RESEARCH ARTICLE

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Application of Modified Walnut Shell With Zinc Oxide (ZnO) Nanoparticles in Removal of Natural Organic Matters (NOMs) from Aqueous Solution

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Background & Aims of the Study: Natural organic matters (NOMs) are a mixture of chemically complex polyelectrolytes produced mainly from the decomposition of plant and animal residues that are present in all surface and groundwater resources. This paper evaluates the aqueous NOMs adsorption efficiency on walnut shell modified with Zinc Oxide (ZnO).

Materials & Methods: This study examined the feasibility of removing NOMs from aqueous solutions using walnut shell modified with ZnO. The effects of NOMs concentration, modified walnut shell with ZnO dosage, and pH on adsorption of NOMs by modified walnut shell with ZnO were evaluated.

Results: The adsorption capacities of modified walnut shell with ZnO in the best conditions were 37.93 $mg.g^{-1}$. The results also demonstrated that adsorption capacity of NOMs on modified walnut shell with ZnO was higher in lower pHs due to significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and negatively charged NOMs. And finally adsorption capacity decreases as adsorbent dose increase.

Conclusions: Walnut shell modified with ZnO can be proposed as a natural adsorbent in the removal of NOMs from aqueous solutions.

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Background

Natural organic matters (NOMs) are a group of linear and cyclic organic materials including humic substances, hydrophilic and hydrophobic acids, and amino acids. This group of organic matter is present in surface and groundwater resources, but their presence at high concentration in the raw water, municipal water utilities are faced with serious problems. High concentrations of these compounds reduce water quality by two ways: (1) reacts with disinfectants and formed disinfection byproducts (DBPs), on this basis these compounds called disinfection byproducts precursors. (2) Intensified microbial regrowth in water distribution networks and destruction of microbiological, physical (taste and odor

formation) and chemical water quality. Among the other adverse effects of natural organic matters, increase the consumption of coagulant and disinfectant in water treatment processes can be noted (1-4).

In the past, the importance of natural organic matter in drinking water was due to aesthetical importance and color formation in water that led to consumer's compliances. But today, due to disinfection byproducts (DBPs) formation such as Trihalomethanes (THMs) which are often carcinogenic. Therefore, survey amount of natural organic matter at influent of water treatment plant regarding to THMs formation potential is essential (5).

Natural organic matters are composed of two parts: hydrophobic and hydrophilic. Hydrophobic part also called humic substances and contains humic acid (HA), fulvic acid (FA) and humins. On average, about 50% of dissolved organic carbon content of the surface water is humic substances. The hydrophobic organic materials have naturally cyclic and phenolic structure and also have double bonds. In contrast, hydrophilic natural organic materials have mainly linear structure and formed nitrogen compounds, carbohydrates, sugars and amino acids (6).

One of the best methods of controlling DBPs formation is to remove the precursor compounds by processes such as adsorption and membrane separation. Because of the complex structure and low concentration of NOM, fully characterizing NOM is very difficult. Thus, to assess the water quality and efficiency of treatment processes, the use of lumped parameters is required. Hence surrogate parameters, total organic carbon (TOC), dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm can be used to quantify the concentration of NOMs (2,7). The most common processes for removal of NOMs from aqueous solution are coagulation and flocculation, ion exchange, nanofiltration, reverse osmosis and adsorption. Recently a great attention has been paid to adsorption process (7).

The adsorption process using activated carbon as adsorbent has been widely used for removal of NOM from water (8,9). Adsorption efficiency depends on several operating variables such as pH, type of adsorbent and organics. In the case of expensive adsorbent application, the adsorption process will also be expensive. Therefore, it is better to use natural adsorbents such as agricultural wastes which are inexpensive and available. Current study was intended to remove NOMs from its aqueous solution using walnut shell modified with Zinc Oxide (ZnO) nano particle as an adsorbent.

Materials & Methods

Preparation of walnut shell modified with ZnO

0.75 g of ZnO powders were carefully weighed and placed into 500 mL Erlen- meyer flask. Then, 200 ml of deionized water is added and the suspension was stirred for 30 min (agitation rate=200 rpm) until the solution turned into colorless. 15 g of walnut shell were added separately to each of the solutions and stirred again properly for 12 hours at 200 rpm. After that, this material was dried in an oven at 110 ◦C for 8 h. Then the temperature of oven was fixed to 185 ◦C for 2 h to dry the adsorbent completely. The dried powder was washed with two distilled water and filtered. Finally, the filter cake is placed in a beaker and then dried in an oven at 100°C for 12 h.

Effect of pH

To study the effects of pH on the adsorption of NOMs onto walnut shell modified with ZnO, 50 mg of adsorbent was dispersed into 100 mL solution containing 50 mg/L of NOMs. The initial pH values were adjusted from 3.0 to 12.0 using various amounts of HCl and NaOH and the suspensions were shaken for 4 h at 20±1 °C. The amounts of adsorbed NOMs were calculated as the difference between the initial

and final concentrations when the equilibrium was reached. The results are based on at least three replicate experiments for each pH value.

Adsorption experiments

The stock solution of NOMs was prepared by dissolving 926 mg of humic acid (purchased from Acros Company) in one liter of distilled water. Regarding to 54% purity of humic acid, the concentration of the stock solution was 500 mg/L.

In all of the adsorption tests, 50 mg of walnut shell modified with ZnO as the adsorbent was placed in the bottles and 100 mL of solution containing a specific amount of NOM were added to the adsorbent. Then, the bottles were sealed with aluminum foil-lined and placed on a rotary shaker and shaken at 180 rpm to ensure that the adsorption process reached equilibrium. In regular time intervals, solution samples were taken and filtered through a 0.45 µm filter. Then NOM residue in the solution was determined by a UV/VIS Spectrometer (+T80) at 254 nm.

Adsorption of NOMs on walnut shell modified with ZnO was calculated using mass balance equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

Where q_e (mg g^{-1}) is the amount of walnut shell modified with ZnO concentration, C_0 and C_e are the initial and final NOMs concentrations (mg L^{-1}), V is the solution volume (L), M is the adsorbent mass (g).To express the NOMs removal efficiency, the following equation was used:

$$\text{Removal efficiency, (\%)} = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (2)$$

Where C_0 and C_f represent the initial and final NOMs concentrations, respectively. All tests were performed in duplicate to insure the reproducibility of the results; the mean of the two measurements is reported.

Results

The results of effect of pH on the adsorption of NOMs by modified walnut shell with ZnO are graphically represented in Fig. 1. According to this figure, the adsorption efficiency of NOMs decreases with the increase in pH. It can be observed from the figure that the maximum adsorption of modified walnut shell with ZnO occurred at pH=3 and q=6.5 mg/g.

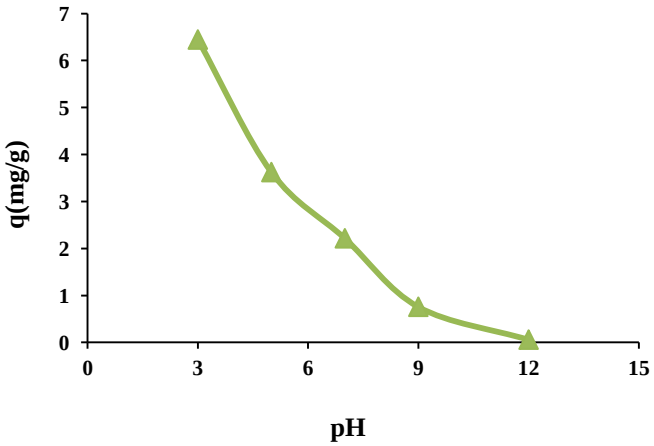

Figure.1) Effect of pH on adsorption of NOMs on to modified walnut shell with ZnO

The adsorption data at different initial NOM concentrations on modified walnut shell with ZnO are shown in Figure 2.

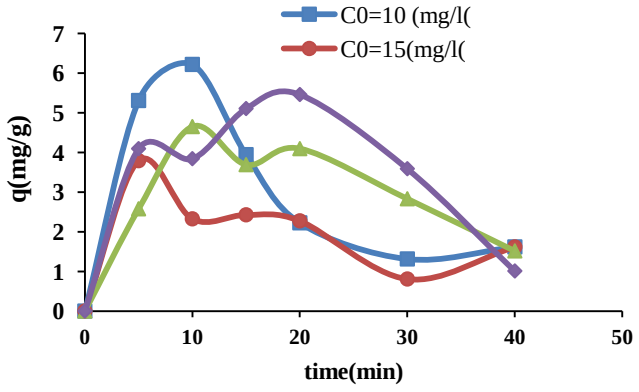

Figure.2) Effect of initial concentration and contact times on NOMs adsorption capacity of walnut shell modified by ZnO with time

The effect of adsorbent dosage on removal of NOMs has been presented in Figure 3.

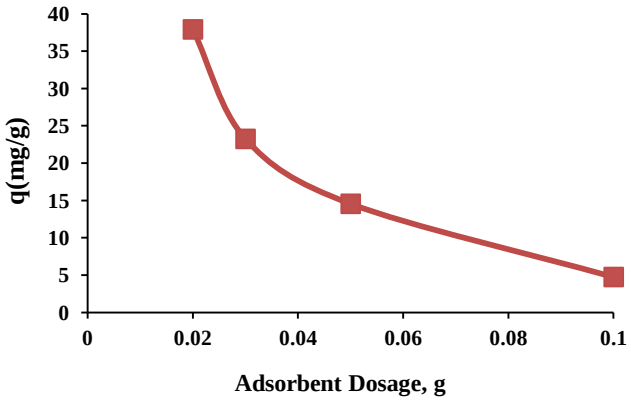

Figure 3) Effect of adsorbent dose on the adsorption of NOMs from aqueous solution

Discussion

It can be observed from the figure 1 that the maximum adsorption of modified walnut shell with ZnO occurred at pH=3 and q=6.5 mg/g. The results are in agreement with Namasivayam and Bhattacharyain that reported the pH=3 was optimum pH for adsorption of Cr onto adsorbents such as activated carbon and low cost adsorbent, respectively (10,11).

As pH increases, the NOM molecules will become less coiled and less compact due to greater charge repulsion, and the adsorption capacity might consequently decrease. In addition, as pH increases, weakly acidic NOM with carboxylic and phenolic moieties becomes more negatively charged (2,12). Thus, at higher pH, repulsion between NOM and modified walnut shell with ZnO surface coated with NOM would increase, hindering further adsorption of NOM.

It can be ascertained from figure 2 that the maximum adsorption capacity of NOMs at a concentration of 10 mg/l and contact time 10 min was equal to 6.21 mg/g. reduction of adsorption capacity after 10 minutes may be due to desorption of NOMs from adsorbent. Previous studies reported similar results (13). The amount of NOM adsorbed onto modified walnut shell with ZnO increased with contact time for all NOM concentrations. The curves reveal that the adsorption kinetics of NOM on modified walnut shell with ZnO mainly consists of two stages: an initial rapid stage related to the instantaneous external surface adsorption of NOM. The second slower stage is the gradual adsorption stage that takes place before NOM uptake attains equilibrium. The high adsorption rate during the initial period of 10 min is due to the number of available adsorption sites of the bare surface of adsorbents. As these sites became progressively covered, the rate of adsorption decreased (14). The masses of modified walnut shell with ZnO used in the removal of NOMs from aqueous solution are critical for the application of this adsorbent in removal of natural organic matters. Whatever the amount of adsorbent used to remove a certain amount of natural organic matter is less; therefore the removal of NOMs with modified walnut shell with ZnO is more economical.

As shown in the figure 3, the maximum adsorption capacity for above adsorbents was determined to be 0.02g per mass of adsorbent.

At 0.02 g of walnut shell, contact time (5 min) and humic acid concentration (30 mg/l), the adsorption capacity was 37.93 mg/g. it can be concluded that the adsorption capacity decreases as adsorbent dose increase. Other studies also show that the humic acid adsorption decreases as adsorbent dose increase which indicates the binding sites on the adsorbents are not fully used (15). Mansoori et al. studied the kinetics and isothermic behavior of SiO_2 nanoparticles in removal of humic acid from aqueous solutions and reported that the adsorption efficiency decreased with an increase in the adsorbent dose (16). Therefore, Walnut shell modified with ZnO due to its availability, cost effectiveness and also its high adsorption efficiency, can be proposed as a natural adsorbent in the removal of NOMs from aqueous solutions.

Footnotes

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Conflict of Interest:
The authors declare no conflict of interest.

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