

APPLICATION OF CORAL SUPPORTED IRON ZERO VALENT NANO SCALE FOR REMOVAL OF NATURAL ORGANIC MATTER FROM AQUEOUS SOLUTIONS

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ABSTRACT

Background: Different materials such as mesoporous silica, carbon and titanium dioxide, chitosan beads, ceramic membranes, kaolin and bentonites have been used as a base for nanoparticles in water treatment industry. In this Research coral supported zero valent iron nanoparticles was applied for the removal natural organic matter from aqueous solutions under different experimental conditions.

Methods: Nanoadsorbent was prepared by wet impregnation method, then characterized using SEM, X-Ray Fluorescence and BET analysis. Adsorption test was done in a batch reactor and effect of different parameters such as initial adsorbate concentration, adsorbent dose effect, adsorption kinetic, and pH, on adsorption of NOMs were studied.

Results: results show that particle size of nanoadsorbent is in range of 53-94 nm, surface area and micropore volume are 16.85 m²/g and 0.023 m³/g respectively, also the most components of adsorbents is composed of lime. Produced nanoadsorbent did not solubility in water. By increasing the nanoadsorbent dose, the removal of humic acid increased, an inverse relationship was found between initial concentration and adsorption capacity. The most fitted adsorption isotherm and kinetic model were Freundlich isotherm and pseudo-second order model respectively.

Conclusions: chemical structure of nanoadsorbent was properly and free of harmful substances. Despite the relatively good condition of the effective surface, due to the large size of the crushed coral, the overall micro pore volume was low. This led to the absorption capacity of humic acid is low.

Keywords: Humic acid, Coral, nanoadsorbent, natural organic matters, adsorption

1. Introduction

Naturally occurring organic materials, a nonhomogeneous mixture of complex organic compounds that include humic acids (HAs), lipids, proteins, hydrophilic acids, carboxylic acids, amino acids, polysaccharides, and hydrocarbons are invariably present in surface and ground waters, in dissolved or colloidal forms [1]. Various environmental and health problems have been reported that may be related to presence of NOMs in natural waters, including the following (a) NOMs have a potential to cause undesirable color and taste [2]; (b) NOMs also contribute to a reaction with heavy metals and biocides to yield high concentrations of these substances and enhance their transport in water [3]; (c) NOMs increased coagulant and disinfectant dose requirements that leads more sludge amounts; (d) in treatment plants, NOMs reacts with chlorine to form harmful organic compounds [2]; (e) NOMs are is an important factor in fouling and affecting various applications of membrane processes [4]; and (f) NOMs have tendency to compete with low-molecular-weight synthetic organic chemicals and inorganic pollutants, reducing their adsorption rates and equilibrium capacities [5, 6].

Notice to harmful effects of NOMs on human health, these compounds should be eliminated from water before the chlorination process in the drinking water treatment train and thus finding reliable methods to remove a wide range of organic contaminants from water can have a great benefit to

the public health and drinking water industry [7]. During the last years a large amount of research has been on the NOM removal from water or to minimize the impacts on water quality [1, 8-12]. Based on these researches, the most conventional options for NOM removal include membrane filtration, ion exchange [13], ozonation [14], biodegradation [15], adsorption, and coagulation [16]. Among the methods, membrane separation and adsorption were the most effective and available processes for removing natural organic matters from water [1]. The main adsorption advantages are high removal efficiency and no harmful by-products so many kinds of adsorbents have been developed for the removal of humic acid from water. During the past few years, nanoparticles have been proposed as a removal method for a wide range of pollutants from water [17]. Some important nanoparticles in water treatment include metal-containing nanoparticles, carbonaceous nanomaterials, zeolites, and dendrimers [18]. As Nanoscale zero-valent iron (NZVI) particles have unique reactive and sorptive characteristics therefore received much attention for the treatment of contaminated water [19, 20]. Several studies have been conducted that used various materials such as mesoporous silica beads [21], carbon and titanium dioxide [22], chitosan beads [23], ceramic membranes [10], kaolin [24], bentonites [11] and so on as a base for nanoparticles. On Iran's southern coast, there is a considerable amount of coral which can be used as a perfect base for Nano adsorbent and considering the possibility of successful production of air-stable ZVI nanoparticles with a high gravimetric ratio, good stability and no harmful matters, it was used as a base for NZVI. This study focuses on the coral supported NZVI application for the removal NOMs under different experimental conditions, in order to application for taste and odor removal from surface water resources in the next studies.

2. Methods

2.1. Preparation and Characterization of Nano-supported coral

The synthesis of the coral supported iron nanoadsorbent was carried out by wet impregnation technique. Coral collected from Persian Gulf coast were transported to lab and after physically cleaning, they were crushed at first and dried in 100°C oven and then sieve with a sieve mesh of 100. To prepare the NZVI coated shell, the shell beads were placed in the reactor during the synthesis of NZVI, by using the reduction of dissolved iron method.

Initially, 5 g of crushed coral were poured in a flask containing 0.1 M FeCl₃·6H₂O dissolved in absolute ethanol and heated at 80°C up to evaporation the solvent to obtain a dry coated beads. The beads were dispersed in 150 mL of absolute ethanol again and then was placed on an orbital Shaker then 100 ml of 0.16 M NaBH₄ aqueous solution was poured into a burette and dropped to stirring flask. During this reaction, ferric iron (Fe³⁺) was reduced to zero-valent iron (Fe⁰) by borohydride and the crushed shell beads started to take black color. This suggested the ferrous ions attached to the support material were successfully reduced to zero-valent state. Afterwards, the contents of the flask using a funnel and filter milipore discharge and suction system, initial dewatering. The shell beads coated with NZVI were washed by ethanol, and then dried at temperature of 50°C, then was kept in desiccators.

Laboratory synthesized adsorbent (nanoadsorbent) was analyzed using Scanning Electron Microscopy (SEM) and XRF to investigation of chemical characteristics. The specific surface areas of nanoadsorbent were analyzed using BET-N₂ adsorption method.

2.2. Batch reactor adsorption system and experiments

Adsorption of HA onto produced adsorbent was carried out by a batch reactor and effect of different parameters such as adsorption, initial HA concentration, adsorbent dose effect (isotherm), solution pH, and temperature were studied.

In order to isotherm study, different doses of nanoadsorbent (0.5gr, 1 gr, 3 gr and 5 gr) were added to the reaction flask containing of 100mL of 5mg/l HA solution in the initial pH of 7 and temperature of 24 to 25°C and mixing during the stirring (100 rpm). At intervals of firstly 5 and 10 min and then at a frequency of every 15 minutes to reach equilibrium, the containers were sampled. After this shaking, and settling for 5 min, the samples supernatant were centrifuged followed by membrane filter (0.45 µm, cellulose acetate), absorbance values of solutions

remaining without adsorption were measured by using UV–Vis spectrophotometer at wavelength of 254 nm.

After determining the adsorption isotherm, using collected data and models related to the absorption kinetics, modeling kinetic of HA adsorption study on the nanoadsorbent were determined. The effect of initial HA concentration on the adsorption rate was studied by contacting a fixed mass of adsorbent (0.5g) at room temperature (24-25oC) and pH (7) using four initial concentrations of HA solution (0.5, 2, 5 and 10 mg/l) in 100ml volume of samples at time=0 and at selected time intervals (up to a maximum of 180 min), were taken and the sample concentration was determined by UV–Vis spectrophotometer.

In order to survey of the pH effect on HA adsorption, the pH of the solution was varied between 5.0 and 10.0 in four intervals (5- 7- 8 and 10) using either 0.1mol/L NaOH or 0.1 mol/L HCl.

3. Results

3.1. Characterization of nanoadsorbent

SEM image of the nanoadsorbent is shown in Fig. 1, the physical properties of the nanoadsorbent is presented in Table.1, and chemical composition of nanoadsorbent are presented in table 2.

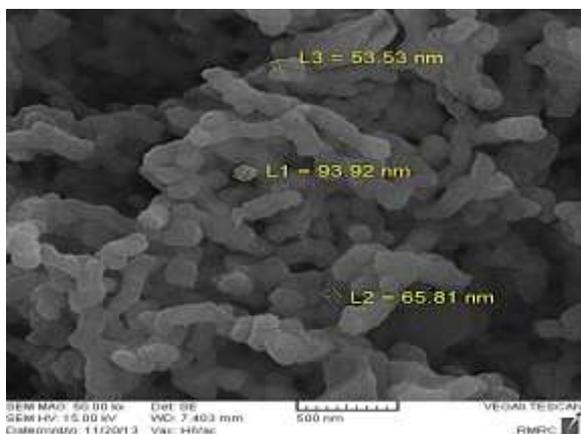


Figure 1: SEM of prepared nanoadsorbent

Parameter	Unit	Value
density	g/ Cm ³	1.69
Particle size	nm	53-94
Micropore volume	m ³ /g	0.023
BET Surface Area	(m ² /g)	16.85
Solubility @(20°C)	%	insoluble

Table 1: physical properties of the nanoadsorbent

Table 2: Chemical composition of the nanoadsorbent

composition	% weight						
SiO2	0.99	Al2O3	0.30	MgO	0.67	Na2O	1.35
CaO	28.35	K2O	0.59	Cl	0.08	SO3	0.19
FeOOH	3.74	CaCO3	62.90	SrO	0.47	Fe2O3	0.291

As shown in the figure 2 (left), most of the sheet structure has been changed to irregular small particles and depicts the synthesized nanoadsorbent with an approximately 53–94 nm diameter. The main elements of adsorbent are Ca, O, Fe and Na and the most components of adsorbents is composed of lime (CaCO₃ and CaO), which is about 93.53 percent of the total weight. None of the adsorbents, did not solubility in water.

3.2. The effect of the adsorbent dose

Although by increasing the nanoadsorbent dose of 0.5 to 10 mg/l the removal of HA (C₀ =5 mg/L) was found to increase from 62.3% to 96.9%, but the amount of removed HA (mg) per mass of nanoadsorbent showed decrease in rate from 0.66 mg/g to 0.09 mg/g.

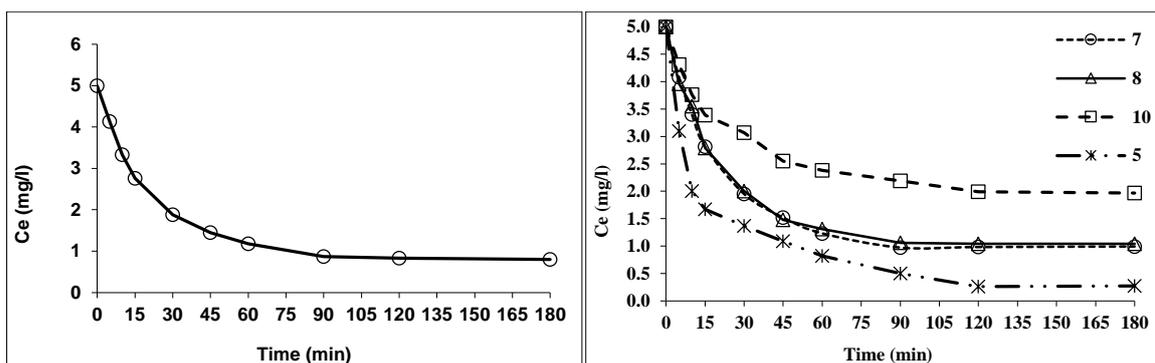


Figure 2: The effect of contact time (left) and pH (right) on HA removal by nanoadsorbent

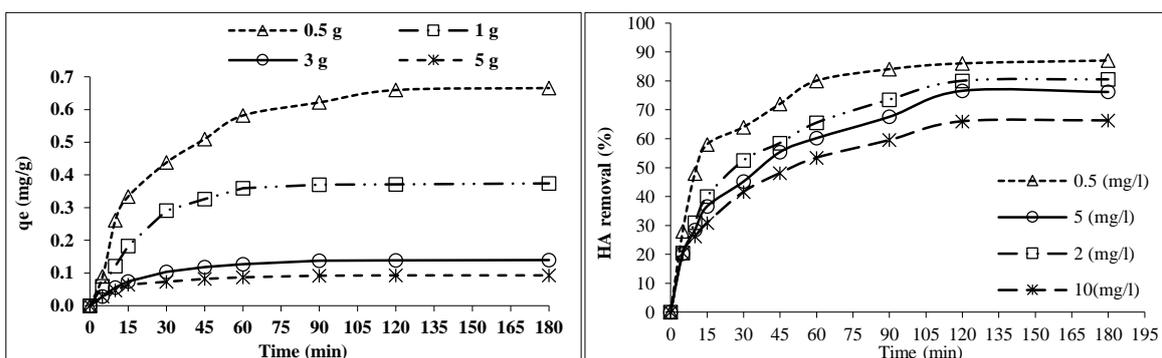


Figure 3: The effect of the adsorbent dose (left) and initial HA concentration (right)

Table 3: Adsorption Langmuir and Freundlich isotherm constants for HA with nanoadsorbent

Freundlich model		Langmuir model			
kf	n	R ²	a	b	R ²
(mg HA/g nanoadsorbent) (L water/mg HA) ^{1/n}	Dimensionless	-	mmol/g	Dm ³ / mmol	-
0.27	0.84	0.87	0.42	-6.23	0.78

Freundlich isotherm had better correlation in HA removal by the adsorbent than Langmuir. In the Freundlich isotherm, correlation coefficients (R^2) reaching a value more than 0.84, indicating that the rate of HA removal fitted well this model. The r-shaped adsorption isotherm indicates that there is a high affinity of contact time with adsorption rate.

3.3. Kinetic of HA adsorption

It found a good correlation coefficient between the kinetics of absorption of HA on nanoadsorbent and pseudo second order model ($R^2 = 0.997$). The removal rate of HA decreased from 0.64 to 0.84, increasing initial HA concentration from 0.5 to 10mg/l.

The equilibration time for the adsorption of HA at different concentrations ranged between 90 and 120 min for 0.5 and 10 mg/l of HA respectively. When an increasing occurs in initial concentrations the adsorption capacity of HA would enhance. Driving force is one of most important factor in the adsorption process so the adsorption capacity of HA is a function of HA initial concentration, because provide an important driving force to overcome the mass transfer resistance of the HA between the adsorbate and the adsorbent. In other words, the increase in the mass driving force allows more HA molecules to pass from the solution to the adsorbent surface. Therefore there is an inverse relationship between initial concentration and adsorption capacity [25].

Adsorption of HA to nanoadsorbent is strongly influenced by pH, so with variations in the initial pH and final pH causing changes in the adsorption rate it can be because of the HA usually

contains a wide variety of functional groups (-COOH, -OH, -NH₂, etc.), which are in uncharged state at lower pH, and hence tend to adsorb more [26]. Increasing the pH increases the ionization of HA and hence the concentration of the negatively charged ions which leads to decreasing amount of H⁺ ions. This was assumed that the system became less hydrophilic and thus HA, would bind hydrophobic compounds more effectively and therefore adsorption will be decreased.

4. Conclusions

The present study shows that surface area and pore volume of nano-adsorbent are 16.85(m²/g) and 0.021 (m³/g), the main elements of adsorbent are Ca, O, Fe and Na and the most components of adsorbents is composed of lime (CaCO₃ and CaO), which is about 94.25 percent of the total weight. None of the adsorbents, did not solubility in water. It was found that nano-adsorbent is an effective adsorbent for the removal of HA from aqueous solution. Under the prevailing conditions, the maximum nano-adsorbent removal efficiency was found to be 84.5% for 2 mg HA with contact of 5 g of nano-adsorbent in contact time of 90 min. Increasing pH from 5 to 10 levels significantly increased HA adsorption; as level of adsorbent dose increases, adsorption level of HA also increases; by increasing the HA concentration, adsorption rate decreases; while temperature increases from 25°C to 40°C, resulting in an increase in HA adsorption from 76.8% to 91.4%. The r-shaped adsorption isotherm indicates that there is a high affinity of contact time with adsorption rate.

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