INVESTIGATION OF ACTIVATED CARBON PRODUCED FROM SUGARCANE BAGASSE AND ITS APPLICATIONS ON SEWAGE WATER TREATMENT

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ABSTRACT

Activation phase was used to produce activated carbon (AC) from sugar cane bagasse (SCB). Whereas, the activation was done by two ways; the first way had crashed granulate AC to fine powder (PAC) and the second was the synthesis process nano-particles from granulate activated carbon (NAC). The surface area of PAC has been estimated by Brunauer–Emmett–Teller (BET) and characterization of NAC by using Transform Infrared spectrum (FTIR) and Trasmission Electron Microscope (TEM).

The efficient adsorbent effects for each products and natural lime stone were tested by its application on sewage water to improve its physiochemical properties which included (pH, TSS, COD, BOD, TDS, ASR, NO3, PO4, Mg, Ca, Na, Cd, Cu, Fe and Ni) through different soaking period (0, 10, 15 and 20 day).

The results cleared that the effects of using individually nano activate carbon was more efficient than PAC and natural lime stone to purified sewage water treatment with 10 days soaking period compared to other soaking periods. Furthermore, NAC exhibited the high efficiency absorbent to remove metal ions (NO3, PO4, Mg, Ca and Na) and heavy metals ion (Cu, Cd, Fe and Ni) and decrement BOD and COD from sewage water. So that, it was selected to test its effects in combination with lime stone on sewage water treatment.

Based on the obtained data the corresponding reduction values for all studied traits were higher as compared to applying each of them separately through soaking period 10 days.

It can be recommended that the combination of (NAC + limestone) are a very good material in the field of sewage water treatment before recycle it, which can be apply for reducing some pollutants in sewage water after disposable.

INTRODUCTION

Nowadays disposal of agriculture more tend to environmental friendly solutions by transforming the unwanted waste to valuable materials and thus, improves and upgrades the technology **Hu** (**2018**). AC used in diverse shapes such as powder, granular, pellet and activated carbon fiber. These types have its specific application **Guo** *et al.* (**2003**). The production of AC around the world is estimated to be around 100000 ton annually (**Ajinomoh**

and **Salahudeen (2014)**. Today, much effort has been devoted to exploiting waste as raw materials in activated carbon production. The pore size of activated carbon can be divided into three categories: the pore size is smaller than 2 nm, the pore size is mesoporous in 2-50 nm, and the pore size is larger than that in 50 nm (**Changjia** *et al.,* **2019**). Generally, AC can be prepared from a large number of low-cost sources and agricultural residues *i.e* corn cob, apricot stone, rice husk and cane bagasse, date palm residue **Nayl** *et al.* (**2017**). The main reason for the strong adsorption ability and adsorption capacity of activated carbon is total surface area in its structure which generally as high as 500-1700 $m^{2/}/g$ and small micropores compared with other adsorption materials (radius<0.02 nm) **Bao** *et.al.,* (**2011**). The pore purview distribution of activated carbon is very wide, ranging from 1 nm to thousands of nm (**Liu** *et al* ., **2012**) whereas, (**Tancredi** *et al.,* **2004**) reported that Powdered activated carbon (PAC), compared to granular activated carbon because it has a much faster adsorption rate and a larger adsorption capacity of various organics usually related to their much higher surface area, pore volume and porosity.

Nowadays nanotechnology has expanded broadly in all science themes. The nanotechnology is one of the new technologies that entered almost all sides of our lives and were used in agriculture production (**Husen** and **Siddiqi, 2014**). Many nano-sized materials (metal oxide, zeolites, carbon-based nanoparticle, nano-clays and nanocomposites) have been used as adsorbent to remove heavy metal ions from wastewater (**Zhao** *et al.,* **2011 and Hua** *et al.* **2012**). The nature of activated carbon surfaces especially the nano size ones have made them promising adsorbents to remove heavy metals from industrial wastewater but they are restricted in use due to their high cost **Kumar and Chawla (2014)** and **El-kady** *et al.,* (**2015**).

Actived carbon which is used in any application must have adequate adsorptive capacity, chemical purity and mechanical strength**.** Furthermore, all these specifications should coexist with a low production cost. The chemical structure of AC could preferentially adsorb organic materials and other non-polar compounds from the gas or liquid streams. Due to these properties, they have been used for removal of COD and BOD, heavy metals removal, and solutions decolorization (**Nayl** *et al*., **2017, Saleh** *et al*., **2015 and Changjia** *et al.,* (**2019**).

Wastewater purification is usually achieved through adsorption on soil, plant uptake, sedimentation, and filtration, microbial and chemical decomposition. Also, wastewater purification could be achieved by the modification in hydraulic loading rate, hydraulic retention time, water depth, and recycling system of crud water. However, to achieve better performance, some highly reactive chemical materials are also being used as a substrate in wastewater purification such as lime stone, shale, activated

carbon, zeolite and fly ash (**Vohla** *et al,.* **2011; Nayl** *et al.*, **2017, , Almuktar** *et al*., **2018, Changjia** *et al.,* (**2019**).

Limestones are rocks predominantly originated from calcite minerals (calcium carbonate with trigonal structure, $CaCO_3$). They are solid and grained sedimentary rocks of organic or chemical origin contain more than 95% $CaCO_3$. **Aziz** *et al.,* (**2001**) found that calcium carbonate ($CaCO_3$) was an effective material to purified water contaminated with heavy metal ions. **Sdiri** *et al*. (**2012**) reported that lime stone contains stains (silica, iron or aluminum oxide and different clay minerals) that enhanced sorption capacity. Also, **Ahmad** *et al*. (**2012**) recorded a remarkable efficiency of calcium carbonate as adsorbent (90%) that significantly remove heavy metal ions from drinking water.

According to the World Health Organization (WHO), the most immediate concern and abundant metals are cadmium, chromium, copper, lead, nickel, and zinc. Copper is an essential micronutrient to the plants but at higher concentrations it may become toxic. Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operation and tanneries. Therefore, mitigated the hazardous effect of heavy metals on the ecosystem is very important (**Rai, 2009**).

The current work aims to produce activated carbon (AC) material by two methods; the first is powder (PAC) and the second is the synthesis process nanoparticles from sugar cane bagasse (NAC). In addition, assess the effects of these methods on the physical properties of the AC as well as their application to the disposal of sewage water.

MATERIALS AND METHODS

MATERIALS:

Raw material

1. Sugar cane bagasse was obtained from pilot milling of Sugar Crops Research Institute, Agriculture Research Center, Giza Agriculture Research Station, Egypt.
2. Limestone was purchased from El-Ahram Company for Mining and Natural Fertilizers, Giza, Egypt
3. Sewage water was obtained from Egyptian station of sewage water collection Co., El-Safe, Giza, Egypt. The chemical compositions of sewage water sample were represented in Table 1.

Table1: Chemical compositions of sewage water at zero time

pH	SAR	COD	BOD	TSS	TDS	PO$_4$	NO$_3$	Ca	Mg	Na	Cu	Cd	Fe	Ni
		mg O$_2$/L					mg/L						µg/L	
7.4	15.4	92.3	63.6	377	12.4	2.41	0.65	38.4	14.8	58.6	17.6	13.6	306.2	45.7
SAR: sodium adsorption ratio, COD: chemical oxygen demand, BOD: biological oxygen demand,TSS: total soluble solids, TDS: total dissolved solids														

METHODS:

 I.   Raw materials preparation:

Bagasse as a by-product of the commercial sugarcane cultivar **(GT. 54-9)** was tested. The sample of 40 millable cane stalks was squeezed by an electric pilot mill belongs to Sugar Crops Research Institute, Agriculture Research Center, Giza Agriculture Research Station, Egypt. Wet bagasse was collected and washed with tap water to remove any debris then sun drying for three days and put in oven at 110 °C till constant weight. The dried bagasse was milled to be in a form of powders.

 II.   Activation phase:

Activation phase carried out according to the method described by **Ajinomoh** and **Salahudeen (2014).** The raw materials were impregnated in phosphoric acid (50% v/v) as an activating agent by 1:1 ratio (bagasse to acid) for 24 hr to cover the whole mass and to give a paste of soft consistency. The impregnated sample was admitted into a muffle furnace at $500^{o}C$ for 3 hr. The obtained granular carbonized mass was left to cool and washed many time with hot distilled water pass through litmus paper to remove washing water**.** The presence of phosphate was recognized in the acid treated sample by the white precipitate of $Pb_3(PO_4)_2$. The AC´s product was dried at $105^{o}C$ in an air oven. Active carbons product (PAC) are milled to pass through a 50-mesh sieve (0.297 mm) then it was stored in polyethylene bags for subsequent characterization and adsorption studies.

 III.   Synthesis of bagasse activated carbon nanoparticles:

Synthesis of bagasse ignoc carbon nanoparticles (powder) was done using the method of up to bottom molecular physical and chemical approach under 2 Mpa pressure. The raw material of bagasse active carbons was grinding continually for 18 hours then soaking in mixed solution of HCl :NaOH: hexametaphosphate in the ratio of (1:1:2) under vigorous stirring. The stirring was continued for 12 h. then 3ml of Tubercidin tridecyl ecosenoin oxolamine serine methyl ester **(TEOS)** solution was add. The resulted material was filtered then exposed to $120^{o}C$ constantly for 24 hours, after that it left under pressure (2 Mpa) for terminated 36 hours; finally ultrasonic was done for 30 minutes to separate nano particles aggregation. The size and shape of bagasse AC nanoparticles were observed directly by Transmission Electron Microscopy (TEM) using an electron acceleration voltage of 60 kV. Transform Infrared spectrum (FTIR – 8400 S Shimadzu, Japan) was used

to determine the change chemical structural of functional groups in NAC has preparation.

IV.   Experimental

16 treatments were carried out on sewage water as follows:

1-   Bagasse active carbon 6 g/l.
2-   Lime stone 6 g/l.
3-   Nano bagasse active carbon 0.5mg/l
4-   0.5mg/l Nano bagasse active carbon + 6 g/l lime stone.

Each treatment was applied at four soaking periods with sample of sewage water (zero, 10, 15 and 20 days) according to **Saleh** *et al*., (**2015)**.

V.   **Evaluation tests**

- Moisture, total carbohydrate, crud fiber, crud protein of raw bagasse were determined according to (**A.O.A.C 2010)**.
- The chemical constituents of raw bagasse, bagasse active carbon and lime stone were determined by using Atomic Absorption Spectrophotometer method (**Helrich, 1990)**.
- Using Multipoint (**BET)** Brunauer–Emmett–Teller to measurements Surface area which performed to get an overview of the porous characteristics of the activated sample included (surface area, pores volume, and pore size distribution). Nitrogen adsorption isotherm (N_2) was produced at 77 K for this purpose using Surface Area Analyzer equipment, BEL-Sorb Max., made in Japan.
- Moreover Transmission Electron Microscopy (TEM) for granular (GAC), powder (PAC) and limestone were used to study the structural features of the carbon surface.
- Several laboratory experiments were carried out to select the optimal dosage for NAC which ended up to 0.5 mg/l sewage water is the most appropriate as dried powder. The whole experiment was repeated 3 times with the same periods during 2020, the average data were analyzed using ANOVA at 5% significance level, the difference between treatments then analyzed using DMRT (Duncan Multiple Range Test) at 5%.
- After each soaking period, samples of sewage water were taken to determine some chemical composition which were (pH, TSS, COD, BOD, ASR, Po4, No3, Mg, Ca, Na, Cd, Cu, Fe and Ni) according to (**Helrich, 1990)**. Sorption studies were conducted in routine manner and adsorption experiments were carried out under room temperature conditions. The standardization dose of adsorbant, agitation time and period of contact with solution were recorded.

RESULTS AND DISCUSSION

The chemical analysis of row dry bagasse, bagasse active carbon and lime stone are presented in **Table (2).** The results showed that sulpher and nitrogen are inferior in raw bagasse than both bagasse active carbon and lime stone. Data observed that hydrogen ratios are rich in raw dry bagasse than the other materials. Meanwhile, active carbon product was highest in carbon contents than the two other materials. The contents of carbon in case of all carbon groups are in the range of 48.9 – 50.49% and are much lower than those in the starting polymers of lignocelluloses materials. Similar relation is observed for nitrogen contents. Oxygen element is presented in the structure of analyzed materials whereas; in the case of polymeric precursor it occurs as a constituent of carbonyl group of the bagasse polymer. This element is also presented in the carbons structure in the form of carbonyl, carboxylic, lactonic, phenolic which can be formed during carbonization and activation processes. In the case of bagasse carbons not only oxygen but also OH groups coming from the residues of lignocelluloses structures. These results are in agreement with those mentioned by **Changjia** *et al.,* (**2019)** who reported that in the preparation of activated carbon, the border chemical bond of the aromatic sheet which formed during shatter stage in carbonization process to form a border carbon atom with unpaired electrons.

These peripheral carbon atoms have unsaturated chemical bonds which can be reacting with heterocyclic atoms such as nitrogen, hydrogen, oxygen and sulfur to form different surface groups. Chemical constituents of lime stone were about 55.51% CaO and ignition loss ratio 42.25% .This results confirmed mineralogical proportion of calcite as well as element oxides is the major source of oxygen while Ca_2CO_3 is the main source for carbons content in lime stone structure. These results are in line with those obtained by **Aziz** *et al.,* (**2001).**

Table 2: Chemical composition of sugar cane bagasse, bagasse activate carbon and limestone

Material	Mois %	pH	T.C %	C.F %	C.P %	Ash %	C %	N₂ %	H₂ %	S %
Row dry bagasse	8.83	-	56	40	2.56	2.53	48.9	0.6	5.2	0.215
Bagasse active carbon		5.6		-		36.5	50.49	0.8	0.76	0.532
Lime stone chemical constituents %	SiO₂	CaO	Al₂O₃	Fe₂O₃		So₃	MgO	Na2O	K2O	
	0.41	55.51	0.24	0.22		0.20	0.15	0.42	0.60	
	Loss on ignition			42.25						
Mois= Moisture, T.C= total carbohydrate, C.F= crud fiber, C.P= crud protein										

Granular Bagasse active carbon   Powder Bagasse active carbon
Fig. 1

Overview of the porous characteristics of PAC and limestone by Multipoint (BET):

The textural characterization of PAC and lime stone samples determination on N2 isotherms that used in mathematical models to quantify the specific surface area, pore volume and size distribution by BET area are shown in Table 2 and fig 1 to 8.

The BET plot in **Fig. 1 and 6** indicated that the PAC has smaller pore size than lime stone meaning that PAC acquires the highest contribution of nanopores in its structure. Meanwhile the total pore volume occurs at about 0.1682 and 1.5847 m^3 g^{-1}, respectively. The samples had pointed out pore diameter of 2.1069 nm for PAC sample and 5.0349 for lime stone (table 2). The practical point of **Fig 2 and 7** illustrated that it is fitting to use NLDFT/GCMC model which had depicted pore size distribution analysis for the used materials. Their pore size distributions in PAC and lime stone have nano pore in its structures. The first small occurs at about 2.1069 nm and the second at 5.0349 nm for mean pore diameter. Density Functional Theory by Model of isotherms pore size distribution analysis by NLDFT/GCMC as a fitting of the integral adsorption equation for description. The shape of adsorption isotherms in **Fig 3 and 8** indicates that bagasse active carbon has the largest specific surface area compared to lime stone. The PAC has remarkable surface area up to 320 m^2/g while the lime stone as expected has low surface area as1.6 m^2/g. These results are in harmony with those obtained by (**Benaddi** *et al.,* **2000, Ordóñez** *et al.,* **2014** and **Changjia** *et al.,* **2019).**

Table (3) BET values for powder active carbon (PCA) and lime stone

Parameters	PAC	lime stone
BET plot		
Mean pore diameter (nm)	2.1069	5.0349
Total pore volume ($m^3\,g^{-1}$)	0.1682	1.5847
a_s BET $m^2\,g^1$	3.1923E+02	1.2590E+00
Model of isotherms pore size distribution analysis by NLDFT/GCMC		
Vp $cm^3\,g^{-1}$	0.1793	1.0762

In fact, it possesses the highest contribution of nano pore in its structure. This result may be due to lime stone has the largest contribution of the micro pore to its structure; unlike the PAC has the largest contribution of the nano pore, which earned it the highest adsorption capacity moreover, the production method which led to build narrow pore systems. Also, these results may be due to the performance indication of AC structure by pore size and the wall of the pore ranges from micro, macro, meso- pores. Eventually their distribution in a matrix depend on the source of the AC as well as the pore size distribution as affected by the nature of the chemical activating agent employed during activation (**Karnib** *et. al.,* **2014).**

Muli point of BET to get (surface area, porous volume, and pore size distribution)
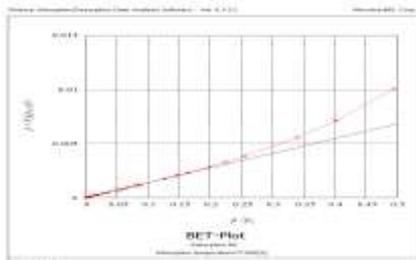
Fig. 1
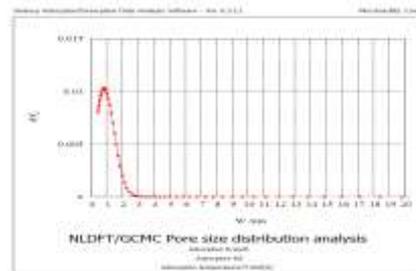
Fig. 2
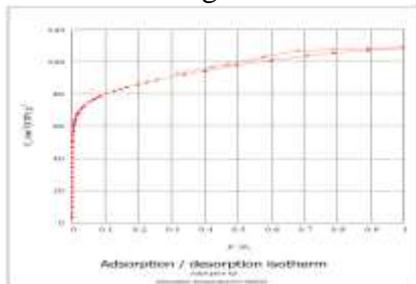
Fig. 3
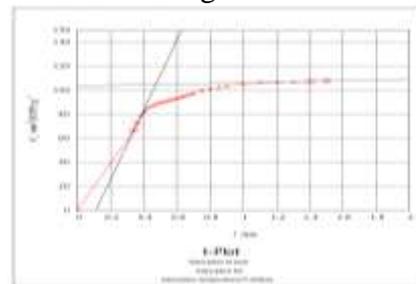
Fig. 4
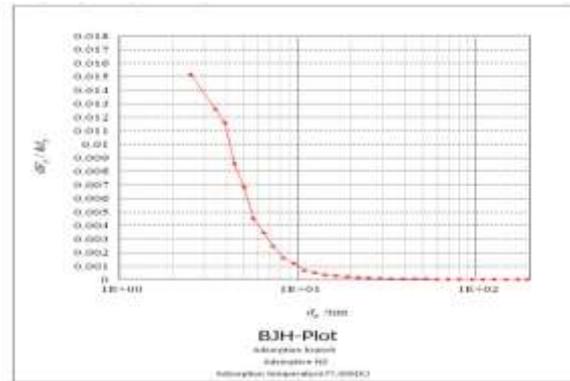
Fi.g 5

Fig: 1,2,3,4 and 5 Characteristics porous of bagasse activated carbon sample (surface area, pores volume, and pore size distribution, NLDFT/GCMC and DFT analyzed by BET area.
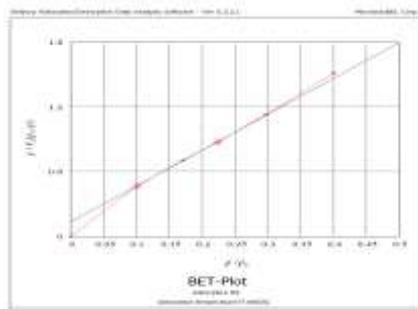
Fig. 6
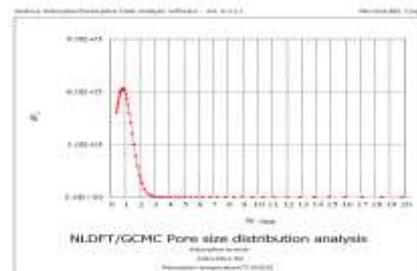
Fig. 7
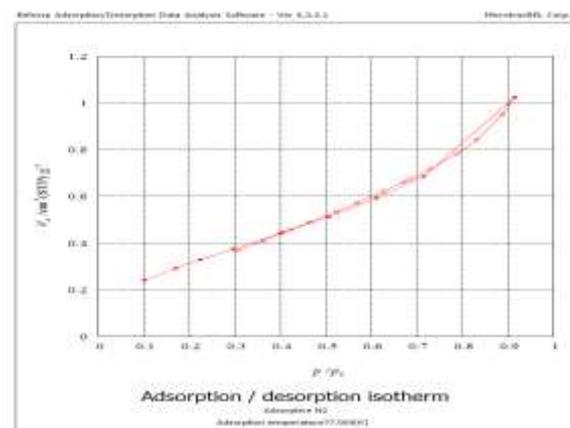
Fig. 8

Fig 6, 7 and 8 Characteristics porous of lime stone sample (surface area, pores volume, and pore size distribution, NLDFT/GCMC and DFT analyzed by BET **area**

Characterization of Synthesized Nano- Bagasse activated Carbon:

Figure (9) show that the FTIR spectra of NAC product sample which point out the nano-particles from granulate activated carbon (NAC) sample revealed visible IR bands between 500 and 2000 cm⁻¹. The large band represented at around 525 cm⁻¹may as a result of overlapping of C–O–C stretching, C–O stretching and O bending modes of alcoholic, phenolic and carboxylic groups. The band at 1570 cm⁻¹is assigned to C═C stretching conjugated with another C═C bond, an aromatic nucleus, or C═O bond. It has been reported that the C═C stretching frequently occurs at approximately 1600 cm⁻¹for carbonaceous materials .The bands at more or less 2012 cm⁻¹are assigned to alkyl groups such as –CH3, ═CH2 and –CH2CH3. The weak band at around 3150 and 3700 cm⁻¹ can assigned to the O–H stretching vibration mode of hydroxyl functional groups. These surface efficient groups can provide active sites where chemical transformations take place via surface reactions. These data demonstrated that the most efficient prepared material represented as **(NAC)**
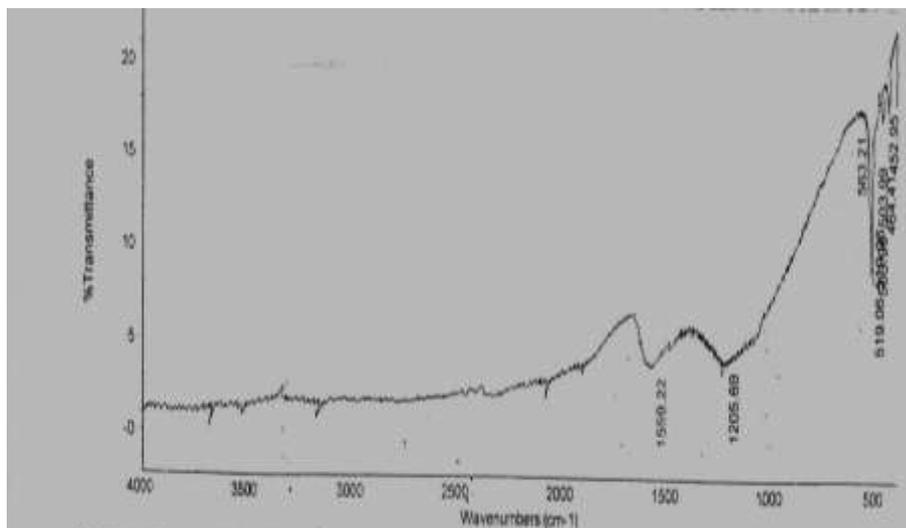
Fig. 9: FTIR spectrums of nano- Bagasse activated carbon

Transmission Electron Microscopy (TEM):

Figure (10) show that TEM images of GAC and PAC products which displayed a well pronounced the average particle size were about 400 to 410 for GAC and ranged from 174 to 200 nm for PAC meanwhile, TEM image of synthesized Nano- Bagasse activated Carbon

I detected that the average of particle size ranged from 7.22 to 14.1 nm. According to above results of BET and transmission electron microscopy (TEM), the most efficient forms is PAC and NAC because it had produced nano-scale by much higher surface area, pore volume, and porosity compared to GAC. These results are in harmony with those obtained by (**Tancredi** *et al.,* **2004).**
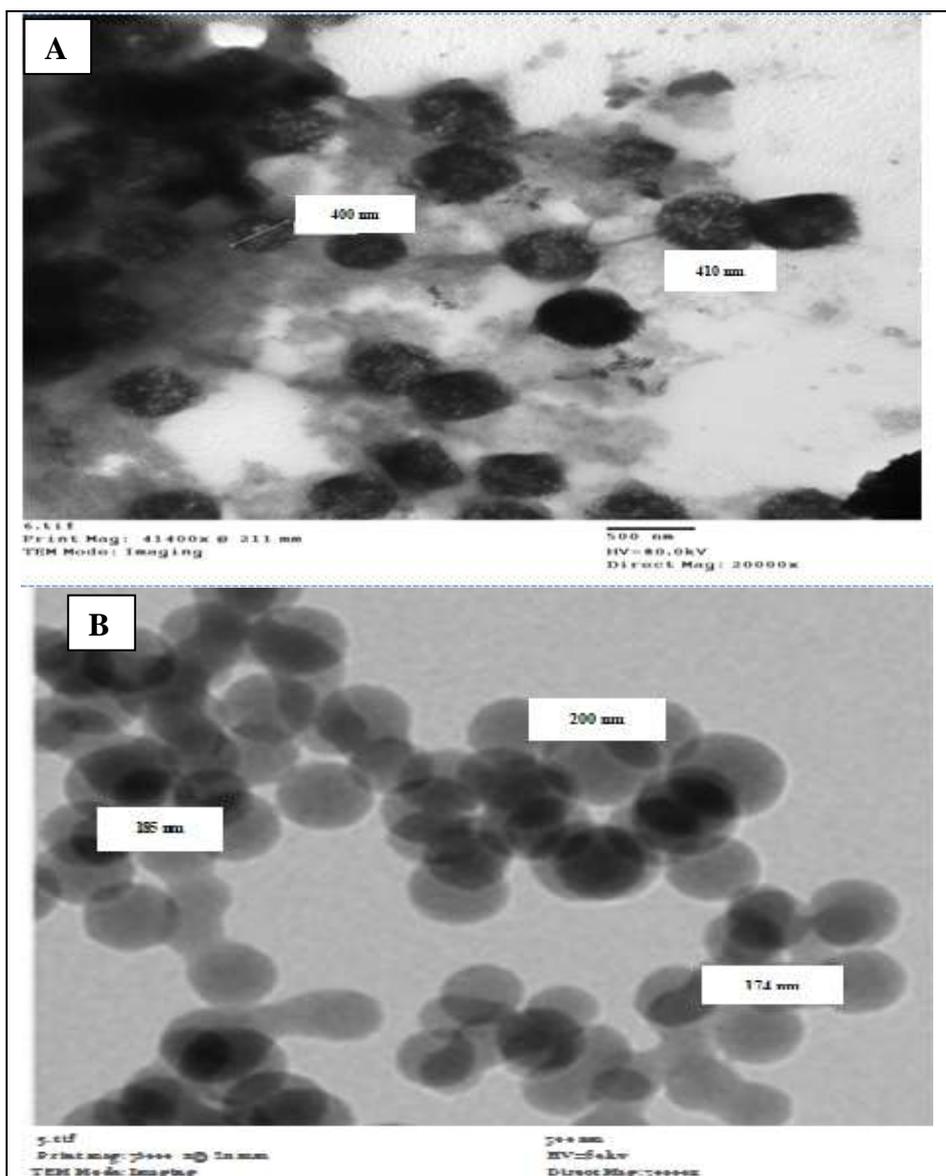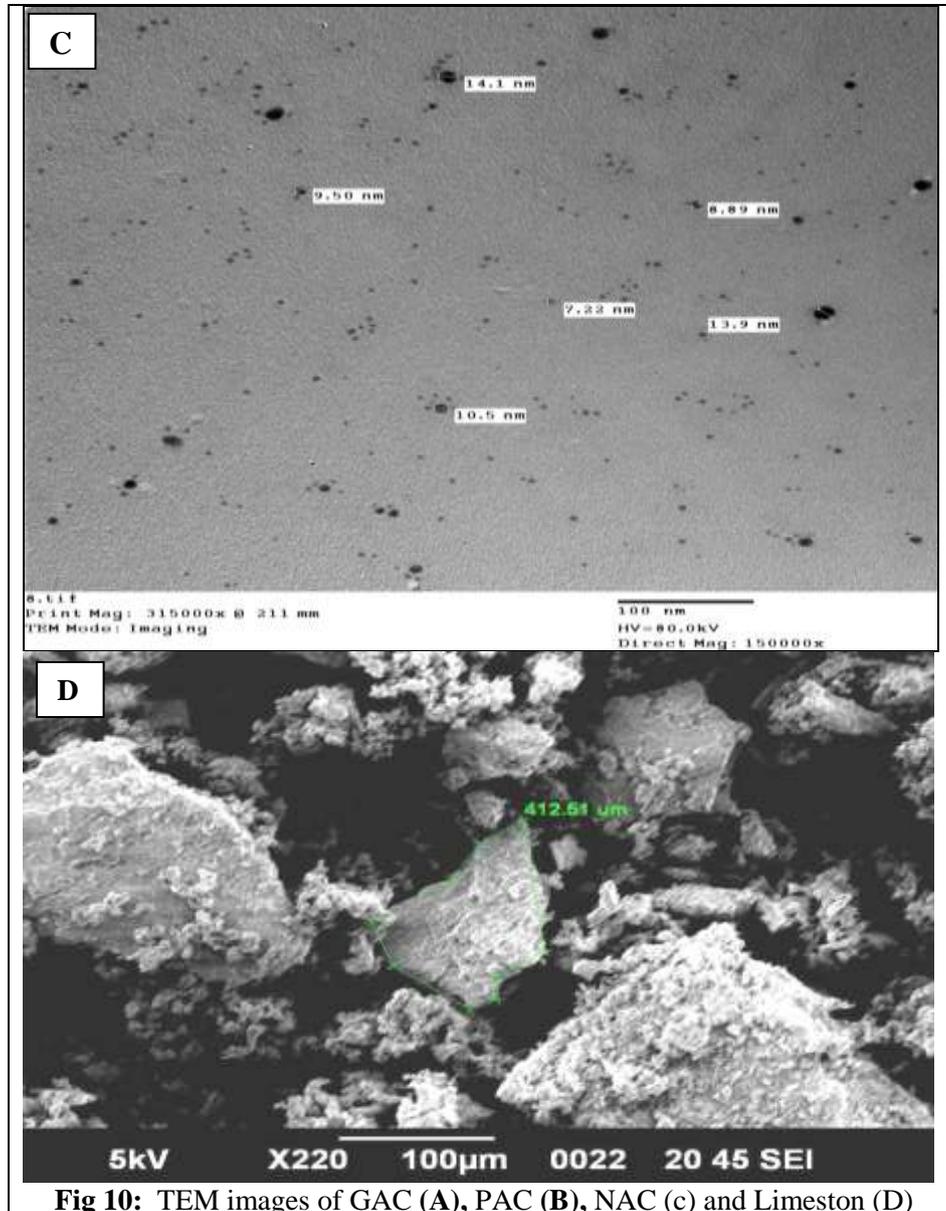
Fig 10: TEM images of GAC **(A),** PAC **(B),** NAC (c) and Limeston (D)

Experimental applications on sewage water:
Treatment sewage water by the fine powder of active carbon (PAC)

Data in Table (4) elucidate that PAC had a appreciable effects on all mention traits of sewage water compared to untreated water except, pH was not affected with all prolonging period under studied .

Significant decreases in COD, BOD, SAR,TSS, NO3, Ca, Na, Cd, Cu, Fe and Ni in sewage water amounted by (14.5, 15.7) mg O2/L and (4.2, 367.2, 0.41, 0.2, 4.6, 1.7 and 4.3) mg/L while, TDS was increased amounted to 299.4 mg/L after soaking period 10 days with zero time and without any significant differences among all soaking period for all traits except between soaking periods 10 and 15 days for PO4 and also between soaking periods of 15 and 20 days for TDS content of sewage water. Data in the same Table also clear that there is no significant difference among soaking periods 10, 15and 20 days for SAR, COD, BOD, TSS, NO3, Ca, Na, Cu, Cd, Fe and Ni. further, the same trend was detected for Mg between results of soaking periods (zero and 10) days and also between soaking periods (15 and 20) days for the same traits while it was found between soaking periods (10 and 15) days for ASR and TDS. These results are in harmony with those obtained by **Ahn** *et al*., **(2009) and Hua** *et al*., **(2012)** they found that PAC due to its high porosity, large surface area and high efficiency has gained more interests than the others. In addition the affected of PAC as a reported explain by **Jung** *et al*., **(2013)** who found that the maximum adsorption capacity of PAC reach to 46.9 mg/g for metal ions removal from aqueous solutions. Furthermore **Tancredi** *et al*., **(2004)** reported that (PAC) compared to granular activated carbon, has a much faster adsorption rate and a larger adsorption capacity of various organics usually related to their much higher surface area, pore volume, and porosity.

Treatment sewage water by limestone:

Data presented in table (5) show that treated sewage water by limestone had significant affect on SAR,TSS, COD, BOD, TDS, PO4, NO3, Ca, Mg, Na, Cd, Cu, Fe and Ni.   Significant reduction resulted in soaking period 10 days in COD and BOD amounted to (3.9 and 4.9) mgO2/L and also was (369.4, 0.3, 0.13, 3.2, 1.7 and 0.8) mg/L for TSS, PO4, NO3, Ca, Mg and Na, respectively while was (13.32, 7.94, 114.8 and 19.2) µg/L for Cd, Cu, Fe and Ni, respectively except the value of TDS was increased amounted by 332.8 mg/L as compared to sewage water at zero time. On the other hand, increasing soaking period from zero to 15 days resulted in significant reduction in PO_4 and NO_3 and caused an increasing in TDS amounted by (0.41and 0.17) and 329.3 mg/L, respectively as compared to zero time. Meanwhile, other values of mention traits between soaking period from10 and 15 in Table 6 was not affect

Table (4) Effect of powder active carbon (PAC) on sewage water chemical composition

S.P/ day	powder active carbon (PAC)														
	pH	SAR	COD	BOD	TSS	TDS	PO$_4$	NO$_3$	Ca	Mg	Na	Cu	Cd	Fe	Ni
			mg O$_2$/L				mg/L						µg/L		
zero	7.4[a]	15.4[a]	92.3[a]	63.6[a]	377[a]	12.4[a]	2.41[a] ±0.1	0.65[a] ±0.03	38.4[a] ±0.2	14.8[a] ±0.12	58.6[a] ±0.2	17.6[a] ±0.2	13.6[a] ±0.02	306.2[a] ±0.12	45.7[a] ±0.3
10	7.2[a]	11.2[b]	77.8[b]	47.9[b]	9.8[b]	311.8[b]	2.00[b] ±0.02	0.45[b] ±0.02	33.8[b] ±0.1	13.1[a] ±0.11	54.3[b] ±0.1	6.75[b] ±0.01	8.81[b] ±0.03	201.6[b] ±0.31	32.6[b] ±0.02
15	7.2[a]	10.8[b]	76.5[b]	47.5[b]	8.5[b]	309.2[b]	1.82[c] ±0.01	0.41[b] ±0.01	33.6[b] ±0.1	12.9[b] ±0.10	54.2[b] ±0.2	6.44[b] ±0.02	8.53[b] ±0.02	200.3[b] ±0.24	32.5[b] ±0.01
20	7.2[a]	10.7[b]	72.8[b]	48.1[b]	8.1[b]	300.7[c]	1.75[c] ±0.02	0.40[b] ±0.01	33.7[b] ±0.1	12.3[b] ±0.11	54.2[b] ±0.1	6.38[b] ±0.02	8.52[b] ±0.03	200[b] ±0.17	32.6[b] ±0.01
S.P: soaking period, SAR: sodium adsorption ratio, COD: Chemical oxygen demand, BOD: biological oxygen demand,TSS: total soluble solids,TDS: total dissolved solids															

Values with different letters show significant differences at P ≤ .05 (LSD).

Table 5: Effect of lime stone on sewage water treatment

S.P/ day	lime stone														
	pH	SAR	COD	BOD	TSS	TDS	PO$_4$	NO$_3$	Ca	Mg	Na	Cu	Cd	Fe	Ni
			mg O$_2$/L				mg/L						µg/L		
zero	7.4[a]	15.4[a]	92.3[a]	63.6[a]	377[a]	12.4[a]	2.41[a] ±0.1	0.65[a] ±0.03	38.4[a] ±0.2	14.8[a] ±0.12	58.6[a] ±0.2	17.6[a] ±0.2	13.6[a] ±0.02	306.2[a] ±0.12	45.7[a] ±0.3
10	7.3[a]	11.8[b]	88.4[b]	58.7[b]	7.6[b]	345.2[b]	2.11[b] ±0.03	0.52[b] ±0.02	35.2[b] ±0.3	13.1[b] ±0.11	57.8[b] ±0.1	8.70[b]± 0.2	11.4[b] ±0.01	249.2[b] ±0.20	41.6[b] ±0.14
15	7.3[a]	11.8[a]	85.7[b]	58.3[b]	7.1[b]	341.7[c]	2.00[c] ±0.02	0.48[c] ±0.03	35.2[b] ±0.4	13.0[b] ±0.11	57.6[b] ±0.1	8.50[b] ±0.3	10.2[b] ±0.01	248.5[b] ±0.22	41.5[b] ±0.12
20	7.3[a]	11.7[a]	80.6[c]	58.5[b]	7.1[b]	341.6[c]	1.98[c] ±0.02	0.48[c] ±0.02	35.1[b] ±0.3	13.0[b] ±0.10	56.4[b] ±0.02	7.66[c] ±0.2	10.0[b] ±0.01	241.6[c] ±0.21	41.0[b] ±0.11

Values with different letters show significant differences at P ≤ .05 (LSD).

Increasing soaking period from zero to 20 days resulted in a significant reduction in COD, Cu and Fe amounted by 11.7 mgO$_2$/L, (9.94 and 64.6) µg/L respectively compared to zero time. Moreover, there is no difference between soaking period from 15 and 20 days for the other values of all mention traits in Table 5. The different absorption capacities of limestone substance through different soaking period zero, 10, 15 up to 20 days may be attributed to various factors such as metal solubility, cationic size, electronegativity, affinity of adsorbent, contact time etc as a mentioned by **Geetha and Belagali (2013).** This results coincides with those found by **Ahmad** *et al*., **(2012)** who reported that CaCO3 showed a good metal binding capability for heavy metals ions and can be used an effective alternative from real wastewater metal removal.

Treatment sewage water by nano active carbon (NAC):

Data in Table (6) elucidate that nano active carbon had a appreciable high effects on all traits of sewage water with increased soaking period from zero to 10 days except pH value was insignificantly affected by the prolonging period from zero, 10, 15 to 20 days after treated. The results also showed that there no detected any significant differences among all other soaking period and zero time for all above traits in Table 6 except, Fe was obtained significant decrease which amounted to (8.9 and 123.7) µg/L in soaking periods10 and 15 days, respectively after treatments as well as increasing soaking period from zero to 20 caused an increase in TDS and reducing NO3 which amounted to (248.9 and0.05) mg/L as a compared to zero time. It worthily to mention the corresponding reduction values for all traits in Table 6 were highest as compared to the other treatment materials. This finding was true when refer to table (2). These results may be attributed to the fact that PAC has a relatively larger particle size compared to NAC and consequently, presents a smaller external surface. These results are in line with those obtained by **Elkady** *et al*., **(2015)** who found that NAC exhibited array of unique performance for improvement properties of sewage water like deodorization and heavy metal removal.

In accordance with previous results in table 3, 4 and 5 about the performance indication of individual effect of each PAC, lime and NAC stone on sewage water chemical composition, the results observed that NAC treatment was high effects than the other materials so that, it was selected to study the effects of using it in combination with lime stone on the disposal of some chemical composition found in sewage water **table 7** and SEM images for combination NAC + lime stone was investigated at **Fig.11**

Table 6: Effect of Nano active carbon (NAC) on sewage water treatment

S.P/ day	Nano active carbon (NAC)														
	pH	SAR	COD	BOD	TSS	TDS	PO$_4$	NO$_3$	Ca	Mg	Na	Cu	Cd	Fe	Ni
			mg O$_2$/L		mg/L								µg/L		
zero	7.4^a	15.4^a	92.3^a	63.6^a	377^a	12.4^a	2.41^a ±0.1	0.65^a ±0.03	38.4^a ±0.2	14.8^a ±0.12	58.6^a ±0.2	17.6^a ±0.2	13.6^a ±0.02	306.2^a ±0.12	45.7^a ±0.3
10	7.1^a	10.1^b	58.3^b	44.2^b	7.6^b	267.5^b	1.61^b ±0.02	0.38^b ±0.02	32.1^b ±0.11	11.8^b ±0.13	51.6^b ±0.3	4.28^b ±0.1	5.66^b ±0.03	191.4^b ±0.45	26.5^b ±0.11
15	7.1^a	10.0^b	56.5^b	42.8^b	7.1^b	267.1^b	1.51^b ±0.01	0.38^b ±0.02	31.5^b ±0.13	11.8^b ±0.11	50.2^b ±0.3	3.06^b ±0.1	5.48^b ±0.04	182.5^c ±0.41	23.6^b ±0.13
20	7.1^a	10.0^b	56.3^b	42.3^b	7.1^b	261.3^c	1.50^b ±0.02	0.33^c ±0.03	31.2^b ±0.20	11.5^b ±0.11	49.1^b ±0.2	2.03^b ±0.2	4.92^b ±0.01	180.1^c ±0.32	20.2^b ±0.11

Values with different letters show significant differences at P ≤ .05 (LSD).
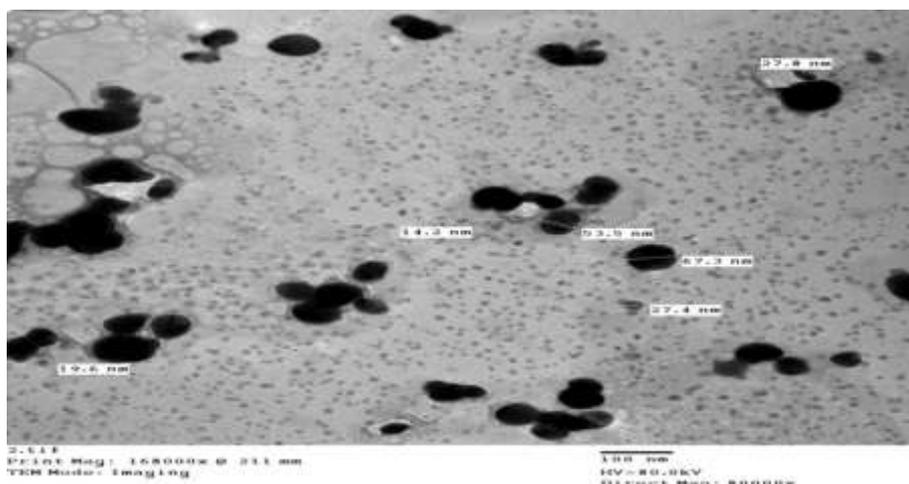
Fig. 11: TEM images of combination NAC + lime stone

Treatment sewage water by combination of (NAC + lime stone):

The results in Table (7) declared that all chemical traits of sewage water were significantly affected by using nano active carbon in combination with limestone. Significant decreasing in all mentioned traits in Table 7 with increased soaking period from zero, 10, 15 up to 20 days excepted, trait of TDS was increase while, pH value was not affected by all prolonging periods. Treatment sewage water by combination of (NAC + lime stone) achieved substantial decrements after soaking period 10 day amounted to (36.9, 26) mg O$_2$/L for COD and BOD and amounted to (5.6, 370.2, 1.67, 0.38, 8.6, 4.5, 10) mg/L for SAP, TSS, PO4, NO3, Ca, Mg and Na and amounted to (13.24, 9.75, 133.6 and 30.9) µg/L for Cd, Cu, Fe and Ni content , respectively and

trait of TDS increasing amounted to 246.4 mg/L compared to that of untreated sewage water. Also in the same Table, it was noticed that insignificant variances were found in SAR, COD, TSS, Ca, Mg and Na traits among their values in soaking period 10, 15 and 20 days. While, the significant difference was detected between soaking periods 15 and 20 days for TDS and PO_4 as well as between soaking period15 and 20 days for BOD, NO_3, Cu, Cd, Fe and Ni. These results may be attributed to various factors such as metal solubility, cationic size, electro negativity, affinity of adsorbent, contact time etc as a mentioned by **Geetha and Belagali (2013)**. This finding meaning using this combination for water treatment it can be achieve impressive results for removal some ions of metal oxides and heavy metals as well as reducing chemical and biological oxygen demand in sewage water.

Table 7: Effect of combination of (NAC + lime stone) on sewage water treatment

S.P/ day	pH	SAR	combination 0.5mg/l NAC + 6g/l lime stone												
			COD	BOD	TSS	TDS	PO4	NO3	Ca	Mg	Na	Cu	Cd	Fe	Ni
			mg O2/L				mg/L						µg/L		
zero	7.4ᵃ	15.4ᵃ	92.3ᵃ	63.6ᵃ	377 ᵃ	12.4ᵃ	2.41ᵃ ±0.1	0.65ᵃ ±0.03	38.4ᵃ ±0.2	14.8ᵃ ±0.12	58.6ᵃ ±0.2	17.6ᵃ ±0.2	13.6ᵃ ±0.02	306.2ᵃ ±0.12	45.7ᵃ ±0.3
10	7.1ᵃ	9.8ᵇ	55.4ᵇ	37.6ᵇ	6.8ᵇ	258.8ᵇ	0.74ᵇ ±0.03	0.27ᵇ ±0.01	29.8ᵇ ±0.1	10.3ᵇ ±0.10	48.6ᵇ ±0.1	4.36ᵇ ±0.04	3.85ᵇ ±0.03	170.6ᵇ ±0.13	14.8ᵇ ±0.3
15	7.1ᵃ	9.9ᵇ	55.1ᵇ	35.5ᶜ	6.3ᵇ	258.1ᵇ	0.72ᵇ ±0.02	0.21ᶜ ±0.02	29.5ᵇ ±0.1	10.2ᵇ ±0.13	46.5ᵇ ±0.2	3.89ᶜ ±0.03	1.81ᶜ ±0.05	162.3ᶜ ±0.11	13.7ᶜ ±0.1
20	7.1ᵃ	9.8ᵇ	54.2ᵇ	35.6ᶜ	6.3ᵇ	253.4ᶜ	0.58ᶜ ±0.03	0.20ᶜ ±0.02	25.5ᵇ ±0.2	8.3ᵇ ±0.05	45.2ᵇ ±0.2	2.81ᶜ ±0.05	1.28ᶜ ±0.05	154.8ᶜ ±0.12	12.1ᶜ ±0.1

Values with different letters show significant differences at P ≤ .05 (LSD).

Data presented in Table 8 show that water treatments under studied were arranged in ascending order according to the removal% of chemical contents. This ranking refer to the good reflect of using NAC in combination with limestone as a better treatment on enhancing sewage water quality. The removals of unwanted traits by the combination (NAC+ Lime stone) may be related to the function activity of surface area and also nano particles has a special properties i.e. high wide specific surface area, high reactivity, tunable pore size, which may allow them access to the maximum adsorption capacity and larger adsorption porosity moreover, the capability of limestone as a tool in water treatment and carriers to nano particles at the same time.

Table 8: Removal % for all sewage water treatments after soaking period 10 days

	Treatments	SAR	COD	BOD	TSS	PO4	NO3	Ca	Mg	Na	Cu	Cd	Fe	Ni
			%				%						%	
1	Limestone	0.23	0.04	0.08	0.98	0.12	0.2	0.08	0.11	0.009	0.51	0.16	0.17	0.09
2	PAC	0.27	0.16	0.25	0.97	0.17	0.31	0.12	0.12	0.07	0.62	0.35	0.34	0.29
3	NAC	0.34	0.37	0.31	0.98	0.33	0.41	0.16	0.20	0.12	0.75	0.58	0.37	0.42
4	NAC + Lime stone	0.36	0.40	0.41	0.98	0.69	0.58	0.22	0.30	0.17	0.75	0.71	0.44	0.67

CONCLUSION

Producing powder activated carbon and/or synthesis of activated carbon nano-particles (NAC) from sugar cane bagasse is considered one of successful trying up grate agricultural waste treatment technologies. Combination treatment (NAC + limestone) exhibited unique performance for reducing some pollutants from sewage water.

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التحقق من الكربون المنشط المنتج من مصاصة قصب السكر وتطبيقه على معالجة مياه الصرف الصحى

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أستخدام مرحلة التنشيط لإنتاج الكربون المنشط (AC) من قصب السكر (SCB). حيث تم التنشيط بطريقتين ؛ الطريقة الأولى تحطمت حبيبات AC إلى مسحوق ناعم (PAC) والثانية كانت عملية تخليق جزيئات نانوية من حبيبات الكربون المنشط (NAC). تم تقدير مساحة سطح PAC بواسطة (BET) Brunauer–Emmett–Teller وتوصيف NAC باستخدام طيف الأشعة تحت الحمراء (FTIR) و .(TEM) Trasmission Electron Microscope.

تم اختبار تأثيرات الممتزات المنتجة وحجر الجير الطبيعي من خلال تطبيقاتهم على مياه الصرف الصحي لتحسين بعض الخواص الفيزيائية والكيميائية التي إشملت على (الأس الهيدروجيني ، TSS، COD، BOD، TDS، ASR، NO3، PO4، Mg، Ca، Na، Cd ، Cu ، Fe ، Ni) خلال فترات نقع مختلفة (0 ، 10 ، 15 ، 20 يوم).

أوضحت النتائج أن تأثيرات استخدام الكربون المنشط النانوي بشكل فردي كانت أكثر كفاءة من PAC والحجر الجير الطبيعي لمعالجة مياه الصرف الصحي مع فترة نقع 10 أيام مقارنة بفترات النقع الأخرى. علاوة على ذلك ، أظهرت المعالجة ب NAC كممتز كفاءة عالية في إزالة أيونات المعادن (NO3، PO4، Mg، Ca، Na) وأيونات المعادن الثقيلة (Cu، Cd، Fe، Ni) وتقليل BOD و COD من مياه الصرف الصحي. لذلك ، تم إختبار تأثيره فى توليفة مع الحجر الجيري على معالجة مياه الصرف الصحي. اظهرت النتائج ان نسب الازالة المقابلة للصفات الكيميائية المدروسة كانت أعلى مقارنة بتطبيق كل منهم منفردا خلال فترة النقع 10 أيام.توصى الدراسة باستخدام التوليفة (NAC+ الحجر الجيري) كمادة جيدة جدًا في مجال معالجة مياه الصرف الصحى قبل إعادة تدويرها والتي يمكن تطبيقها لتقليل بعض ملوثات مياه الصرف الصحي بعد التخلص منها.