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SYNTHESIS, CHARACTERIZATION AND ANALYTICAL APPLICATIONS OF BIOCHAR NANOCOMPOSITES FOR DECONTAMINATION OF KOHAFA WASTEWATER TREATMENT PLANTS, FAYOUM, EGYPT.

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Abstract

A new synthesis was developed to create highly porous nanocomposite material that has high sorption ability for water contaminant. Physical and chemical properties of the synthesized nanocomposites were investigated at 600 and 800°C using the BET surface area analyzer and transmission electron microscopy. Batch sorption experiment was conducted to determine the sorption ability of MgO-biochar nanocomposites to ammonia solution. Adsorption studies were modeled with Langmuir and Freundlich adsorption isotherms. According to the obtained results, Freundlich isotherm model was the best fit. Careful evaluation for using rice straw biochar (RSB) as nano-absorbent material was performed in Kohafa wastewater treatment plants (QWWTP), Fayoum, Egypt. The RSB give maximum removal (89.66 and 82.86%) for BOD_5 and COD, respectively at contact time one hour and weight 0.7 g. However, NO_3^--N reached up to 57.78%, while for NH_3-N, the maximum removal reached 62.86 %. For total phosphorus, Cu(II), Zn(II) and Pb(II), it reached 77.26, 97.92 , 99.38 and 100%, respectively. In addition the physical parameter TSS the highest value reached 93.84% and TDS increases due to the presence of ash in the RSB samples. The study concluded that the use of RSB in the Kohafa Wastewater Treatment Plants served in the elimination of the different pollutants, save power, time and coast.

Key words: Biochar nanocomposites, Characterization, Isotherm, Wastewater treatment.

Introduction

Recently, many studies have been directed toward the use of biochar for the removal of the contaminants to decrease sewage pollution. Hence, the use of advanced treatments to improve wastewater effluents is not feasible, due to its capital and operational costs, as well as the lack of specialized operators. Conventional water resources in Egypt have its limitation on use, these limitations related to quantity, quality, time and/or use coast (Mostfa *et al*., 2005). Biochar is a form of charcoal prepared through a thermochemical condition of biomass under poor oxygen conditions, known as pyrolysis or calcinations. (Maebh *et al*., 2016).

The physicochemical characteristics of biochars are not identical and the technologies used to produce this material have not yet been united (Sohi, S.P., 2012). Consequently, types of feedstock, where biochars are produced and pyrolysis conditions are the main factors influencing the sorption ability of these materials (Ahmad M. *et al*., 2014 and Chen B. *et al*., 2008). Improvement of water properties depends on the mineral content of biochar, its composition and structure, as well as biochar stability and surface chemistry. Conversion of rice harvest byproduct (biochar) provides another way for handling these crop residues that are traditionally burned in open field (Sobhy M. *et al.,* 2014). Residue burning practice in rice cultivation is also common in many countries, especially in Egypt. It is considered the source of the black sky in different places inside Egypt (Abeer M. Adel, *et al*., 2013). Nowadays, powerful research efforts have additionally been carried out on biochar-based adsorbents for elimination of aqueous contaminants that can exert useful win-win consequences for carbon sequestration and water pollution treatment as well (Tan, X.F. *et al*., 2015 and Ahmad M. *et al*., 2014). Biochar exhibited a notable capacity to adsorb water contaminants due to its huge availability of feedstocks, low coast and favorable

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physical/chemical surface properties (Meyer S. *et al.*, 2011). Synthesizing a biochar-based nano-composite is not a way just to improve the physical or chemical properties of biochar, however to reap a new composite and combine the blessings of biochar with other nano-substances. Recently, exceptional substrates based nanocomposite materials were advanced for decontamination of wastewater (Awual M.R., 2016). In comparison with different nanocomposite substances, a couple of advantages of the use of biochar because the substrates material for nano-composites manufacturing are existed. Firstly, the feedstocks of biochar production are ample and occasional-fee, which in particular received from agricultural biomass and solid waste (Sohi S.P., 2012). Sewage water needs to be purified and recycled as another source of water for possible reuse in irrigation, which is now commonly acknowledged (Maebh *et al.*, 2016).

The present study aims to assess the impact of using RSB on the physical and chemical pollutants removal from waste water treatment plant**,** after ensuring its ability to remove ammonia from aqueous solution.

Materials and Methods

Materials

Rice straw (RS) was obtained from a local agricultural farm in El-Fayoum Governorate, Egypt. Ground rice straw was dipped in bidistilled water with a mass-to-volume ratio of 1: 3 for 2 h., dried at 110°C (2 times) then was dipped in ($MgCl_2.6H_2O$) similarly and pyrolyzed at 600 and 800°C, respectively in nitrogen gas for 0.5 h. (Ming Zhang *et al.*, 2012). The pyrolysis sample was cleaned by bidistilled water, dried at 60°C, sieved through 0.315 mm mesh and sealed in a container before use (Ci Fang *et al.*, 2014). The magnesium chloride solution was prepared by dissolving 40g $MgCl_2.6H_2O$ in 60 mL bidistilled water sampling, preservation procedures and wastewater parameters were assessed according to APHA, (2012). Waste water samples were collected from new and old Quhafa wastewater treatment plants (QWWTP), El-Fayoum Governorate**.**

Characterization

Total amount of carbon C, H and N in the RBC samples was analyzed at the two different temperatures using an elemental analyzer. The surface area were measured for the pores and surface characteristics using BET analyzer by N2 adsorption. Determination of cation exchange capacity (CEC) was achieved according to Sumner and Miller method (Sumner, M.E., *et al.*, 1996). TEM was used for assessing the microscopic and morphology features of the samples.

Adsorption tests

In the single component system, a stock solution of ammonia was prepared from (Merck, 1000 ppm). Using the batch experiment: 60 mL of ammonia solution with initial concentration ranging from 5 to 200 mg/L were placed in 100 mL conical flasks with a required dose (0.1g) of biochar and shaken at constant speed 180 rpm for 3 h. at 28°C ± 2 °C and pH = 9. Each sample was centrifuged at 4000 rpm and then filtered. The concentration of ammonia in the residual solutions was analyzed for calculation of the removal percentage and adsorption capacity (q) according to the flowing equations (Vieira R.H. *et al.*, 2000 and Vijaraghavan *et al.*, 2006 b):

$$\text{Removal } \% = (C_0 - C_e / C_0) \times 100 \quad (1)$$

$$q = (C_0 - C_e) \times v/m \quad (2)$$

Where C_0 and C_e are the initial and equilibrium concentrations of ammonia in solution respectively. q: the adsorption capacity, v : suspension volume (L), m: mass of biochar (g). The adsorption data of ammonia in RBC samples were analyzed using the Langmuir (Eq. 3) and Freundlich isotherm (Eq. 4) models.

• Langmuir isotherm model

$$q_e = q_o K_L C_e / (1 + (þ K_L C_e) \quad (3)$$

Where q_e is the adsorption capacity at equilibrium (mg/g). The constant q_o (mg/g) and K_L are the characteristics of the Langmuir equation (L/mg) and can be determined from its linear plot (C_e / q_e vs. C_e).

• Freundlich isotherm model

$$q_e = K_F \times C_e^{1/n} \quad (4)$$

Where K_F is the Freundlich adsorption capacity (mg/g), 1/n is the Freundlich constant related to the surface heterogeneity. The above equation can be linearized to calculate the parameters K_F and n (plots of log q_e vs. log C_e).

RSB dose and contact time effects

The biochar doses impact on contaminant sorption were investigated with intervals ranging from (0.5-1g) biochar in one liter influent of the QWWTP, the mixture was shaken in rotatry shaker at 50 rpm at pH= 7 and temperature (30 ±2°C) for 3 h., followed by precipitation. The supernatant was taken and analyzed for the optimal RSB dose determination. Contact time was studied similarly at constant RSB dose and ranging time from 1- 6 h.

Application of RSB in wastewater

The removal efficiency of contaminants from QWWTP influent samples were determined by using 0.7g RSB dose and contact time one h as the best condition for the experiment.

Table 1: Characteristics of rice straw biochar at 600 and 800°C.

Item	600 ºC	800 ºC
Biochar yield %	22.3	15.3
BET surface Area ($m^2.g^{-1}$)	63	141
Total pore volume ($cm^3.g^{-1}$)	0.10	0.16
Average pore size(nm)	6.5	6.3
Bulk density $gm.cm^{-3}$	0.32	0.44
CEC ($cmol_c$/kg)	26.9	24.9
C%	33.78	20.17
H%	0.60	0.25
N%	0.41	0.25
O%	13.68	3.71
O/C	0.30	3.71
H/C	0.21	3.71
pH	10.04	10.84
Ash%	39.8	80.19
Fe (ppm)	170	511.3
Mn (ppm)	112.9	147.4
Zn (ppm)	17.7	58.5
Cu (ppm)	41.5	174.7

Results and Discussion

Bulk physicochemical properties

The results of the analysis of bulk physicochemical properties of 2 biochars produced at different temperatures (600 and 800°C) are shown in table 1. The data revealed that the content of carbon ratio (C %) shows relatively variance, as a function of temperature for feedstock tested. The biochar yield significantly decreased as the final pyrolysis temperature increased from 600 to 800°C, ranged from 22.3% to 15.3% (Liao R., *et al*., 2013 and Sun Y., *et al*., 2014). Also, the pH and bulk density of the prepared biochar increased slightly with increasing temperature. This can be attributed to the presence of great ash content in biochar prepared at high pyrolysis temperature (J.W. Gaskin, *et al*., 2008). High surface area and pore volume of the RSB 800°C may be ascribed to lowering the average pore diameter.

Morphology and crystalline structure of biochar nanocomposite

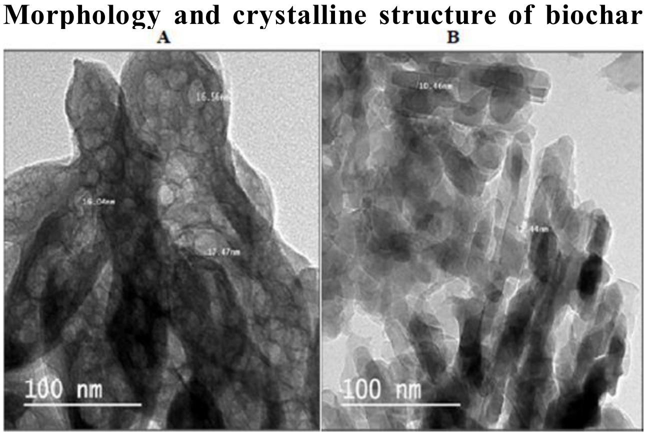

Fig. 1: TEM images of rice straw biochar: A at 600 and B 800°C.

The TEM images (Fig. 1) showed pores on RSB morphology. The micro porosity on the surface favors the opening, which creates large pores on the surface and a porous structure. Rice straw biomass had a more porous and disintegrated structure, with increase in pyrolysis temperature from 600 to 800°C, the biomass surfaces were found to rupture radically. The biochars produced at 800°C had a more fragmented structure caused by thermal cracking of their parent biomass at higher temperatures.

Adsorption isotherm

Excessive nitrogen (N) releases into runoff from human activities is considered as the major cause of eutrophication, which degrades fresh water and imposes great risk to the ecosystem therefore increase the risk of animal and human life (Ming Zhang, *et al*., 2012 and Cei Ping Wu. *et al*., 2010).

Adsorption capacity (q mg/g) of ammonia on RSB increases as the initial concentration increases to reach (35.82 and 32.10 mg/g) at the two RSB temperatures (600 and 800°C), respectively at initial concentration 200 mg/L.

Langmuir and Freundlich equations were applied in the current research. The results indicated that the Freundlich isotherm model was the best fit (Fig. 2) for ammonia adsorption on to RSB surfaces (R^2 (0.994 and 0.995), K_F (0.594 and 1.01 mg/g) and n (1.22 and 1.37)) at 600 and 800ºC, respectively whereas for Langmuir isotherm model (R^2 (0.936 and 0.989), Q_m (55.6 and 62.5 mg/g) and K_L (0.012 and 0.0073 L/mg)) at 600 and 800ºC, respectively.

It is of great interest to note that similarity of the adsorption results at the two RSB pyrolysis temperatures can be attributed to decreasing in the particle size with increasing pyrolysis temperature from 600 to 800°C

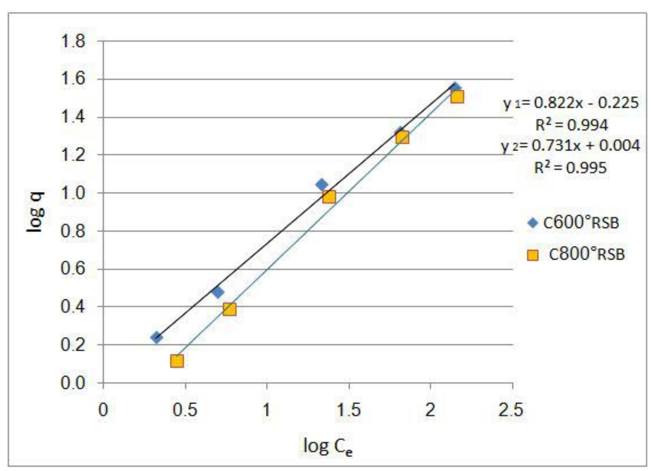

Fig. 2: Freundlich adsorption isotherm of Ammonia.

Table 2: RSB dose effect on wastewater parameters.

Parameter	Influent	Effluent						Limit
		0.5 g	0.6 g	0.7 g	0.8 g	0.9 g	1 g	
pH	7.40	8.99	9.02	9.04	9.26	9.33	9.34	6-9
BODmg/L	208.4	45.8	36.1	31.5	30.8	29.7	28.9	60
CODmg/L	328	94	80	67	65.5	64.6	63.4	80
NO_3^--Nmg/L	15.3	9.7	8.8	8.0	8.4	8.2	7.8	50
NH_3-Nmg/L	20.4	12.6	12.5	11.3	11.3	10.9	10.4	-
Pmg/L	34.2	13	10.1	7.60	7.65	7.5	7.55	-
Cu (II)mg/L	0.170	0.019	0.010	0.010	0.009	0.010	0.009	0.5
Zn (II)mg/L	0.740	0.059	0.049	0.015	0.014	0.013	0.009	2
Pb(II)mg/L	0.155	0.063	0.054	0.000	0.000	0.001	0.000	0.1
TSSmg/L	122	11	13	15	21	22	27	50
TDSmg/L	510	612	614	671	623	644	724	2000

(Wetzel, R.G., 1983) with decreasing in the carbon ratio. Consequently, application of rice straw biochar at 600°C was selected for contaminant removal from QWWTP aiming to provide low energy consumption as reported recently (Meyer, S. *et al*., 2011).

RSB dose samples effect

RSB optimum dosage to remove contaminants is considered crucial for its cost-effective application. The adsorption percentage of QWWTP pollutant (Table 2) increases with the increasing of the adsorbent dose from 0.5 to 0.7 g and then a slight increase was observed above 0.7 g. This can be ascribed to the increase in the availability of the surface active sites resulting from the higher dose and conglomeration of the adsorbent (D. Kołodyn´ska, R. *et al*., 2012). Based on the obtained results, 0.7 g RSB sample was established as optimal dosage for contaminants removal.

RSB phase Contact time effect

Also, the contact time influence between RSB and waste water samples is an important factor decreases the energy consumption. The data (Table 3) revealed that, there is no significant difference in removal percentage for most wastewater parameters at contact time ranged 1-6 h. Therefore, applications were conducted at one hour contact time.

Table 3: Effect of RSB contact time on wastewater parameters.

Parameter	Influent	Effluent						Limit
		1 h	2 h	3 h	4 h	5 h	6 h	
pH	6.9	9.15	9.16	9.16	9.18	9.23	9.32	6 - 9
BODmg/L	110	28.7	28.6	28.6	28.4	28.3	28.0	60
CODmg/L	306	68	67.8	66.1	66	64.5	64	80
NO_3^--Nmg/L	13.8	12.2	12.1	9.2	9.8	9.4	10.2	50
NH_3-Nmg/L	23.9	11.2	11.8	12.6	12.2	12.8	13.1	-
Pmg/L	28.7	11.9	11.3	11.3	11.2	11.1	11.0	-
Cu (II)mg/L	0.370	0.012	0.010	0.010	0.009	0.009	0.008	0.5
Zn (II)mg/L	0.650	0.010	0.009	0.009	0.010	0.010	0.009	2
Pb(II)mg/L	0.130	0.008	0.007	0.007	0.005	0.005	0.005	0.1
TSSmg/L	120	20	20	20.5	20.7	20.8	21.0	50
TDSmg/L	523	585	584	584	592	606	621	2000

Analytical applications

The results (Table 4) showed that the pH values for the influent and effluent are (7.09-7.41) and (8.77-9.07), respectively, achieving the limits of pH in the Egyptian law no 48, 1982 which regulate the discharge of the treated wastes to the drain. It is worthy to mention that high effluent pH value may be due to the influence of the biochar sample pH (10.04), as mentioned in table 1.

The 5-days biochemical oxygen demand method (BOD_5) is a real measure of the polluting amount of the effluent due to the dissolved oxygen taken up by organisms in the organic matter decompositions (Carlsberg, S.R., 1972). Chemical oxygen demand (COD) for effluent samples achieved the limit (80mg/L “Dichromate), except sample no. 3 (108 mg/L). This odd behavior can be attributed to the high COD concentration (504 mg/L) in the influent. The data (Table 4) revealed a high and successful BOD_5 and COD removal efficiencies (80 - 89.7%) and (72.2 - 82.86 %), respectively.

It is well known that nitrate is the final oxidation product of nitrite and nitrogen compounds in water (Horna, R.A., 1972). The influent nitrate concentrations were extremely high varied (13-66 mg/L), this may be related to nitrosamines bacteria that plays an important role in the establishment of nitrification processes. The nitrate concentration increased relatively with increasing the nitrification process (Esteves, F.A., *et al*., 2001). Nitrate and ammonia removal efficiency were (34.6-57.8%) and (44.57 %- 62.86 %), respectively.

The influent total phosphorus concentration, varied from (14-75.2 mg/L), high concentration is mainly attributed to the excretions of phosphorus as by-products from various metabolism processes. These processes play a vital role in phosphorous loading contribution (Hunter, D.A. *et al*., 1993 and Hunter, D.A. 1996). Total phosphorus removal efficiency (55-77.26%), which indicated that RSB is affective for phosphorus removal compared with nitrate, because magnesium nanoparticles can increase the surface charge, thus improving and

Table 4: Effect of RSB samples on QWWTP parameters..

Parameter	Sample 1		Sample 2		Sample 3		Sample 4		Maximum Removal	Limit
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent		
pH	7.11	9.04	7.09	8.77	7.26	9.05	7.41	8.83	-	6-9
BODmg/L	223	44.6	146	15.1	226	43.1	92.0	17.3	89.66	60
CODmg/L	319	70.0	315	54	504	108	234	65	82.86	80
NO_3^--Nmg/L	27.4	13.9	36.0	15.2	66.0	28.4	13	8.5	57.78	50
NH_3-Nmg/L	34.9	14.0	26.6	12.4	33.2	18.4	14	5.2	62.86	-
Pmg/L	25.5	9.60	23.4	8.3	75.2	17.1	14	6.3	77.26	-
Cu (II)mg/L	0.252	0.009	0.317	0.011	0.390	0.019	0.192	0.004	97.92	0.5
Zn (II)mg/L	0.580	0.006	0.410	0.008	0.610	0.010	0.320	0.002	99.38	2
Pb(II)mg/L	0.138	0.002	0.129	0.001	0.156	0.009	0.098	0.00	100	0.1
TSSmg/L	176	14.0	146	9.00	222	31.0	132	20.0	93.84	50
TDSmg/L	545	629	521	656	670	725	560	675	-	2000

accelerating Phosphorus adsorption (Ci Fang, *et al*., 2014).

Metals exist in wastewater in soluble or particulate forms (Ewa, L.K*., et al.,* 2009). In QWWTP, three elements (Zn(II)- Cu(II)- Pb(II)) were analyzed using ICP-OES instrument. The removal efficiency is highly affected by pH in which the removal efficiency increases with increasing pH until they precipitated as hydroxides at pHH"9 (Ewa, L.K*., et al.,* 2009). The order of removal efficiency for the three metal is Pb(II) > Zn(II) > Cu(II) with ratio 100, 99.4 and 97.9%, respectively.

Total suspended solids (TSS) are the portion of solids remaining after the filtration and include organic residues (Wetzel, R.G., 1983 and Horna, R.A., 1972). RSB showed higher removal efficiency of TSS ranging (84.85 - 93.84%). The influent and effluent concentrations of total dissolved solids (TDS) varied from (521 - 670 mg/L) and (629 - 725mg/L), respectively. The increase of the effluent TDS concentrations can be attributed to the addition of RSB with high ash content prepared at higher pyrolysis temperature raising the electrical conductivity (Mukome, *et al*., 2013).

Economic evaluation

The plant of new kohafa (60000 m^3/day) consumes 26400 KW per day with a coast of 23760 L.E., while the old kohafa plant (3 stages) (each stage 20000 m^3/day) consumes 5280 KW per day with a coast of 4752 L.E. for each stage. The contact time will be reduced, with the biochar addition, from 18 h. for new kohafa and 4 h. for each stage of old kohafa to one hour for the two plants. This will save a lot of money, time and power.

Conclusion

In the present work it was found that rice straw biochar had a strong affinity for adsorption of ammonia at the two pyrolysis temperature (600 and 800°C). Adsorption data were strongly correlated with the Freundlich adsorption isotherm. Similarity of ammonia adsorption results at 600 and 800°C, led to the selection of the former pyrolysis temperature saving energy. 0.7 g RSB sample and one hour were the best conditions for contaminants removal. Adsorption of rice straw biochar for wastewater pollutants is effective, environmentally friendly sustainable and reduce energy consumption, compared with the traditional treatment of wastewater. In future, our research program will be oriented towards studying the bacteriological analysis for clear supernatant resulting from RSB addition to wastewater samples.

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