Research Article

The Treatment of Waste water by Modiied Nano Hydroxyapatite: Synthesis, Characterization and Studying the Influence of using the Treated Waste water on some plants and Soil Properties

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Received: 10-01-2018; **Revised:** 27-01-2019; **Accepted:** 08-02-2019.

ABSTRACT

The reuse of treated wastewater (TWW) in agriculture has become an attractive option for expanding and conserving available water supplies which suffer from scarcer. In this paper, using synthetic nano hydroxyapatite (nHAp) powders, which is prepared by microwave heating based wet chemical method and its modification with humic acid (HA) as a sorbent for wastewater treatment (WWT). The nHAp and nHAp-HA complex (modified nHAp) were characterized by different techniques. Parameters such as a sodium adsorption ratio (SAR), salinity (EC), soluble sodium percentage (SSP) and residual sodium carbonate (RSC) were used to assess the suitability of water for irrigation purposes. Moreover, pots experiment was conducted to study the effect of irrigation with non- and TWW by adsorption onto nHAp and modified nHAp by using the fixed bed column model on some soil and Jew's mallow plant properties. The results showed that TWW by modified nHAp was suitable for irrigation. Plant and soil analysis showed significant changes in plant and soil properties due to irrigation with TWW where the results showed that WWT by modified nHAp had a significant reduction of total dissolved solids, heavy metals and organic contaminants which in turn enhanced chemical properties of TWW.

Keywords: Wastewater treatment, modified nHAp, Jew's mallow plant.

INTRODUCTION

The scarcity of water supplies to meet the needs of population growth and rapid development in agriculture have given cause for concern in semi-arid and arid countries towards the use of non-conventional water resources in particular the sewage effluent. Moreover, the population growth has not only increased the fresh water demand, but also increased the volume of wastwater generated.[1] Therefore, in arid and semi-arid areas, recycling of wastwater may have a greater impact on future usable water supply than any of the other technologies aimed for increasing water supply such as water harvesting, desalting of sea water, weather modification of artificial rain jets.

Wastewater reuse in agriculture has substantial benefits for agriculture and water resources management, but can also pose substantial risks to public health-especially when used non treated for crop irrigation. There can also be chemical risks to plant health, and risks to the environment in the form of soil and groundwater pollution. Therefore, we must reduce the risks of wastewater reuse in agriculture, in particular those to public health through properly planned and managed wastewater irrigation practices.

Wastewater pollutants could be eliminated by several traditional techniques, including chemical precipitation[2], reverse osmosis[3], electrochemical treatment techniques[4], ion exchange[5], membrane filtration[6], coagulation[7], and adsorption[8]. However, adsorption technology is regarded as the most promising one to remove pollutants from effluents among these techniques due to its low cost-effective, high efficiency, and simple to operate for removing trace levels of pollutants. Although traditional sorbents could remove pollutants from wastewater, but its sorption capacities and efficiencies are low and limited. To solve these defects of traditional sorbents, nano materials are used as the novel ones to remove pollutants from wastewater where nanostructure adsorbents have exhibited much higher efficiency and faster rates in water treatment due to their large surface area and high reactivity.

As a member of apatite mineral family, hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, nHAp] is an ideal adsorbent material for long-term containment of contaminants because of its high sorption capacity for dissolved organic matter and heavy metals[9, 10], availability, low cost and high stability under oxidizing and reducing conditions.[11] Sorption mechanisms of metal ions from polluted wastewater onto nHAp based materials are diverse and include mainly the ion exchange, dissolution/precipitation, and formation of surface complexes processes.[12]

To enhance the sorption capacities, nHAp particles are modified by using HA[13] where, HA is a subclass of soil organic matter, generally contains both hydrophobic and hydrophilic moieties as well as many functional groups (−COOH, −C=O, and −OH) bonded to the aliphatic or aromatic carbons in the macromolecules. For that, HA can react with inorganic and organic contaminates where the hydrophobic fraction of HA interacts with organic contaminates by hydrophobic-hydrophobic interaction mechanism while carboxylic and hydroxyl group interact with heavy metals by electrostatic and complexation mechanisms.[14,15]

Accordingly, the objective of this study is to investigate WWT by adsorption onto nHAp and modified nHAp and studying the influence of using the TWW on some plant and soil properties.

MATERIALS AND METHODS

MATERIALS

Wastewater samples

Wastewater samples were collected from Sohag (Eldare area), Egypt, after second treatment. Chemical analysis of wastewater "EC, heavy metals, pH, TOC, TDS and major ions" before and after treatment process had been occurred. [16]

Nano hydroxyapatite

The nHAp powders were synthesized from high purity calcium chloride 2-hydrate $CaCl_2.2H_2O$ (99%) and orthophosphoric acid H_3PO_4 (85%), as the main reactant materials, while solution pH was controlled by the addition of NH_4OH solution (30%).

Humic acid

Humic acid in its potassium salt was obtained from Sigma-Aldrich Co., Germany.

Soil samples

Soil material was taken from the surface layer (0-30 cm) of an experimental farm, at the Shandwell Agricultural Research station, Sohag Governorate, Egypt.

Seeds

Egyptian Jew's mallow (cv. Balady) seeds were used in the experiment. These seeds were obtained from the Ministry of Agriculture.

METHODS

Synthesis of nHAp

The nHAp powder in the current work was produced according to the wet chemical method with the use of precipitation from the aqueous medium through a titration process by reacting high purity calcium chloride 2-hydrate $CaCl_2.2H_2O$ (99%) and orthophosphoric acid H_3PO_4 (85%), as the main reactant materials in accordance to the molar ratio of Ca/P = 1.67.[17]

Preparation of modified nHAp

The modified nHAp was carried out by mixing 25 g of nHAp and 0.25 g/L of HA solution in a orbital shaker at 5000 rpm for 1 day at pH 6.0 and ionic strength, 0.001 mol dm^{-3} as KCl.[18] The precipitated material was ground and stored for future experiments.

Wastewater treatment

The treatment of wastewater was carried out by adsorption on nHAp and modified nHAp by using the fixed bed column model as described before in reference.[18] The data were subjected to analysis of variance (f-test) using a statistical analysis system (SAS) and the means were separated using least significant difference (LSD 0.05).

Soil analysis

Some physical and chemical properties of soil such as: mechanical analysis, pH value, calcium carbonate content, organic matter, EC, soluble cations and anions have been determined as previously reported.[19]

Irrigation with non- and TWW

Pots experiment was carried out between June and August during the seasons of 2016 and 2017 at the experimental station of Agriculture Research Centre, Sohag Governorate, Egypt to investigate the effect of irrigation by non- and TWW on the soil's chemical and physical properties and the vegetative growth of Jew's Mallow plant. Pots were filled with 1 Kg of soil sample. Then, the seeds were cultivated in pots and were irrigated during planting with three types of wastewater; non- and TWW by nHAp, and modified nHAp from stock TWW. Plants were irrigated using the same volume of water at each time during the experiment. Throughout the vegetative growth stage (growing stage was 80 days), three random plants were taken after the experiment end from each pot per treatment for determination of plant height (cm), number of leaves per plant, fresh and dry weight per plant (g), leaf area per plant (cm^2) according to Ghoneim and El-Araby.[20] The data collected were subjected to analysis of variance (ANOVA) using Statistical Analysis System (SAS) and means were separated using least significant difference (LSD 0.05).

RESULTS AND DISCUSSION

Characterization of nHAp

The characterization of nHAp and modified nHAp was consistent with the literature data.[18] XRD patterns of the prepared nHAp are shown in Fig.1, the prepared nHAp was in good agreement with the reference pattern of pure nHAp.[21] The result explained that well crystallized of nHAp was prepared. The average particle size (D) of nHAp was estimated using Debye Scherer equation.[22]

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where λ, β, and θ is X-ray wavelength light, the complete width of the half maximum of diffraction peak, and the diffraction angle respectively. K is a shape factor and usually taken as 0.89. It was found that the particle sizes were on the nanoscale (about 35 nm).

FTIR analysis demonstrated that the surface modification of nHAp by HA has been carried out successfully as displayed in Fig. 2 where the modified nHAp spectrum shows a main absorption peak at 1583 cm^{-1} corresponding to stretching frequency of carbonyl group in COO^{-} group of HA. However, the intensity of peaks at 1583 cm^{-1} and 1385 cm^{-1} in the FTIR spectrum of the modified nHAp is less in comparison with the intensity of the same peaks in the pure HA spectrum. This behavior refers to the reaction of the carboxylate group with nHAp surface[18]. Moreover, the statistical studies using t-test ($t_{0.05}$) have shown a significant improvement in the surface area of nHAp after the reaction with HA where the surface area of nHAp and modified nHAp were 60.618 and 78.165 m^2/g, respectively. Therefore, we can say that the modification of nHAp by HA has enhanced the surface area of nHAp dramatically.

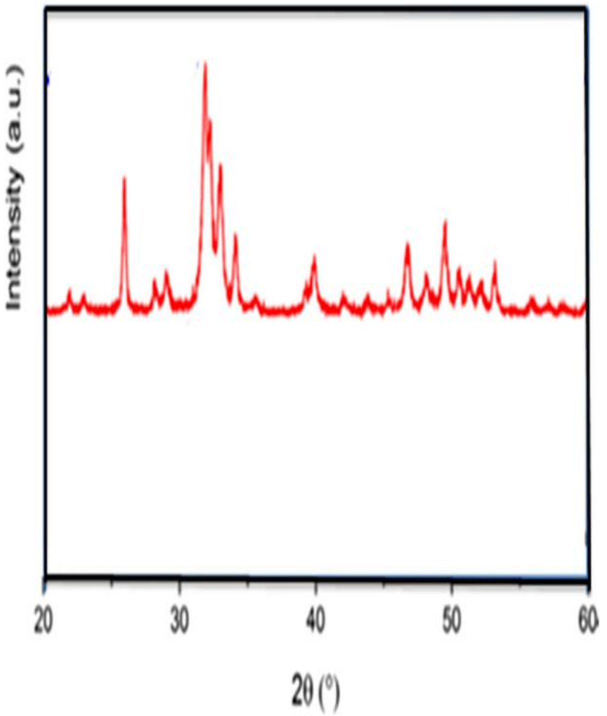

Figure 1: The XRD patterns of nHAp

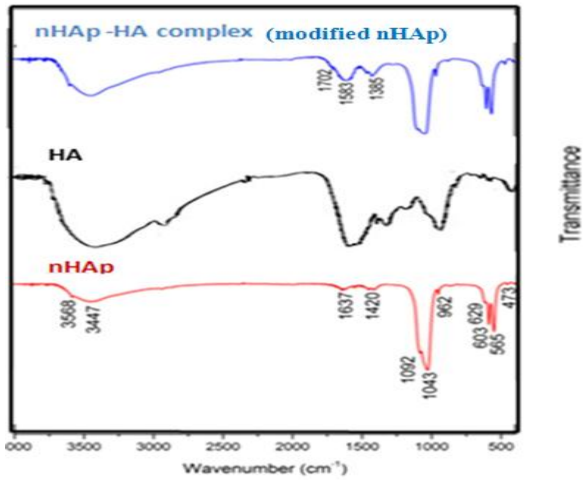

Figure 2: FT-IR spectra of HA, nHAp and modified nHAp

Wastewater treatment

The wastewater treatment process was done by adsorption onto two sorbents "nHAp and modified nHAp" by using fixed bed column model[18].

The results in Table 1 obvious that modified nHAp presents a better activity compared to nHAp in WWT from heavy metals and organic contaminants. This refers to highly BET surface area and active site contents of modified nHAp rather than of nHAp. Furthermore, f-test results showed that the treatment process by the nHAp and modified nHAp had a significant effect on all heavy metals concentration and TOC of wastewater except on Cr^{+6} had insignificant. In addition, treatment by modified nHAp had a significant effect on Se^{+4}, B^{+3}, Co^{+2}, Mn^{+2}, Cu^{+2} and Fe^{+2} than nHAp due to LSD results (C.f. table 1).

The results in table 2 showed that modified nHAp enhanced the chemical analysis (EC, pH, TDC, major cations, and major anions) of wastewater rather than of nHAp. Moreover, f-test results showed that the treatment process by the nHAp and modified nHAp had a significant effect on the chemical analysis (EC, pH, TDC, major cations, and major anions) of wastewater except had an insignificant effect on Ca^{+2} and SAR. This insignificant effect refers to the highly composition of nHAp with calcium. Furthermore, there was a significant effect on some chemical analysis after treatment by modified nHAp than nHAp due to LSD values.

Table 1: Heavy metals concentrations and TOC of non- and TWW.

Samples	Cd^{2+} ppm	Fe^{2+} ppm	Zn^{2+} ppm	Cu^{2+} ppm	Mn^{2+} ppm	Co^{2+} ppm	Cr ppm	Pb^{2+} ppm	B^{3+} ppm	Se^{4+} ppm	TOC %
Non TWW	0.019	0.965	0.109	0.075	0.082	0.179	0.049	0.054	0.132	4.030	0.40
TWW by nHAp	0.00	0.352	0.000	0.049	0.019	0.047	0.000	0.000	0.053	0.194	0.01
TWW by modified nHAp	0.00	0.065	0.000	0.000	0.000	0.000	0.000	0.000	0.015	0.022	0.00
$LSD_{0.05}$	0.0014	0.0377	0.0057	0.0064	0.0058	0.0118	0.1133	0.0028	0.0192	0.2297	0.0288

Table 2: Major cations and anions concentrations of non- and TWW.

Samples	Ph	Ec ds/m	TDS mg/l	SAR	Na^+ meq/l	K^+ meq/l	Ca^{2+} meq/l	Mg^{2+} meq/L	Cl^-meq/l	SO_4^{2-} meq/l	NO_3 meq/l	HCO_3^- meq/l
Non TWW	8.58	0.95	$0.61*10^3$	2.48	4.08	0.40	1.61	3.80	4.60	1.77	0.49	2.48
TWW by nHAp	8.01	0.81	$0.52*10^3$	2.26	3.36	0.32	1.23	3.20	4.11	1.70	0.30	2.00
TWW by modified nHAp	7.62	0.74	$0.48*10^3$	1.98	2.80	0.27	1.00	3.00	3.80	1.57	0.10	1.60
$LSD_{0.05}$	0.2088	0.1073	16.9687	3.22	0.2336	0.0860	1.675	0.2007	0.3324	0.1696	0.0702	0.1945

Evaluation of non- and TWW quality for irrigation

Some parameters such as SAR, EC, SSP and RSC presented in table 3 had been used to assess the suitability of water for irrigation purposes.

Sodium adsorption ratio (SAR)

The main problem with high sodium concentration is its effect on soil permeability and water infiltration. The results in table 3 indicated that the non- and TWW from the study area is an excellent water class (S1) in water classification according to SAR and can be used for irrigation on almost all soils, with little danger of the development of harmful levels of exchangeable sodium.[23]

Salinity (EC)

As well as sodium effects on soil permeability and water infiltration. Sodium also contributes directly to the total salinity of the water and may be toxic to sensitive crops. Data in table 3 showed that the non- and TWW by nHAp samples lie in the class of C3 in table of the irrigation water classification according to salinity indicating high salinity water, which can be used for soil with restricted drainage and plants with good salt tolerance should be selected but TWW by modified nHAp sample lies in the class of C2 in same table of the irrigation water classification according to salinity indicating medium salinity water, which can be used if a moderate amount of leaching is occurs and plants with moderate salt tolerance can be growth without special practices for salinity control.[23]

The Soluble Sodium Percentage (SSP)

The SSP was calculated by the following equation[24]

$$SSP = \frac{(Na^+)\times 100}{Ca^{2+} + Mg^{2+} + Na^+ + K^+}$$

Where all the ions are expressed in meq/L.

The SSP also used to evaluate the sodium hazard of irrigation water like SAR, but it expresses the percentage of sodium out of the total cations and not as SAR correlating the sodium with the Ca^{2+} and Mg^{2+}only. The calculated SSP values of non- and TWW by nHAp in table 3 indicated that this water is permissible class in table of classification of irrigation water based on SSP while the calculated SSP value in case of TWW by modified nHAp indicated that this water is good class for irrigation in the same classification.[25]

The residual sodium carbonate (RSC)

The RSC can be calculated as follows[26]

$$RSC = \left(CO_3^{2-} + HCO_3^{-}\right) - \left(Ca^{2+} + Mg^{2+}\right)$$

All ion concentrations are reported in meq/l.

The water with high RSC has high pH and land irrigated by such waters becomes infertile owing to deposition of sodium carbonate as known from the black colour of the soil. The calculated RSC values in table 3 showed that all samples have RSC less than zero and are good suitable for irrigation purposes where RSC value less than 1.25 meq/l is safe for irrigation, a value between 1.25 and 2.5 meq/l is of permissible quality and a value more than 2.5 meq/l is unsuitable for irrigation according to the USSL.[23] Hence, non TWW and TWW by nHAp are permissible for irrigation, but TWW by modified nHAp is good for irrigation.[24]

Effect of using non – and TWW in irrigation

In order to evaluate the influence of irrigation with non- and TWW on some plant and soil properties under pots experiment. Jew's mallow seeds were sown in pots and were irrigated under different irrigation sources with non- and TWW by nHAp and modified nHAp in three replicated.

Table 3: Some parameter values of non- and TWW.

Sample	SAR	EC (ds/m)	SSP	RSC (meq/l)
non treated wastwater	2.48	0.95	41.4	< 0
TWW by nHAp	2.26	0.81	41.3	< 0
TWW by modified nHAp	1.98	0.74	39.6	< 0

Effect of irrigation with non- and TWW on some physical and chemical properties of soil samples

Data in table 4 shows the soil physical properties (soil texture, $CaCO_3$, saturation percentage (SP) and organic matter (OM)) before and after irrigation by non- and TWW. The results indicated that slightly change in physical properties of soil under different irrigation sources with little increasing in OM contents, $CaCO_3$ and SP in case of using non TWW than TWW. Although, these results refer to EC values of non- and TWW as described before in table 2 are not high enough to change the physical properties of soil, but the change in physical properties will be significant after long-term using non TWW while it will become much better after irrigation with TWW by modified nHAp.

Table 4: Physical analysis of soil samples under investigation

Sample	SP ml/100gm	OM %	$CaCO_3$ %	Mechanical analysis			Texture class
				Clay %	Silt %	Sand %	
Blank	56	0.81	4.97	20.6	57	22.4	Silt Loam
Non TWW	59	0.99	5.31	20.6	57	22.4	Silt Loam
TWW by nHAp	56	0.67	4.90	20.6	57	22.4	Silt Loam
TWW by modified nHAp	56	0.60	4.88	20.6	57	22.4	Silt Loam

Data in table 5 shows values of pH, EC(ds/m), cations (meq/L): Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and anions (meq/L): CO_3^{2-}, HCO_3^{-}, Cl^{-}, SO_4^{2-} before and after irrigation with non- and TWW. The results explained that there change in the chemical properties of the soil samples under investigation.

Soil pH and EC are important factors that affect nutrient availability and absorption by plant roots. The soil pH and EC had significantly increased by using non TWW as compared to using TWW in irrigation of soil under investigation. This is probably due to the alkaline nature and high concentrations of major cations and anions in non TWW[27]. The highest values of EC, pH, major cations and major anions were after irrigation with non TWW while the smallest values were after irrigation with TWW by modified nHAp.[28] Moreover, the results showed that the chemical properties of soil such as EC, pH and major cations and anions decreased after irrigation by TWW by modified nHAp than nHAp. Consequently, soil chemical properties became much better after irrigation with TWW by modified nHAp than nHAp. Hence, the irrigation with non TWW seems to increase salinity, pH and major ions in soil.

Table 5: Chemical Analysis of soil samples under study (in the peast extractable)

Soil sample	pH	EC ds/m	Cations meq/l				Anions meq/l			
			Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}
Blank	7.90	1.02	8.69	0.78	0.82	0.25	-	4.25	5	2.30
Non TWW	8.3	1.3	8.62	1.3	3.93	0.26	-	4.80	4.69	2.98
TWW by nHAp	7.70	0.8	6.3	1.00	2.93	0.15	-	4.01	3.33	1.62
TWW by modified nHAp	7.60	0.67	4.8	0.82	2.01	0.10	-	3.66	3.02	1.07

Effect of irrigation with non- and TWW on JEW's Mallow properties (vegetative growth characters)

Means of vegetative growth characters of Jew's mallow: plant fresh weight (g), plant dry weight(g), number of leaves per plant, number of branches per plant, plant height (cm), leaf area (cm^2), RWC % and photosynthetic pigments under non- and TWW are presented in table 6. The results showed that plant fresh weight (g), number of leaves per plant, number of branches per plant, plant height (cm), RWC %, photosynthetic pigments parameters measured except plant dry weight (g) and leaf area of plot were significantly affected by the TWW. It is obvious that using TWW by modified nHAp in irrigation gave the highest values of all studied characters followed by using TWW by nHAp then non TWW. The significant reduction in some plant vegetative growth characters under irrigation with non TWW may be due to increasing EC values in non TWW as well as toxicity resulting from excessive concentration of major ions such as: Na^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, SO_4^{2-}, and HCO_3^{-}. Moreover, the availability of some plant nutrients is greatly affected by soil and irrigation water pH. It has been found that most plant nutrients are optimally available to plants within this 6.5 to 7.5 pH range, plus this range of pH is generally very compatible to plant root growth.[29] From table 2, the non TWW pH was 8.58 while pH value was 8.01 and 7.62 of TWW by nHAp and modified nHAp respectively. Therefore, the nutrients availability and plant growth were highly affected under irrigation with non TWW than TWW by nHAp and nHAp-HA complex.

Table 6: Means of vegetative growth characters of Jew's mallow.

Sample	fresh weight (g)	dry weight (g)	No of leaves	No of Branches	Plant height (cm)	Leaf area (cm^2)	RWC %	Photosynthetic pigments		
								Chlorophyll a (µg/ml)	Chlorophyll b (µg/ml)	Carotenoid (µg/ml)
Non TWW	5.02	2.93	6	3.66	31.5	5.71	73.9	8062.1	4311.7	2037.18
TWW by nHAp	11.86	6	7	3.34	38	7.55	76.8	9074.06	5041.8	2100.26
TWW by modified nHAp	20.70	9	8.5	4.19	43	9.94	80.6	10715.31	6337.2	2163.08
$LSD_{0.05}$	0.024	1.111	0.654	0.023	0.654	1.494	0.453	0.958	0.346	0.159

Accordingly, the treatment of wastewater by adsorption onto modified nHAp in the fixed bed column model is very economic, simple and safe method to WWT and reusing it in agriculture where TWW had a highly significant effect on plant and soil properties due to improvement of wastewater properties.

CONCLUSION

In this paper, the potentially using nHAp and modified nHAp as a sorbents for WWT. The prepared nHAp powders were prepared successfully by microwave heating based wet chemical method and also nHAp was modified with HA to improve its surface properties.

The results indicated that TWW by modified nHAp was better than nHAp in WWT from some heavy metals, organic contaminants, EC, pH, TDC, and major anions. Also, some parameters such as: SAR, EC, SSP, and RSC were used to assess the suitability of water for irrigation purposes and showed that TWW by modified nHAp is good for irrigation while non TWW and TWW by nHAp are permissible for irrigation but may be causing problems for soil and plant on long term. Furthermore, the result showed that after using TWW by modified nHAp in irrigation, soil properties became much better and gave the highest values of all studied characters of plant properties. Hence, WWT by modified nHAp considers safe, simple and economic method to wastewater reuse again with highly significant effect on plant and soil properties.

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Source of Support: Nil, **Conflict of Interest:** None.