Removal of Humic Acid from Contaminated Water by Nano-Sized TiO₂-SiO₂: A Case Study of Baba Sheikh Ali Treatment Sit of Isfahan-Iran

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Abstract: Humic substances in drinking water react with chlorine and form carcinogenic compounds. This study investigates application of SiO₂-TiO₂ nano particles and determines removal of Humic acid from an aqueous solution and also was conducted on both synthetic and actual water samples, was collected from Isfahan located in center of Iran. The effects of various parameters such as pH, contact time and adsorbent concentration were searched for isotherms. The adsorption kinetics data of HA on SiO₂-TiO₂ Nano-particle were well described by a pseudo-second-order model. The Langmuir isotherm model fitted the equilibrium data better than the Freundlich isotherm model and the model parameters were evaluated 0.25g of SiO₂-TiO₂ Nano-particle is found enough to remove 85 and 97% of Humic acid in synthetic and actual water samples respectively. The sample is prepared from an aqueous solution of 1.5 mg L⁻¹ at pH 3 with a shaking time of 30min.

Key words: Humic acid • Titanium dioxide • Nano particle • Silicon • Adsorption

INTRODUCTION

Amphiphiles molecules contain a polar head and a non-polar head. The most common Amphiphiles substances found in surface water are natural organic matters (NOMs), Humic acids (HAs) and Fulvic acids (FAs) [1]. Humic acid (HA) is one of the main components of Humic substances. Humic substances constitute the major part of dissolved organic materials in surface water and account for 90% of the dissolved organic carbon [2, 3]. Humic substances are abundantly found in the environment; in freshwater, they make up about 40-60% of the dissolved organic carbon [4]. Humic substances can react with Chlorine during water treatment and produce disinfection by products (DBPs) such as Trihalomethane (THMs) which have been shown to cause cancer in laboratory animals [5]. These substances can deteriorate the water quality by imparting color (yellowish to brownish) to the water [6]. So, it is important to remove HA from drinking water. There are many ways to remove Humic acid of water such as: coagulation/ flocculation, advanced oxidation, membrane separation, ion-exchange and adsorption [3, 7]. Of them, adsorption has been interested as an effective process due to its simplicity of design, ease of operation and high efficiency [8, 9]. Recently, there is a great interest in development of new adsorbents for effective removal of HA from water [8-22]. Nano-particles are a new group of materials with fast growing production and application [23]. Several studies have shown that natural mineral elements have high adsorption capacity for the removal of heavy metal ions [24]. Silica Nano-particles as one of the most important natural mineral particles due to the non-toxicity, high specific surface area and porosity are used.
This material due to its high polarity of the surface hydroxyl groups on appropriate interactions with the aquatic environment [25]. Therefore, to improve the interaction of these particles is modified. Surface modification is to reduce the surface energy of the particle and its hydrophobicity properties [26, 27]. Because Titanium is inert, non-toxic, high density as well as a photo catalyst, it has been used for water and wastewater treatment. Nano-Hybrid Silica and Titanium oxide with different surface characteristics are conducive to the adsorption capacity is increased [26]. When the surface is modified, Nano-particle uptake occurs faster than the previous state. Different methods have been used for surface modification and surface modification that can be deduced from the results of the surface modification of nano-particles with a smaller size improves the electrostatic properties of the particles. Since it depends on the material properties such as shape, size and geometrical parameters of Nano-particles in matter that has caused so many combinations of triple TiO$_2$-SiO$_2$ is used [27, 28]. During the research conducted indicated that Nano-particles SiO$_2$-TiO$_2$ side walls of hollow layers created in and around the surrounding selective exclusion and thus contribute to a better removal of material. Use SiO$_2$-TiO$_2$ has demonstrated high performance in the removal of environmental pollutants. During this study it was found that the silica-coated magnetite Nano-particles on the removal of heavy metals (mercury) are effective [29]. A study in 2005 by Takeshi Moriguchi et al. [30], conducted in China showed that the Nano-particles were also effective SiO$_2$-TiO$_2$ addition of. Mahmoud et al [31]. Shaheen [32] in 2009 in Egypt use of various soils of the silicone composition comprises, for the removal of cadmium and lead. Boparai et al. [33]. The aim of the present work was the examined and compare the adsorption of HA on SiO$_2$ nano particle with different factors including pH, contact time, different amount of adsorbent (TiO$_2$-SiO$_2$Nano-particle) and determine sorption isotherms and analyze regressively experimental data with the linear, Langmuir and Freundlich model.

**MATERIALS AND METHODS**

**Experimental**

**Adsorbent and Chemicals:** All chemicals used in this study were of analytical grade without further purification, also all stock solutions were prepared with double-distilled water. Glass materials and plastic bottles were washed with double-distilled water and exposed overnight to a 5% nitric acid solution. Stock solutions (1000 ppm) of Humic acid were prepared by dissolving the appropriate amount of Humic acid sodium salt (C$_{11}$H$_{14}$Na$_2$O$_4$), in double-distilled water. Solutions of required lower concentrations were prepared by diluting the stock solutions. Sodium hydroxide and hydrochloric acid was used for adjusting the pH. SiO$_2$ and TiO$_2$ adsorbent respectively in amount of 10 nm and 20 nm and also Sodium salt of Humic acid was prepared from Aldrich Company. The adsorbent was obtained by mixing molar ratio of 3/1 from SiO$_2$ and TiO$_2$ with a purity of 99% of Aldrich Company’s productions (20% w). For the preparation of Hybrid Nano-particles by sol-gel, the bottom-up process was used. This process generally involves the following steps:

In the first step, an initial solution including raw material and solvent was held at room temperature and stirred the complex mechanism of polymerization mechanism (citric acid - ethylene glycol) for preparation of tuberculosis for about 2 hours. In the second step to homogenize the tuberculosis transparent Reflux, the solution was held in the oil bath for 3 hours at temperature of 100 °C (to heat indirectly and uniformly). Postoperative reflux and achieve the final sol-gel process was carried out for 24 hours to form a hybrid. In the third step the gel was dried at a temperature of 120 °C for 1.5 hours in the furnace. The dried gel calcined in 550 °C to obtain the final nano powder [34, 35]. To investigate the surface characteristics and morphology of adsorbents were obtained by TEM.

**Methodology:** The experiments were carried out on synthetic samples and then on the water samples. Water samples of Baba sheikh Ali treatment site transferred to the laboratory in dark brown glass containers with a temperature of 4°C under standard conditions. Characterization of the water samples was undertaken according to the standard procedures. The concentration of HA in the water was directly determined by using a UV-visible spectrophotometer at 254 nm (Schimadzu /UV-1800). pH of water was analyzed by using (EDT-RE357 pH Meter. The amount of water parameters as pH, hardness, conductivity, total dissolved solid, turbidity, humic acid concentration was also measured as per described methods [34].

**Batch Experiments:** The effect of pH on the removal of HA was determined over the pH ranges of (3, 5, 7, 9) an initial HA concentration of 1.5 mg L, adsorbent dose 1 g/L and 60 min. The pH was adjusted by adding 0.1 or 0.01 mol/ L HCl or NaOH solutions. After the isothermal
RESULTS AND DISCUSSION

Characteristics of the Adsorbent: Fig.1 TEM (Transmission Electron Microscopy) images of Nano-particles TiO$_2$-SiO$_2$ produced by the Microscope has been developed, produced average particle diameter in the range of 50 nm. According to Fig.1, the average diameter of the particles was produced in the range of 50 nm. The results show that adding SiO$_2$ particles will increase the thermal stability of TiO$_2$ particles. SiO$_2$ Nano-particles can effectively grow within the TiO$_2$ particles and deal to Hydrocele stability of TiO$_2$. Also, studies have shown that the proper molar ratio of mixture of Titanium - silica gain additional stability. Silica Nano-particles with honeycomb structure hybridize on a uniform structure of TiO$_2$ and due to more adsorption. The reason for this criteria is that silica Nano-particles forced the Titanium particles to transfer to the Anatase phase (is one of the three mineral forms of titanium dioxide) to increase surface and improve absorption of it [35, 36].

Tests for Chemical Quality of Water: The general raw water characteristics in terms of parameters such as, pH, hardness, conductivity, total suspended solid, turbidity, humic acid concentration are presented in Table 1.

Effect of pH: The effect of pH of contact solution on HA sorption was investigated in different acidic, neutral and alkali solutions with pH 3, 5, 7, 9. The efficiency of Nano hybrid SiO$_2$-TiO$_2$ sorbent towards HA removal was strongly affected by the pH of primary solution. The results of this study are shown in Fig. 2. Maximum removal for actual and synthetic sample water were achieved in pH = 3 (97%) and pH = 3 (85%) respectively. Moreover, the HA sorption was found to increase from

Fig 1: TEM (Transmission Electron Microscopy) images of Nano-particles TiO$_2$-SiO$_2$ produced by the microscope has been developed, produced average particle diameter in the range of 50 nm. Pictures taken from various sites are shown.
Table 1: Average concentration of chemical quality parameters of water of Baba sheikh Ali Isfahan.

<table>
<thead>
<tr>
<th>parameters</th>
<th>pH</th>
<th>Electrical Conductivity</th>
<th>Total hardness</th>
<th>Total Dissolved Solids</th>
<th>Humic acid</th>
<th>Turbidity</th>
<th>So$_2$ \cite{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>7.7</td>
<td>365</td>
<td>185</td>
<td>22.5</td>
<td>1.6</td>
<td>28.5</td>
<td>31</td>
</tr>
<tr>
<td>Minimum</td>
<td>7.5</td>
<td>355</td>
<td>181</td>
<td>221.8</td>
<td>1.4</td>
<td>27</td>
<td>30</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>7.6±0.0066</td>
<td>355.33±0.22</td>
<td>183±2.66</td>
<td>222.03±0.108</td>
<td>1.5±0.0066</td>
<td>27.83±0.388</td>
<td>30.66±0.22</td>
</tr>
</tbody>
</table>

*Measurement unit: $^1$ µs/cm; $^2$ mg/L (CaCO$_3$) and $^3$ mg/L.

At higher pH values, dissociated HA molecules will be adsorbed due to electrostatic attraction HA showed high adsorption at low pH and decreasing adsorption as the pH increased \cite{37}. Similar behavior has been observed for HA by other adsorbents such as modified zeolite, clay minerals, activated carbon, iron oxides and chitosan \cite{38-48}.

**Effect of Adsorbent Dosage:** The results of this study are shown in Fig. 3. The effect of adsorbent dosage and the removal rate shows a decreasing trend with rising. This decline with increasing absorber to absorb the large number of unsaturated sites is absorbed. In fact, by increasing the amount of absorption that can absorb a large number of adsorption sites due to the limited number of companies remain free HA ions. Results show that increasing in concentration of SiO$_2$-TiO$_2$ Nano-particles to 2g/l deal to increase the efficiency of removal of HA. According to the adsorption process, the efficiency is dependent on surface area and achievable active sites due to weight of adsorbent. In fact, dynamic parameters like increasing of interactions and free bonds affect on adsorbent and HA adsorption. Yang et al. \cite{49}. Cardin and Rasheed Al investigated that increasing in concentration of SiO$_2$-TiO$_2$ Nano-particles more than 2.5g/L deal to increase the efficiency of removal in 2003 \cite{50}. Hung et al. \cite{51} studied the use of TiO$_2$ Nano-particle to decompose organic materials by photo catalytic oxidation and showed that the optimum concentration of TiO$_2$-SiO$_2$ Nano-particle is 0.1 to 1 g/L, increasing amount of catalyst decreases the efficiency of removal.

**Effect of Contact Time:** In order to find out the equilibrium time for HA adsorption, by TiO$_2$-SiO$_2$ nano particle adsorbent batch experiments were conducted over a contact time range of 30 to 120 min. According to Fig. 4 the amount of HA adsorbed decreased with increasing the contact time. The adsorption rate was very high for the first 30 min reaching the equilibrium after 120 min. This is because that in the initial stage a large number of empty surface sites are available for adsorption during and over time, the remaining empty surface sites are difficult to be occupied due to repulsive forces between the adsorbate molecules in the aqueous solution.
Fig 4: Effect of Contact Time on Adsorption of SiO2/TiO2 Nano Particle  SiO2/TiO2 = 1g/l, Ha=1.5mg/l, pH=3

and those on the adsorbent surface [52]. On the other hand the rapid adsorption observed during the first 30 min was perhaps due to the plentiful availability of sorption sites and large surface area available for the adsorption of the Humic acid on the TiO2-SiO2 nano particle surface. adsorption time depends on adsorbent capacity and equilibrium time [53]. The results, from the adsorption of humic acid by activated sludge, showed that the equilibrium adsorption levels were attained after about 20 minutes of exposure for activated sludge [54].

**Modeling of Adsorption Isotherms:** The equilibrium data were modeled with linearized Langmuir, Freundlich expressions. At first the experimental values of q and C are arranged with the linearized equations in order to determine the model parameters and the isotherms are reconstituted using the determined values. Linear correlation coefficients (R^2) calculated from linear regression analyses are the most extensively used criteria in evaluating good experimental data and linearized forms of isotherm Equations (Table 2). Reveals that the Langmuir isotherm yielded best-fits to the experimental data, probably due to the homogeneous and monolayer nature of surface sites involved in the humic acid uptake [54].

**Adsorption Kinetics:** Adsorption kinetic is one of the most important factors for designing adsorption system and determines the residence time of the adsorbent in the adsorption process. Adsorption Kinetic depends on physical and chemical properties of the adsorbent. In this work adsorption kinetics of HA on TiO2-SiO2 Nano-particles were described with the pseudo-first-order model and pseudo-second-order model. It can be concluded that the pseudo second order kinetic model can produce better fitting to the experimental data of HA adsorption. According to the calculated kinetic Parameters shown in Table 3.

**CONCLUSIONS**

The TiO2-SiO2 Nano-particle was investigated as an adsorption material for Humic acid removal. Humic acid adsorption by Hybrid TiO2-SiO2 nano particle was studied in batch mode and it was strongly dependent on adsorbent dosage, initial pH and contact time. The isotherm study indicates that adsorption data fit well with the Langmuir model. Values from the Langmuir model indicate that the removal of Humic acid was favorable. 0.25 g of TiO2-SiO2 nano particle was found enough to remove 97% and 85% of the humic acid respiratory in synthetic and actual sample from an aqueous solution containing 1.5 mg L of humic acid at pH 3 with shaking time of 30 min. The kinetic process was well predicted by pseudo second-order model. The experimental isotherm data of HA adsorption on to nano particle TiO2-SiO2 were

| Table 2: Parameters of Langmuir and Freundlich for adsorption of Humic acid on TiO2-SiO2 Nano-particle. |
|-----------------------------------------------|-----------------------------------------------|
| Langmuir \((1/q =1/k Q (1/C)+1/Q )\)             | Freundlich \((logq =1/n)logC +logk )\)          |
| \(K_1\)                                      | \(K_f\)                                      |
| 0.51                                         | 4.7                                           |
| \(Q_m\)                                      | \(N\)                                        |
| 10.21                                        | 0.976                                         |
| \(R^2\)                                      | \(R^2\)                                      |
| 0.94                                         | 0.93                                          |

| Table 3: Parameters of kinetic models for HA adsorption onto TiO2-SiO2 Hybrid Nano-particle. |
|-----------------------------------------------|-----------------------------------------------|
| log\((q-q_p)\)=log\(k_{1}t/2.303t\) first-order kinetic | \((1/q =1/k_q (1/t)+1/q)\) second-order kinetic |
| \(K(1/min)\)                                     | \(K(1/min)\)                                 |
| 0.003                                          | 1428.6                                       |
| \(q_p\)                                        | \(q_e\)                                      |
| 0.922                                          | 0.0075                                       |
| \(R^2\)                                        | \(R^2\)                                      |
| 0.788                                          | 0.99                                         |
well fitted to Langmuir models. This study revealed that this adsorbent is an efficient, available and cost effective alternative sorbent material for removing humic acid from humic acid contaminated water.

REFERENCES


