REMEDIATION OF ARSENIC CONTAMINATED WATER BY A NOVEL CARBOXYMETHYL CELLULOSE BENTONITE ADSORBENT

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Abstract. Suitability of bentonite clay modified with sodium carboxymethyl cellulose (Na-CMC) for the removal of arsenic(III) ions from aqueous solution was tested in batch adsorption studies and complemented by theoretical modeling with Langmuir, Freundlich and Temkin isotherm models. The effects of various factors, such as the initial adsorbate concentrations, pH, and temperature of the solutions were investigated in series of experiments. FTIR analysis was used to detect functional groups typical for cellulose and bentonite. Scanning electron microscope was used to analyze the surface morphology of the composites. It was established that the removal process was fast in the beginning and adsorption equilibrium was attained in around 20 minutes with good fittings to both Langmuir and Freundlich model. Maximum adsorption capacity (Q_{max}) obtained from experiments was 9.4 mg/g. No influence of solution pH and temperature on the sorption was noticed. The series of conducted experiments showed that synthesized composites are suitable for the removal of arsenic from wastewaters by adsorption as efficient and low-cost technique.
Keywords: *pollution, waste waters, composite, isotherm model, sorption capacity*

Introduction and literature review

Water contamination by arsenic salts is regarded as a critical issue in growing environmental pollution due to arsenic's toxicity, its abundance and difficulties to

remove it from contaminated sources. For several decades, arsenic is the contaminant of priority interest by the European Union (Council of the European Communities, 1976) and by the Environmental Protection Agency of the United States (EPA) (Environmental Protection Agency, 1982). Arsenic gets at water bodies from natural deposits, smelters, glass industry, electronic waste, mining, combustion of fossil fuels, orchards where arsenical pesticides were used, disposal of chemical wastes, etc. (Mar et al., 2013; Pandey, 2017). It causes serious diseases, such as cancer, neurological disorder, nausea, hyperkeratosis, muscular weakness, and others (Pandey, 2017). US EPA has established a maximum contaminant level (MCL) for arsenic of 0.010 mg/l in drinking water (U.S. Environmental Agency, 2018).

There are many methods for arsenic removal from water sources, such as chemical precipitation, coagulation and flocculation, ion exchange, adsorption, electro deposition, advanced oxidation, membrane filtration, etc. Adsorption seems to be one of the best techniques for this purpose since it is known for its high-removal efficiency, profitability, simplicity, easier and sludge-free operations, and the possibility to recycle (Mar et al., 2013). Numerous materials have been used as adsorbents, such as activated carbon, fly ash, clays, muds, various oxides, polymeric resins, biomaterials, composites, etc. In the last three years, many novel adsorbents have been reported for efficient arsenic removal including zeolitic imidazolate framework-8 (ZIF-8) (Liua et al., 2018), graphene oxide@iron aluminium oxide composite (Majia et al., 2018), α-FeOOH decorated graphene oxide-carbon nanotubes aerogel (Fu et al., 2017), magnetite sub-microparticles (Mejia-Sentillan et al., 2018), cerium loaded cellulose nanocomposite (Santra and Sarkar, 2016), iron oxyhydroxide on the root powder (Lin et al., 2018), etc. There is a pronounced tendency that adsorbents should be more economic. For these reasons, the most desired adsorbents originate from the various by-products and low-cost raw materials locally available in huge amounts.

Sodium carboxymethyl cellulose (Na-CMC) is a white granular powder that is colorless, odorless, non-toxic and water soluble. It is used as thickening agent, emulsion stabilizer, or suspending agent in the food industry but it is also often found in water-based paints, detergents, and paper products. As a typical polymeric derivative of cellulose, it contains carboxylate anion and hydroxyl functional groups (Yan et al., 2014) which are responsible for good complexation ability for some metal ions, such as Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Pb^{2+} (Petrox et al., 2002). Up to our best knowledge, there are no reported studies about arsenic removal by carboxymethyl cellulose.

Herein, we present study based on the removal of As^{3+} ions from aqueous model solutions by acid activated bentonite clay impregnated with Na-CMC as an adsorbent in the batch system. Sorptive features of powdered adsorbent were estimated by analyzing the impact of varying complex experimental conditions and employing theoretical modeling of adsorption. The goal of the work was to elucidate the mechanism of As removal and correlation between structural, functional and sorptive properties of Na-CMC-bentonite composite.

Material and methods

Preparation of Na-CMC-bentonite composite (adsorbent)

Three bentonite clay based adsorbents containing 1, 3, and 5% of Na-CMC were synthesized in our laboratory at Department of Chemistry, Faculty of Science and Mathematics, University of Niš, Serbia. Na-CMC was purchased from Weifang Lude

Chemical Co., Shandong, China. Bentonite was used in experiments as an adsorbent in native form (natural clay, purchased from "Riznica Prirode", Serbia). 15 grams of bentonite clay was suspended in 300 ml of deionized water and mixed with 0.15 (1%), 0.45 (3%) or 0.75 (5%) g of Na-CMC in order to achieve desired weight ratio. Suspensions were agitated on a magnetic stirrer at 90 ºC for 2 h. During stirring, 5 ml of concentrated HCl was added in drops. Prior to adding acid, pH of the suspension was 9.2 while after adding pH dropped down to 1.35. Probes were left to cure overnight and then filtered by vacuum with constant rinsing by using deionized water. Rinsing was carried out until negative reaction for chlorides. Modified clay was dried overnight at 110 ºC, crushed and used in experiments. Composites were designated as: GI (1% Na-CMC), GII (3% Na-CMC), and GIII (5% Na-CMC).

Characterization of adsorbent

FTIR spectrometer BOMEM MB-100 (Hartmann & Braun, Canada) with detector DTGS/KBr was used for recording FTIR spectra in a spectral range from 4000 to 400 cm^{-1} with the resolution of 4 cm^{-1}. Morphology of the samples was analyzed by the scanning electron microscope JSM-5300 (Jeol, Japan). For SEM analysis, composite samples were prepared by using instrument JFC-1100E ION SPUTTER for sputtering gold particles for better conductivity. Samples were recorded at magnifications of 1000, 2000, and 5000 times. For EDS analysis which revealed the presence of chemical elements, detector Linx Analytical QX 2000b was used on the same microscope.

Adsorption experiments

Adsorption experiments were carried out in a batch system by contacting mass of 1 g of adsorbent and arsenic solutions of concentrations from 10 to 200 mg/l for 20 minutes. Suspensions were agitated by magnetic stirrer at defined temperature and filtered through quantitative filter paper. The residual concentrations of arsenic in solutions were determined by ICP-OES spectrometer iCAP 6000 (Thermo Fisher Scientific). In order to investigate the influence of experimental conditions on the removal process, initial arsenic concentration, temperature and pH value were considered. Adsorption capacity, Q (mg/g) was determined by the *Equation 1*:

$$Q = \frac{(C_0 - C)V}{m}$$
(Eq.1)

where C_0 is the initial concentration of arsenic ions, V is the volume of the solution, m is the mass of bentonite composite and C is the residual concentration of arsenic ions at the equilibrium. Previously it was established that contacting time of 20 min was enough to reach equilibrium of the process.

Effect of solution pH was investigated at values 1, 3, 5, 7 and 9 by stirring 100 mg/l arsenic solution with 1 g of the adsorbent for 20 minutes. After this time, suspensions were filtered and analyzed for remaining arsenic. In order to examine the impact of different temperatures on the sorption process, the same procedure was followed at 20, 30, 40, 50, and 60 ºC.

For all analyses, the stock solution of arsenic (1 g/l) was prepared by a diluting proper amount of arsenic (III) nitrate in deionized water.

According to manufacturers specification, bentonite clay has the chemical composition presented in *Table 1*. Along with dominant ratios of silicon and aluminum

oxides, oxides of potassium, iron, titanium and calcium are also present. These "heteroatoms" are responsible for numerous structural deformations in the clay structure, especially those related to forming non-stoichiometric moiety filled with vacancies and charges compensated with suitable ions. Such defects are prone to electrostatic interactions with grafting or dopping agents, and among the rest for forming thin films with proper modifiers. In this case, carboxymethyl cellulose is used for this purpose and with the goal to introduce reactive hydroxyl groups which are proven to be responsible for complexation with some metals.

Table 1. Chemical composition of bentonite

Oxide	SiO_2	Al_2O_3	K_2O	Fe_2O_3	TiO_2	MgO	CaO
Mass ratio (%)	67.81	24.73	3.25	1.89	1.06	0.93	0.33

Three theoretical isotherm models were used to analyze the sorption data. Each model is briefly described below. Langmuir isotherm is usually used to describe monolayer adsorption where all reactive sites on the sorbent's surface are energetically homogenous. Here no lateral interaction and steric hindrance between the adsorbed molecules is assumed. This model is in its linearized form represented by *Equation 2*:

$$\frac{c_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}}c_e \qquad (Eq.2)$$

where K_L is Langmuir equilibrium constant (l/mg), and Q_{max} (mg/g) is maximum adsorption capacity. The useful feature of Langmuir isotherm is separation factor, R_L defined by *Equation 3*:

$$R_L = \frac{1}{1 + K_L c_0} \qquad (Eq.3)$$

The value of the R_L defines the types of isotherms as unfavorable ($R_L > 1$), linear ($R_L = 1$), irreversibile ($R_L = 0$), and favorable $0 < R_L < 1$ (Karagoz et al., 2008).

Freundlich isotherm best describes adsorption onto heterogeneous surfaces which is the opposite to Langmuir's model. This implies that each molecule of the sorbate is bound at the surface with the different binding energy. It means that stronger binding sites are occupied first and then the binding strength decreases for the rest of the available sites. *Equation 4* defines Freundlich model as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \qquad (Eq.4)$$

where K_F ((mg/g) (dm^3/mg)$^{1/n}$) is Freundlich constant and $1/n$ is the heterogeneity factor (Haghseresht and Lu, 1998).

Temkin isotherm model considers that adsorption takes place through indirect adsorbate-adsorbate interactions. The linearized form of equation (*Eq. 5*) is given as:

$$q_e = B \ln K_t + B \ln c_e \qquad (Eq.5)$$

where K_t (dm³/mg) is the equilibrium binding constant corresponding to the maximum binding energy and constant $B=RT/b$ represents the heat of adsorption, while $1/b$ indicates the adsorption potential of the adsorbent (Hameed and Ahmad, 2009).
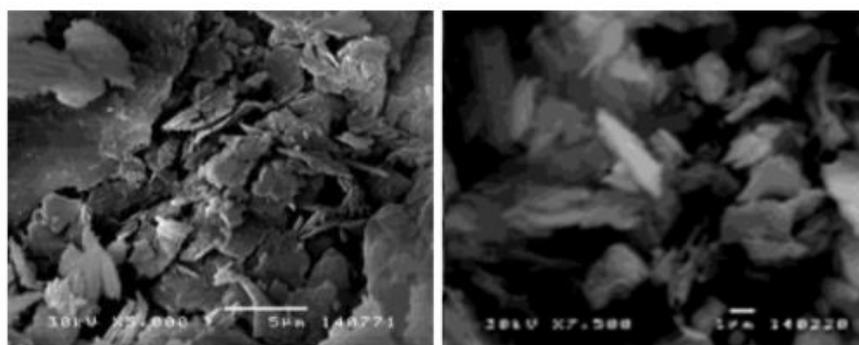
Linear fitting of experimental data was carried out by using software Origin 8.0. For each isotherm model, corresponding values were plotted and fitted by applying option Analysis/Fitting/Fit linear. All sorption parameters were calculated from the parameters which apply to the slope and the intercept of the linear form of isotherm equation.
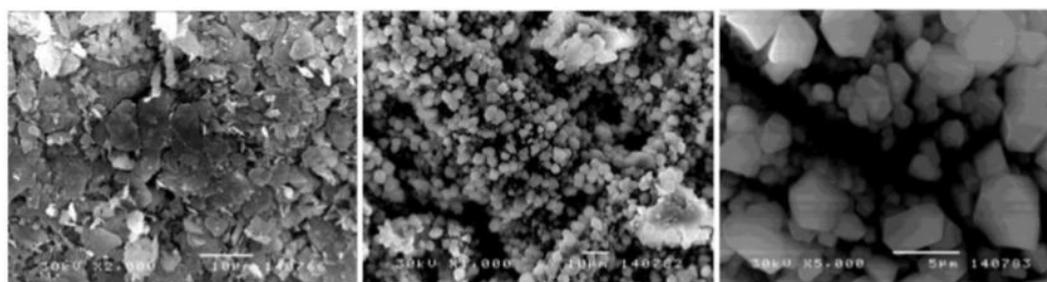
Results and discussion

Characterization of adsorbents

Scanning electron microscopy

The SEM micrographs of native bentonite clay and carboxymethyl cellulose bentonite based composite are given in *Figures 1 and 2*, respectively.

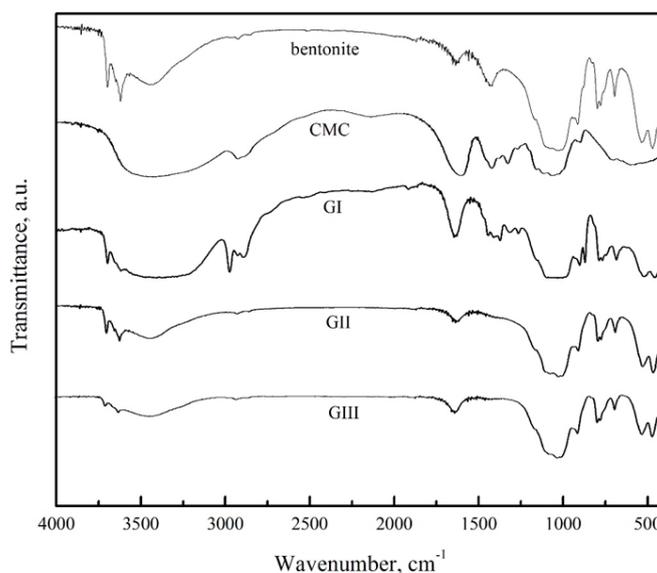*Figure 1. SEM micrographs of native bentonite at magnifications of a) 5000x and b) 7500x*

Figure 2. SEM micrographs of carboxymethyl cellulose bentonite based composite with a) 1% b) 3% and c) 5% of modifier

Laminar crystals noticed at magnifications of 5000x are typical for bentonite clays (*Fig. 1*). These particles arranged in a layered manner form the aggregates with diameters of 5 µm on average. Composites with carboxymethyl cellulose show smaller structure changes since thicker crystals are noticed with the higher degree of agglomeration especially in case of the sample where 3% of modifier is applied (*Fig. 2*). Fine grains instead of the dominant laminar structure are attributed to forming of the sticky organic film at the surface of the clay particles.

The SEM-EDS analysis shows that predominant elements in unmodified clay are: Fe, Al, Si, and O. In samples GI, GII and GIII aluminum is the most dominant, due to leaching of Fe during the synthesis of composites.

FTIR spectral analysis

Fourier-transform infrared spectra of native bentonite clay and modified composites which include various ratios of carboxymethyl cellulose are given in *Figure 3*. Two distinctive peaks in bentonite spectrum corresponding to OH stretching vibrations which originate from the Al–Al–OH stretches are observed at 3625 cm^{-1}. The wide peak at 3400 cm^{-1} belongs to the OH stretching of H-bonded water. The bend at 1330 cm^{-1} is due to Si–O bending vibrations. This peak is noticed in native bentonite and GI composite. For samples GII and GIII noticeably weaker peaks for all functional groups are present. For the sample GI, the peaks at 2926 and 2854 cm^{-1} are from C-H vibrations coming from carboxymethyl cellulose. The additional bend corresponding to Al–Al–OH is observed at 925 cm^{-1}. A peak around 800 cm^{-1} with the inflexion at 780 cm^{-1} corresponds to quartz. Carboxymethyl cellulose confirms typical peaks for hydroxyl groups, C-H vibrations and nothing more of interest.
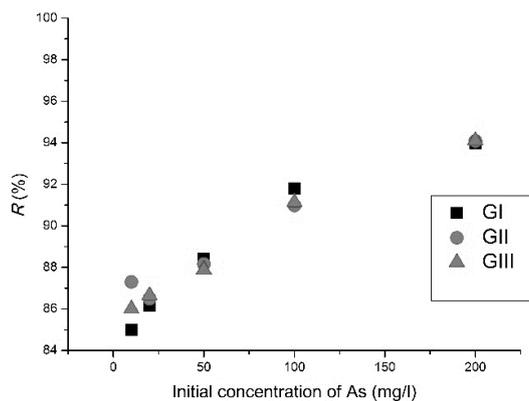

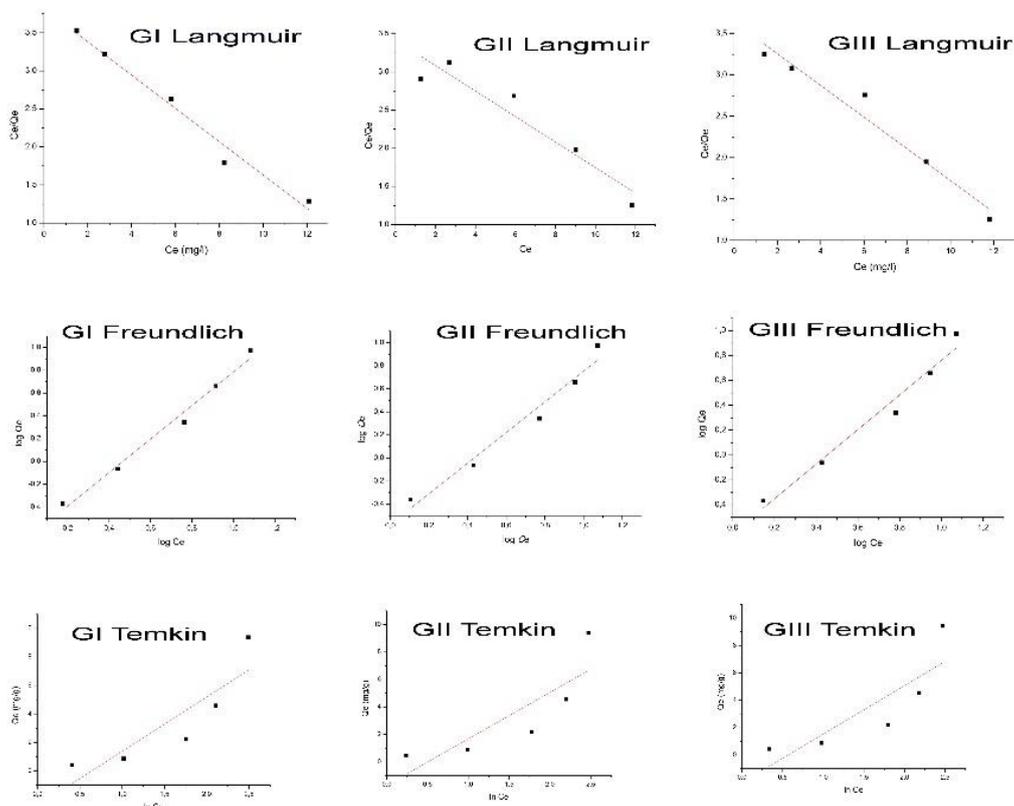*Figure 3. FTIR spectra of native bentonite clay, carboxymethyl cellulose and corresponding composites*

Adsorption experiments

Removal degree of arsenic is represented by the *Figure 4*. It is seen that removal degree for the different initial concentrations and for all composites is in the range from 85 to 94%.

In order to analyze the equilibrium condition of arsenic adsorption onto prepared adsorbents three theoretical isotherm models were applied including Langmuir, Freundlich, and Temkin model. Parameters of these models were estimated with the aid of the linear fitting in Origin 8.0 (OriginLab Corporation, USA). Results of the fitting are given in *Figure 5*.

Figure 4. Removal degree of As onto bentonite composites

Figure 5. Linear fitting to Langmuir, Freundlich and Temkin isotherm model

Parameters which apply to the slope and the intercept of the linear form of isotherm equation were used for calculation of sorption parameters which are presented in *Table 2*. It is noticed that Freundlich model fitted well for all three composites, followed by Langmuir and Temkin model. Freundlich model assumes multilayer adsorption and heterogeneity of the process. This model was reported to be the most suitable also in the case of arsenic adsorption onto mesoporous bismuth-impregnated aluminum oxide
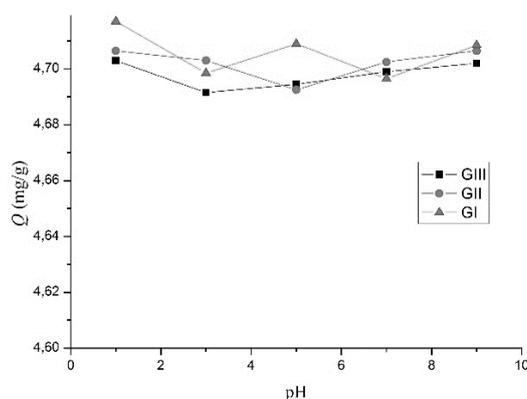
although the process was studied by using the lab-scale column (Zhu et al., 2018). In addition, experimental results were also fit well with this model in case of arsenic adsorption onto alum sludge (Jeon et al., 2018). However, there is a hint which distrusts this model as physically relevant. Namely, strong interactions between the adsorbate and adsorbent are observed when the reciprocal Freundlich constant (n) is above 1, as in our case. This basically indicates an unsuitable adsorption process (Komy et al., 2014; Lee et al., 2010). Such statement is in contrast to results attained it this study where with current experimental set-up removal degree was 85% or higher (*Fig. 4*).

Table 2. *Equilibrium model parameters for adsorption of arsenic onto bentonite based adsorbents*

Equilibrium model	Parameter	Composite GI	Composite GII	Composite GIII
Langmuir	K_L (l/mg)	0.056	0.05	0.052
	q_{max} (mg/g)	4.56	5.88	5.26
	R_L	0.019	0.017	0.018
	R^2	0.972	0.876	0.948
Freundlich	K_F (l/g)	0.21	0.27	0.23
	n	0.68	0.76	0.72
	R^2	0.981	0.956	0.964
Temkin	A	0.53	0.61	0.56
	b (J/mol)	650.6	733.4	700.2
	R^2	0.686	0.608	0.625

Langmuir model is less suitable to interpret experimental data. Although fair values for correlation coefficients were obtained, estimated values for maximum adsorption capacities for GI, GII, and GIII (4.56, 5.88, 5.26 mg/g, respectively) are far below the experimentally obtained ones (9.4 mg/g for all three composites). The low values of K_L indicate a poor affinity and thus weak bonding of arsenic to the surface of composites at examined conditions. Value for R_L in Langmuir model shows favorable adsorption for all composites.
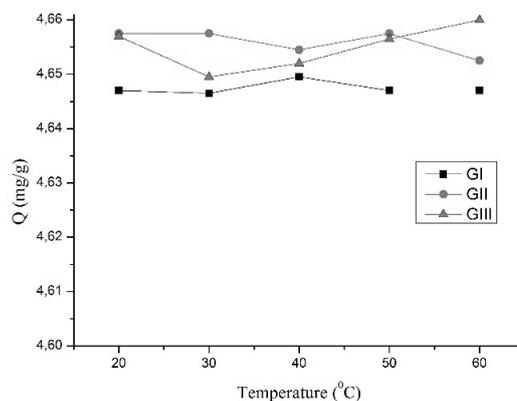
From *Figure 6* it is seen that pH value of solutions has no impact on the removal efficiency of arsenic since adsorption capacities for all three composites differ on the second decimal.

Figure 6. *Effect of pH on arsenic adsorption onto bentonite composites*

This result is most probably related to the nature of interactions between arsenic ion present in the suspension and electrostatic neutrality of the composites. In case if there is no non-compensated charge on the adsorbent surface the nature of sorptive binding of the As ions are not influenced by electrostatic forces. Hence, the purely physical process takes place. It is conducted by the spontaneous orientation of sorbed ions on the reactive centers of the adsorbent by weak physical forces. However, it is the fact that the number of these sites (for the employed experimental conditions) is not small and it is certainly enough to adsorb great majority of adsorbate.

Another topic which explains the nature of As binding to the porous structure of all three composites is the analysis of temperature impact on the sorption process. From *Figure 7* it can be seen that there are almost no differences in adsorption capacity at different temperatures. To conclude, there is no meaningful influence of thermal energy on the binding of As ions onto surfaces of the composites. It is also in favor of the assumption that arsenic ionic species are bound to the surface of the adsorbent by the weak physical forces and excessive energy does not result in better sorption.

Figure 7. Effect of temperature on arsenic adsorption onto bentonite composites

In order to rate sorptive potential for As(III) removal by Na-CMC-bentonite composite, *Table 3* given below lists achieved maximum adsorption capacities (Q_{max}) obtained from various sorbents in defined experimental conditions.

From *Table 3* one can conclude that significant scientific effort is dedicated to arsenic removal from aqueous media since it is already established that arsenic is very persistent and ubiquitus pollutant. In *Table 3* are presented low cost sorbents obtained from materials that are cheap and abundant. Interesting material is Fe(III)-loaded celulose which gave twice higher sorption capacity than our material. However, one should bear in mind that we used sodium salt and not the pure cellulose and we certainly lowered the prise of the final product by forming a composite which involves the very cheap and easily available bentonite clay. Generally, it is noticed that Na-CMC-bentonite composite achieved moderate success in the sorption of arsenic from solutions. However, if one considers the fact that this composite was produced easily and in short period of time, by using low cost ingredients which are locally available in large amounts, certain feasibility of its production on large scale and applications for treating contaminated water sources could make sense especially in terms of economic profitability.

Table 3. *Comparison of As^{3+} maximum adsorption capacities (Q$_{max}$) for various sorbents*

Biosorbent	Experimental conditions	Q_{max} (mg g^{-1})	Source
Iron-impregnated chitosan	C_i=1.007 mg/l; pH=8	6.48	Ref. [5]
Fe-sericite composite beads	C_i=5-25 mg/l; m_{ads}=0.12 g; 200 rpm, 12h, pH=6.82	9.02	Ref. [11]
Synthetic iron sulphide	pH=6.5	0.2	Ref. [27]
Fe(III)-loaded celulose	pH=9	18.0	Ref. [20]
Commercial adsorbents (goethite)	pH=7.5	10.1	Ref. [12]
Commercial adsorbents (mosoporous alumina)	pH=7	47.2	Ref. [12]
Tea fungal biomass	pH=7.2; C_i=1.3 mg/l	1.11	Ref. [21]
Atlantic Cod fish scale	pH=4	0,027	Ref. [25]
Hydrous ferric oxide incorporated diatomite	pH=7	267	Ref. [8]
Chitosan extracted from shrimp waste	pH=4,5,6; t=30-90 min; dosage=2,3,4 mg/l; C_i=200, 300, 400 mg/l	1.3	Ref.[2]
Perilla leaf biochar	pH=3-10; dosage=1g/l; C_i=0.05-7.0 mg/l;	3.8 – 11.01	Ref.[22]
Na-CMC-bentonite	C_i=10-200	9.4	This study

In contrast to compared studies listed in *Table 3*, Na-CMC bentonite clay composite is material which is very easy and practical for common day practice since it can be employed with no additional adjusting of the pH of the suspension and contacting time is around 20 minutes. This is considered as the main advantage of this sorbent. In addition, preparation of this composite material is fast, safe and involves no harmful ingredients or complicated synthetic procedures.

Conclusion

Composite adsorbents obtained by modification of bentonite showed significant sorptive potential for removal of arsenic(III) ions from water sources. The maximum adsorption capacity, experimentally obtained from isotherm studies, equals 9.4 mg/g. The adsorption process is considered to be fast since the equilibrium is fully attained in only 20 minutes. Good fitting to Freundlich isotherm model pointed out to complex processes at the boundary of the phases liquid-solid which involve multilayer adsorption with different energies of bindings between adsorbate and adsorbent. In the case of presented experimental set-up, high removal degree was attained. This pronounced great affinity of the Na-CMC-bentonite composites towards the dissolved arsenic ions. Bearing in mind low cost of the raw materials which were used to produce this adsorbent, the simplicity of the synthesis and expressed removal feasibility of As^{3+}, this comparative study conveys direct stimulus for practical applications of this composite material and their further examinations in associated frameworks.

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