTMA$_{3\text{-}CEC}$	14.0	28	
Bentonite	66.7	0.2	40	100	5.4	-	0	0	
Kaolinite	9.8	0.2	40	100	5.4	-	0.17	0.8	
Halloysite	10	0.2	40	100	5.4	-	0.54	2.7	
Bentonite	66.7	0.2	40	100	5.4	HDTMA$_{2\text{-}CEC}$	12.8	64	
Kaolinite	9.8	0.2	40	100	5.4	HDTMA$_{2\text{-}CEC}$	1.54	7.7	16
Halloysite	10	0.2	40	100	5.4	HDTMA$_{2\text{-}CEC}$	1.78	8.9	
Bentonite	66.7	0.2	40	100	5.4	HDTMA$_{4\text{-}CEC}$	14.7	73.5	
Kaolinite	9.8	0.2	40	100	5.4	HDTMA$_{4\text{-}CEC}$	4.87	24.5	
Halloysite	10	0.2	40	100	5.4	HDTMA$_{4\text{-}CEC}$	1.93	9.6	
Bentonite	89	0.2	10	100	7.3	HDPy$_{1.7\ CEC}$	4.65	93	
Bentonite	89	0.2	10	100	7.3	HDTMA$_{1.2\ CEC}$	4.8	72	14
Bentonite	89	0.2	10	100	7.3	BE$_{1.2\ CEC}$	4.2	84	

CEC: cation exchange capacity; HDTMA: hexadecyl trimethylammonium; HDPy: hexadecyl pyridinium; BE: benzethonium

(4) The effects of specific organic surfactant into different clay minerals are not equal because of different cation exchange capacity[9]. For example, removal of nitrate into three different clay minerals, bentonite, kaolinite and halloysite, using hexadecyl trimethylammonium as surfactant are 73.5, 24.5 and 9.6 %, respectively.

(5) Although the organic surfactant and adsorbent, hexadecyl trimethylammoniumand bentonite[16] were almost the same, nitrate removal was different, 64 and 72 %, respectively[22]. The ratio of volume solution to the amount of adsorbent and contaminant removal has inverse relation[22]. The ratios were 200 and 50 mL/g for[14,16], respectively.

Conclusion

Change of surface properties from hydrophilic to hydrophobic and increases anions adsorption capacity are two positive points of using organic surfactant as clay minerals modifier. The present review reports that modified clays are more effective than unmodified clay to remove nitrate in water. Review of the performance of different surfactants of various clay minerals reveals that modified bentonite with hexadecyl pyridinium is the most efficient absorbent. The operating conditions for the organic surfactants, such as the ratio of the volume of water to surfactant, pH and pollutant concentration should be further examined to improve the efficiency of clay mineral as absorbents.

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