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Preparation and Evaluation of a Material Containing Both Micropores and Mesopores as a Dual-Function Adsorbent for Removal of Cationic and Anionic Species from Aqueous Solutions

E. A. Abdel-Galil, M. M. S. Ali* and Mostafa M. Hamed

Hot Laboratories and Waste Management Center, Egyptian Atomic Energy Authority PO.13759, Cairo, Egypt.

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ABSTRACT

The sorption potency of any material toward different radionuclides is closely related to porous structures and the surface functional groups. In this research, we report the process conditions to attain a new low-cost carbonaceous adsorbent from mint waste (CAMW) containing both micro- and meso-pores. The new sorbent was analyzed using various analytical techniques. From the study of surface properties, it was found that synthesized material possesses a high surface-area (BET) of 735.75 m²/g, Langmuir surface area of 1015.0 m²/g, total pore volume of 0.596 cm³/g, and the average pore diameter of 0.60 nm with a reasonable yield, 32.4%. Radionuclides contamination in the aquatic environment has become a dangerous threat today. Removal and recovery of these species (anionic and cationic radionuclides) before extrusion into the environment is essential for the safety of organisms. Therefore, we evaluated removal efficiencies of this new carbonaceous material as a dual-function sorbent for the retention of cations (Cs(I), Co(II), Sr(II) and Eu(III)) and anions (Cr(VI) and Mo(VI)) from aqueous solutions. Sorptive removal of various radionuclides (cationic and anionic species) from environmental samples confirmed the validity of results gained in these studies. All these values indicate that prepared CAMW possesses excellent adsorption capacity for both cationic and anionic radionuclides and can generally be considered as an advanced adsorbent.

INTRODUCTION

To date, the release of radioactive effluents (or any radionuclides), specifically from nuclear reactors, NORM, TENORM, and medical litter remains a hotly contested agenda from a global point of view. Nuclear energy production generates many radionuclides that must be managed safely to maintain the safety of humans and the environment around them. To solve this serious problem, modern technologies must be used and developed to remove radioactive species from the environment (mainly from wastewater) [1-7]. These combined reasons led to a general determination to remove radioactive isotopes and nuclear materials from wastewater before discharging them. [6, 7].

There are three methods that can be applied to treat radioactive wastewater, such as biological, chemical and physical methods [6-8]. Amorphous carbonaceous materials have been open utilized as an all-purpose sorbent for their unique characteristics, such as high

physicochemical stability, elevated degree of porosity, electrical conductivity and high surface-area. Moreover, it is nonpoisonous, recyclable and the cheap [7, 8]. Its precedent, activated carbon and charcoal, was first used in the industry of sugar in the United Kingdom in 1794 to remove color of sugar syrup, in respect of its capacity to efficiently adsorb various types of contaminants. The great improvement occurred in the First World War, for their application in air filters to delete toxic chemicals. The commercial manufacture of these materials has taken its current form since the 1930s [8].

The ability and efficiency of prepared carbon material are evidenced by the physical properties and chemical temperament of the surface, that is, the nature and quantity of the functional groups present. The surface nature of the carbonaceous material evolves through various modifications resulting from the oxidation process with H₂O₂, HNO₃, N₂O or O₂ and thermal modifications [7, 8].

The capability (mg/g) of carbonaceous materials is greatly affected by the pore-size- distribution of different materials subject to their molecular sizes [9]. According to many scientists interested in studying the adsorption of different types of radioactive materials on activated carbon (AC), the capacity of carbon (mg/g) is increased by the presence of micro-pores together with meso-pores in the structure of the prepared carbon [7-9]. This paper point out that the pore-size- distributions of carbonaceous materials evaluate their possibility utilization. Therefore, it should be noted that the pore-size-distribution and the surface chemistry synergize together to have a positive effect on the adsorption process [8-10]. Nevertheless, the high production cost of these carbonaceous materials hinders their popular apply. Biomass and agricultural residues are a cheap sources of low-cost activated carbon production [11].

Manufacture of ACs from agricultural residues (such as cotton, coconut husk, rice by-product, fruit skins) is a promising solution by converting discarded waste into useful (environmentally friendly) adsorbent materials.

There are a lot studies on the fabrication of carbonaceous sorbents such as activated carbons from many types of wastes as precursors. These wastes were counted to be undesirable starting materials for ACs because their composition was variable and heterogeneous. So, these relatively carbon-rich wastes are advantageous for producing different types of ACs that have large surface-area [8-12].

Two types of methods are frequently applied to produce these carbonaceous materials (AC): the method of physical-activation embrace the pyrolysis or thermal decomposition (carbonization process) of raw species (biomass wastes) and activation step of char by using gaseous activating agents (steam, CH₄, C₂H₄ and C₃H₆, CO and CO₂); and the chemical-activation method is completed by mixing carbonized materials together with activating agents (KOH, ZnCl₂, NaOH, K₂CO₃, AlCl₃, FeCl₃, NH₄Cl and H₃PO₄) [13].

Mint (*Mentha arvensis*) is one of the significant trade crops. It is spread almost universally around all continents and is immensely utilized in pharmaceuticals and cosmetic manufacturing. Following the extraction of the essential oil, mashed spearmint (distillation residue or mint waste) is usually used as a fuel [14]. Mint waste, as a type of renewable resource (agricultural), could be utilized an ideal precursor to obtain a new carbonaceous sorbent utilized in removing and recovering different radionuclides forms from solutions.

The objective of these studies was to synthesize a carbonaceous sorbent from mint waste (CAMW) to explore its use as a dual-function novel sorbent for the removal of different forms of radionuclides (cationic- and anionic- species) from waste solutions. Nitrogen sorption, FT-IR, SEM, TGA & DTA analyses were examined to assess the physicochemical properties of CAMW adsorbent. The model ionic species such as Cs(I), Co(II), Sr(II), Eu(III), Cr(VI) and Mo(VI) (for example of cationic and anionic species) are sorbed onto different CAMW samples. The current study indicated the wide applicability of this carbonaceous adsorbent (CAMW) in removing and recovering species of anionic and cationic radionuclides from different radioactive wastewater.

Experimental

Chemicals & Reagents

The reagents and salts used in this research were of analytical grade and used without further purification. Double distilled water (DDW) was used in all practical experiments. Mo (VI) and Cr (VI) solutions used in this study were prepared by dissolving ammonium molybdate and potassium dichromate in DDW, respectively.

Europium, cesium, strontium and cobalt solutions were obtained by mixing suitable amounts of their nitrate salts in DDW. Radioactive tracer ⁶⁰Co ¹⁵²⁺¹⁵⁴Eu, ¹³¹I and ⁹⁹Mo were gained from the second Egyptian Nuclear Reactor, while ¹³⁷Cs and ⁹⁰Sr were obtained from Amersham. Phosphoric acid solution was used as an activator during the preparation, and appropriate amounts of NaOH and/or HNO₃ solutions were also used to adjust the pH of the solution to the desired value.

Preparation of Carbonaceous Adsorbent (CAMW)

Mint waste was collected from the local market in Cairo, Egypt. Then, it was air-dried in sunlight for one week. The dried mint waste was crushed to suitable parts. CAMW adsorbent was prepared via impregnating the raw mint waste with 70% H₃PO₄ for about 24 hours, and then it was filtered via cotton membrane, and placed in stain-less steel tube “(4-cm×60-cm)” with thin ports (diameter of 1cm) at both ends, electrically heated, in absence of air, from ambient temperature to 600°C and kept at the final temperature for 2 hours. In the end, the carbonized material was taken away from the furnace and allowed to cool. The trial tests showed that the carbon produced under these conditions is economically preferable as a product with distinct surface properties. The carbonized material was subjected to repeated

washing with tap water to adjust the pH, then placed in a drying oven at 80 °C for 1 day, then ground, sieved and stored in a plastic bottle for further processing. The CAMW output was calculated from the following relationship:

$$Yield (\%) = \frac{CAMW}{RMW} \times 100, \quad (1)$$

Where CAMW is the carbonaceous adsorbent from mint waste (g) and RMW is the raw mint waste (g).

Instruments and Apparatus

Some of the characteristic chemical and physical properties of CAMW prepared using the following techniques have been demonstrated:

Scanning Electron Microscope (SEM)

The surface morphology was determined with scanning-electron-microscopy (SEM) and using the Jeol electron microscope of JSM-6510A Model, Japan.

N₂ adsorption-desorption

The specific surface-area, pore-volume, and pore-size-distribution of CAMW adsorbent were measured applying nitrogen adsorption & desorption isotherm (at 77 K) via Brunauer-Emmett-Teller (BET)-equation and Quantachrome Nova device (Model 184 Nova1000e series), USA. CAMW adsorbent was de-gassed (250 °C) under nitrogen flow for 3 h. before analysis so as to remove any adsorbed moisture or other impurities bound to CAMW surface sample followed by their analysis to evaluate the porous parameters. The amount of nitrogen adsorbed onto the adsorbent samples (CAMW) was used to compute the specific-surface-area (S_{BET}) according to BET-equation. The total-pore-volume (V_T) of the CAMW sample was deduced at a relative-pressure of $P/P_0 = 0.991$ from the adsorption data based on the manufacturer's software. The micropore-volume (V_{micro}) was computed by applying Dubinin-Radushkevich equation and meso-pore-volume (V_{meso}) was computed from the difference between $V_T - V_{micro}$. Pore-diameter and pore-size-distribution were computed by using the DFT-method.

Infra-red Absorption Spectrum

This spectrum has been recorded utilizing a Nicolet spectrometer (Meslo, USA) to identify the functional-groups using the KBr-disc method. In this test, CAMW sample was fully mixed with KBr as a matrix, the mix was ground and then pressed (to give a disc of standard diameter) . The disk formed was examined in FTIR-spectrophotometer (4000 - 400 cm^{-1}).

Thermal Analysis

Differential-thermal and thermo-gravimetric analyses (DTA/TGA) of CAMW were analyzed using DTA and TGA with a sample holder made of platinum using a Shimadzu DTG-60/60H thermal analyzer, Japan. It was applied for measurements of the changes and weight losses of the sample at heating rate of 10 °C/min in presence of nitrogen gas to avoid thermal oxidation of the CAMW sample. CAMW was heated in the platinum crucible from 25°C up to 600°C.

Determination of Adsorbate Ions Concentration

The pure liquid phase was gained by centrifugation and concentration of different adsorbate ions were measured utilizing an inductive-coupled-plasma-spectrometer (ICPs-7500) and/or spectrophotometry[5-7].

Analysis of Radioactive Samples

The pure liquid phases were obtained by centrifugation and the activity of ¹³⁷Cs, ⁶⁰Co ¹⁵²⁺¹⁵⁴Eu, ¹³¹I and ⁹⁹Mo were measured utilizing a high-resolution (7.5%) NaI(Tl) scintillation-detector, Model 802-3 × 3, Canberra, USA. As for the ⁹⁰Sr, it is measured using a liquid-scintillation counter (TRI-CARB model, 2700TR series, PerkinElmer) [5].

Sorption Studies

Batch experiments were investigated in thermostated shaker at 20 ±2°C to determine sorption behavior of the newly prepared material (CAMW) towards Cs(I), Co(II), Sr(II), Eu(III), Cr(VI) and Mo(VI) from aqueous media. The adsorption process was completed inside suitable-sized bottles in presence of a certain amount of adsorbate ions and CAMW adsorbent with the respective radiotracer ions (in the case of using radioactive isotopes). The bottles were locked and then shook until equilibrium was accomplished. The mixtures were centrifuged unto the supernatant was free from CAMW particles. Removal percentage (%R) and amount of ions, q_t (mg/g) retained on the CAMW were computed applying the following equations respectively [15, 16]:

$$\% .R = \frac{A_o - A_e}{A_o} \times 100 \quad (2)$$

$$q_t = \frac{\% R}{100} \times C_o \times \frac{V}{m} (mg / g) \quad (3)$$

Note that, A_o and A_e are the initial and equilibrium concentrations (or activities) of the aqueous phase before and after sorption process, respectively; C_o is basic concentration (or activities) of adsorbate ion (mg/L); V is the volumes of the solutions (L); and m is the masses of CAMW adsorbents (g).

RESULTS AND DISCUSSION

Main Characteristics of CAMW as A new adsorbent

The interactions between solid and aqueous phase are an essential substrate in retaining different species of adsorbates from aqueous media in sorption systems. In these reactions, the adsorption efficiency of any adsorbent is generally affected by the functional-groups present in its structure. These groups are closely related to the chemical assembly of the solid adsorbent. In addition, the extent of adsorption of the ion species from the solutions is positively proportional to the physical properties of the surface of the solid adsorbent material. So, the capacity of any solute of any solutions using a solid-phase sorbent material is affected by its physical and chemical properties [17-23].

SEM Micrograph

In numerous fields, such as geology, materials science, and chemistry the investigation of surface and interior morphology of solid phases is extremely important. One of the methods utilized to gain this information is the SEM. The SEM analyses supply a useful insight concerning the shape and surface of solid phases. Studies on CAMW material's surface details could specify important data on the degree of reciprocal action within the CAMW and adsorbate species [23]. To identify the morphological frames of the prepared CAMW, SEM images for the produced CAMW material were investigated in Fig. 1.

The images of CAMW offered a well-clear porosity, with a set of unequal cavities disseminated over the surface. These pores are gained from vaporizing the chemical activation molecules (H_3PO_4) during the step of carbonization of mint waste, leaving different spaces prior occupied by acid-chemical activator on surface of CAMW. There are plentiful cracks and small pits disseminated over the surface, indicating the severe interaction of the chemical enhancer with raw mint waste through step of carbonization [23].

There are different fluffy tablets or layers within the CAMW particles, between which are some pores due to the liberation of volatile compounds. The white species may be due to the existence of H_3PO_4 remnants or other impurities [23]. Obviously the rough exterior of the CAMW particles is an indication of a large surface-area. SEM-images of CAMW confirm the porous shape of this sorbent which could promote the retention of different adsorbate species.

Porous Characterization

The pore nature characters, including surface-area (S_{BET}), pore-volume, and pore-diameter of different

adsorbents, played a crucial function in the operation of adsorption [21]. To gain the surface-area of the prepared CAMW, N_2 adsorption-desorption isotherm was done at liquid N_2 (at temperature 77 K) and plotted as adsorbed volume (mL/g) versus relative pressure (P/P_0). The format of nitrogen gas adsorption isotherm may tool up a qualitative acquaintance on sorption step and the magnitude of the surface-area available to the sorbate species. Almost all analysis of adsorption equilibrium starts by matching the obtained adsorption isotherm with the classical one [7,22]. First endeavour to explicate adsorption isotherms of gas/solid phase equilibrium was made by (BDDT) in 1940, which classified these isotherms in five Types or patterns. The BDDT tabulation became the beginning point for modern IUPAC tabulation or classification for adsorption isotherms that included also a sixth type of isotherm[22].

In present studies by using chemical activation via H_3PO_4 , surface-area was greater than $730m^2/g$ wick is favorably comparable with commercial one and activated carbons produced from agricultural waste [23]. The N_2 isotherm and corresponding pore-size-distribution of the prepared CAMW was listed in Fig.2 and Fig.3.

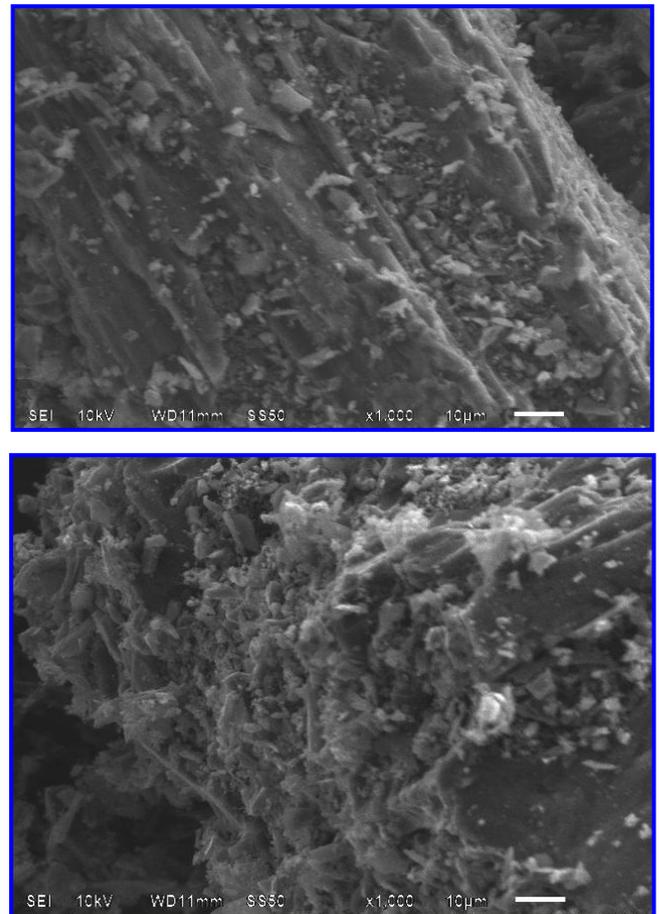


Fig. (1): SEM images of CAMW material

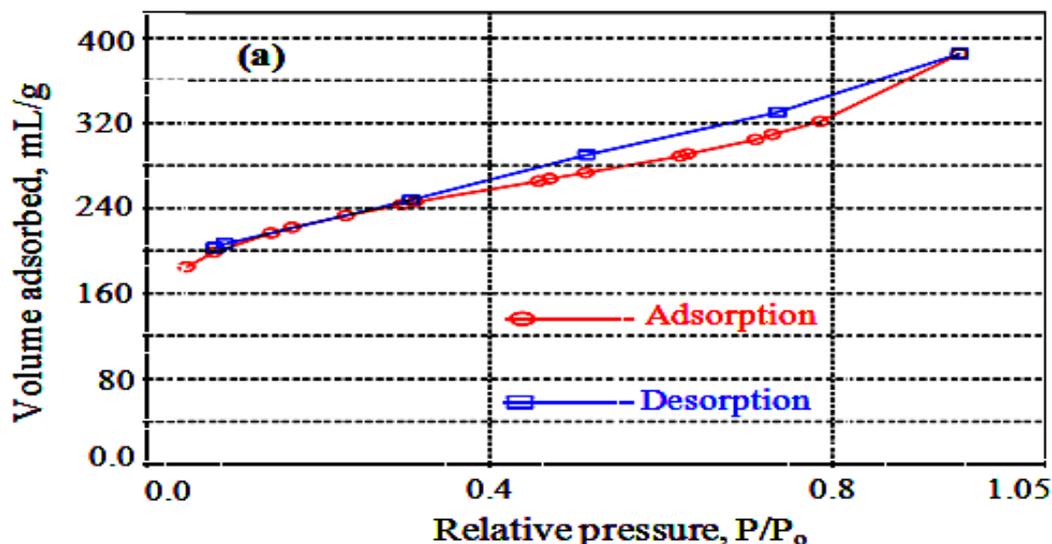


Fig. (2): Nitrogen adsorption/desorption isotherm of CAMW material

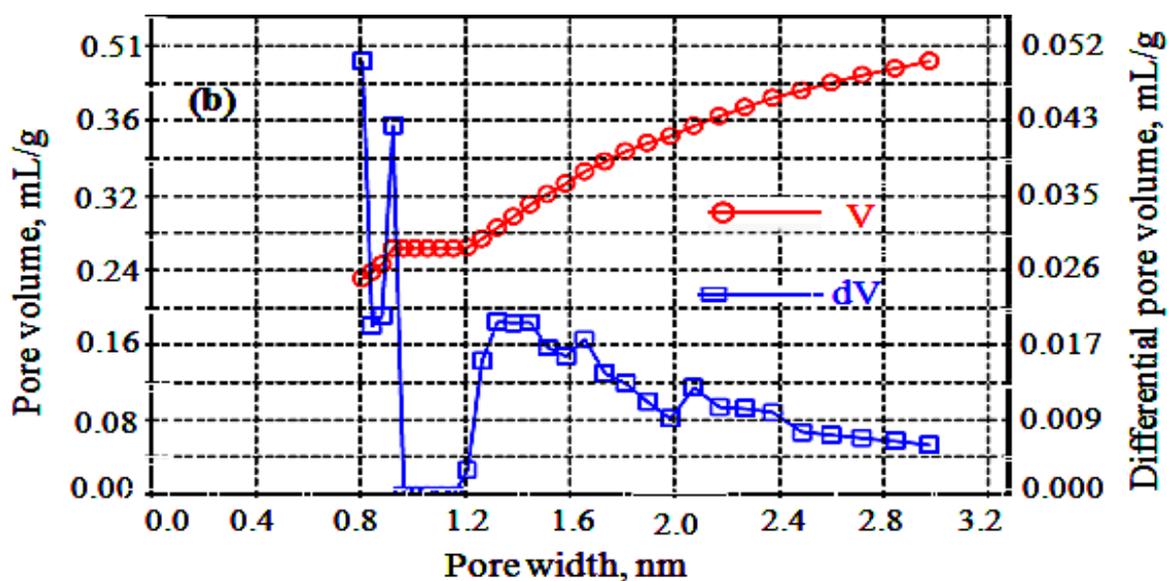


Fig. (3): Pore-size-distribution of CAMW material

Figure 2 displays the N_2 -isotherm of the prepared CAMW. According to IUPAC classification, the isotherm obtained for CAMW is composite *Types I* and *IV*, showing that CAMW abundant with both micropores and mesopores is obtained. [24]. It can be found that the sorption value increases at low-relative pressure (P/P_0), demonstrating the being of micropores (*Types I*); and there exists a hysteresis loop after $P/P_0 = 0.3$ but no adsorption plateau near $P/P_0 = 1.0$, illustrating presence of mesopores (*Types IV*).

Indeed, the CAMW possessed a combination of both *Type-I* and *Type-IV* of IUPAC-isotherm, indicating the simultaneous presence of micropores (<2 nm) and mesopores (2–50 nm). CAMW exhibits a broad knee

and clear desorption hysteresis loop of type H4, which is linked with capillary condensation that occurred in mesopores. The appearance of this loop indicates a *Type-IV* isotherm which was evidenced by the presence of mesoporous texture in the CAMW. The hysteresis loop has no sharp knees indicating the presence of different sizes from mesopores.

Generally, the pore-size-distribution is one of the characteristics of porous sorbent that displays the structural not matching and represents a model of sorbent internal-composition. Figure 3 presents the pore-size-distribution curve. This figure scouts the being of micropores and mesopores in CAMW. Most of the pore-size is ranging from 0.8 to 3 nm are distributed in

the CAMW texture, around 55% -of the pores are between 0.8 and 2 nm (super-micropores) and around 45% -of the pores are 2-3 nm, which confirms the micro-porous and meso-porous nature of this prepared carbonaceous material. The smaller particle-sizes of a porous sorbent the greater rate of diffusion and removal [25]. Those further indicate that CAMW is an effective retention material for many adsorbate species.

In the chemical activation step (using H_3PO_4), pore-size and pore-volume increase, and new pores are created due to reaction of carbon and H_3PO_4 . During the process of pyrolysis, pores are left after the volatilization of moisture and volatile. The activation of mint waste, and subsequent pyrolysis, leads to the-production of carbonaceous CAMW with a highly specific surface-area ($735.80\text{m}^2/\text{g}$) and has 0.596 mL/g of total pore volume, which is highly advantageous for adsorption applications, Table 1 [25].

Table (1): N_2 adsorption/desorption analysis of CAMW

Parameter	Value
S_{BET} Surface-area (m^2/g)	735.75
Langmuir surface-area (m^2/g)	1015.0
Total pore-volume (cm^3/g)	0.596
Average pore-diameter, APD (nm)	0.60
Yield of carbonaceous CAMW, %	32.40

Functional Groups of Carbonaceous CAMW

It is well known that carbonaceous materials have a huge variety of surface functional-groups and the nature of these groups counts on the precursor and activation type method [26]. FT-IR is a vibrational spectroscopic technique usually used to identify functional groups that exist in solid phase's surface which could be probably interested during the interactions/ sorption of different adsorbate species. These groups on-the surface are one more effective factor on the capacity (mg/g) of the material. Fig.4 shows FT-IR the spectrum of the prepared carbonaceous CAMW gained by H_3PO_4 activation at 600°C .

The multiple bands observed from 3696 to 3588 cm^{-1} followed by a broad band at 3444.88 cm^{-1} in the CAMW is given to -NH stretching, -OH stretching (from carboxyls, phenols or alcohols) vibration modes & H_2O present in CAMW respectively sample [23, 27]. The vibration modes appear at about 2925 cm^{-1} and 2855 cm^{-1} are given to asymmetric $-CH_2-$, $-CH_2-$ stretching and symmetric $-CH_3$ vibrations [23]. The absorption

peak at around 2100 cm^{-1} may be ascribed to the alkynes group [23].

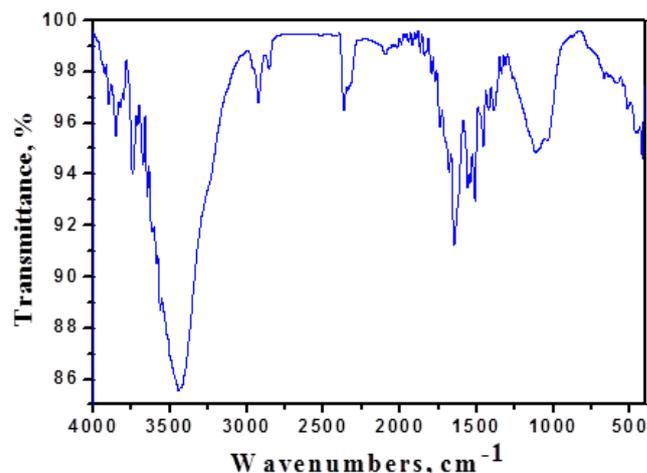


Fig. (4): FT-IR spectrum of CAMW

The bands observed from 1670 cm^{-1} to 1820 cm^{-1} may be referred to $-C=O$, in addition to bonding of $Si-O$ and $P-O$ [27]. It is noteworthy to mention that the $-C=O$ groups, $-COOH$ groups, and $-OH$ groups in addition to bonding of $Si-O$ and $P-O$, play an important part in the step of sorption to different adsorbate species [27]. The vibration modes appear at about 1550 cm^{-1} and 1650 cm^{-1} is given to $-NH$ of amide groups, where the peak at around 1458 cm^{-1} may be due to $C-H$ bending (in CH_3 groups)/aromatic $-C=C$ stretching vibrations. The band at 1559 cm^{-1} is given to $C=N$ or $C=C$ stretching vibrations [23]. The absorption from 1300 to 900 regions is difficult due to the overlapping of absorption peaks from many oxygen & phosphorus molecules in this range, an unambiguous assignment is intricate. Nevertheless, based on these data, absorption in-the range $1300-900\text{ cm}^{-1}$ could be temporarily linked to the phosphorus species [23]. It suggests that various functional-groups formed on CAMW surface could be affected by the H_3PO_4 activating agent. The small bands located at the range from 400 to 700 cm^{-1} are related to modes of $O-C-N$, $Mg-O$, $Ca-O$, $Si-O$ or $Si-O-Si$ vibration bonds. The existence of these absorptions was due to the being of Si , Ca , Fe , Mg or Zn [23]. From this study, we may say that the prepared new CAMW material contains various functional-groups on its surface.

Thermo-gravimetric Analysis (TGA&DTA)

Thermo-gravimetric analysis (TGA and DTA) is the extreme vastly utilized thermal analytical techniques in

the characterization of retention materials. In the TGA, mass of samples from these materials is measured as a function of temperature increment over a period time. The consequence from this analysis supplies facts related to chemical and physical phenomena, including thermal decomposition and sorption [26]. The TGA & DTA of CAMW were elaborated to explore its thermal-stability at towering temperature operating case. The thermal analysis of CAMW sample was tested from about 30°C to 600°C. Figure 5 shows thermal curves (TGA and DTA) of CAMW sample in N₂ atmospheric gas. During the thermo-gravimetric analysis (TGA), two weight loss stages were observed in CAMW sample, Fig.5.

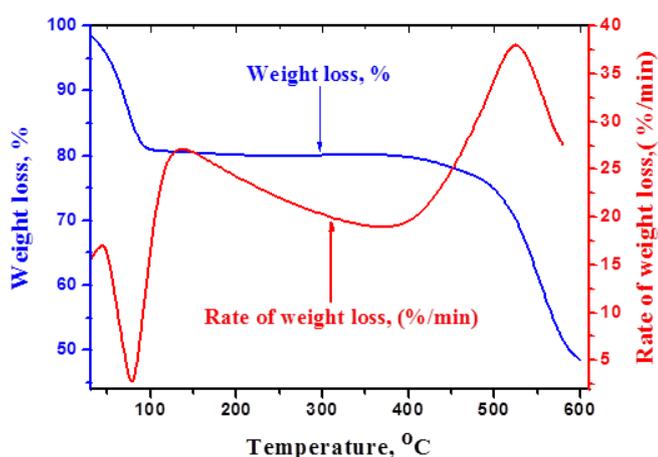


Fig. (5): TGA & DTA for the CAMW material

Weight loss initially, which is lesser than 20% at the temperature range 30 to about 100 °C could be referred to releasing of molecular-bound free H₂O and some volatile species (hydrocarbons compounds) from the surface and pores of CAMW sample. Then weight loss remains constant till temperature of about 500°C. A mass loss of around 23% from 500°C to 600°C may be resulting from the thermal decomposition of CAMW sample. Volatile gasses products such as carbon dioxide (CO₂) and carbon monoxide (CO) are possibly generated at this step. The DTA curve shows the endo-thermic and exo-thermic reactions of CAMW at their respective temperatures. From the thermogram (Fig.5), it is spotted that CAMW carbonaceous material is extremely stable up to about 500 °C.

CAMW-Production

In the present research, CAMW production was done at 600°C using H₃PO₄ as activating agent. Several activating agents have been stated for use in the chemical activation process. Among them, H₃PO₄ is excessively applied in the generation of carbonaceous

adsorbents because of few energy costs and high carbon contents moreover easy recovery of the activating agent. While the general mechanism in chemical activation isn't so well understood as that in physical activation, the activator is notified to act as an acidic/alkaline catalyst to support bond break down, hydrolysis, dehydration and condensation, accompanied by cross-linking reactions between acid/alkali and bio-polymers [28, 29].

An increase in activation temperature can hurry the activation process, extra carbon atoms react with H₃PO₄ (activating agent). The carbonization of mint waste at a selected temperature, 600 °C in the presence of H₃PO₄ resulted in the configuration of the carbonaceous adsorbent (CAMW) in yield of 32.40 %. This yield is comparable to some work on carbon adsorbents prepared from different tailings where a similar yield above 30% has been reported [28, 29].

Physical change happens in the internal composition of carbonaceous sorbent with an increase in thermal treatment. The growth of definite crystals is advanced and the orientation of these crystals is uniformly, and these alterations improve the graphitization degree. It was noted that the augmentation of carbonization-temperature causes a progressive dwindling of the final yield. A decrease in the final product (yield) was observed at temperatures of 800°C for activated carbons (ACs) prepared from fruit stones and other carbonaceous precursors [28, 29]. This can be referred to a thermal-decomposition for the carbonaceous-phosphorus species and reduction of the phosphates present to elemental phosphorus having, as a result the figuration of gases or volatile phosphorus species likes phosphorus oxide (P₄O₁₀) and elemental phosphorus. Volatile phosphorus compounds may be formed according to the equations below [28]:



Evaluation of Adsorption Behavior of CAMW as A dual-function Adsorbent

In recent years, the removal of different radioactive isotopes has been further increased by the growth of new ACs or carbonaceous adsorbents of different modifications. It is well established that sorbents with highly sorption capacity need the being of micro- and meso-sized pores, high thermal and physical stability, and less cost for commercial production [22, 23, 29].

The actual application of currently available sorbents to environmental treatment is restricted by their ability to sorb and remove only one radioactive type (anionic or cationic), which reduces their real environmental treatment [30]. Motivated by these worries, we prepared a new cheap porous sorbent for removal of anionic and cationic radionuclides concomitantly. Through the conclusion we gained from the step of characterizing the newly prepared carbonaceous material, it was revealed to us that CAMW (the new material prepared) has important characteristics. As it holds a relatively small and suitable particle-size and its surface has many holes and cracks. From a study of nitrogen adsorption/desorption, it was found that CAMW carbonaceous material contains two important types of pores concomitantly, they are micropores and mesopores, and it also has a large surface-area of 735.75 m²/g. This makes it suitable for the sorptive removal of many ions of different sizes. The study also showed that the exterior (surface) of this carbonaceous material is rich in plentiful different functional groups. This makes it able to easily bond with any cation or anion species. It also has thermal stability that makes it work under difficult conditions. In general, all these features possessed by the prepared material make it a unique adsorbent that can easily adsorb many radioactive isotopes of different charge and size. And all of this is because this material can work by a new than one mechanism in removing the various species. After all, it has unique properties that qualify it for that. This makes this new material capable of treating both liquid radioactive wastes, moreover environmental water contaminated with radioactive isotopes.

Sorption Behavior of CAMW for Anionic Radionuclides Species

Removal of Cr (VI) and Mo (VI) Anions

With the immediate evolution of power plants (nuclear), removal of several radionuclides such as ⁹⁹Tc, ⁹³Mo, ¹³⁷Cs and ⁹⁰Sr turned into a prime environmental security problem. Sorption of these isotopes, especially anionic ones such as ⁹⁹Tc ($t_{1/2}$ 2.13×10⁵ y) and ⁹³Mo ($t_{1/2}$ 4×10³ y) has been challenging. ⁹⁹Tc and ⁹³Mo are weakly sorbed by most solid phases [22, 31].

In this experiment, removal of Cr(VI), a non-radioactive analogue of ⁹⁹TcO₄⁻, from various solutions by CAMW was investigated [32]. Chromium (VI) anions sorption was studied from solution (concentration 100 mg/mL) onto CAMW (0.03 g). The concentration C_e

was obtained when the solution reached equilibrium. According to Eq.2 and 3 we could get the q_e (equilibrium sorption capacity of CAMW) [33-35]. The removal process was tested at 25°C. Sorption of Mo(VI) anions was studied in the same way (of nuclear power plants).

From the results found in **Fig. 6**, Cr(VI) sorption reached the equilibrium in about 60 min and maximum amount of sorption (q_e) was 35 mg/g.

As for Mo(VI) sorption, it can be seen from **Fig. 6**, Mo(VI) sorption reached equilibrium in about 50 min and uptake (q_e) was 30 mg/g. Generally, the obtained sorption results of anions indicated that CAMW has excellent sorption capacity towards Cr(VI) and Mo(VI) species.

Sorption Behavior of CAMW for Cationic Radionuclides

Sorption of Cs(I) and Sr(II) Cations

Following the Fukushima nuclear disaster (Japan 2011) the levels of isotopes such as, ¹³⁷Cs, ¹³⁴Cs, ⁹⁰Sr and ¹⁴⁰Ba in the ocean have been noted [23]. Exposure to these isotopes has serious consequences such as damage to humans and the surrounding environment also through genetic mutations. For instance, ¹³⁴Cs and ¹³⁷Cs can inflow into the human body with ease by virtue of food consumption because of its high-water solubility. In addition, ⁹⁰Sr, the second greatest radionuclide after ¹³⁷Cs, poses a risk of osteosarcoma, chondrosarcoma, and Ewing sarcoma. Thus, the evolution of an effective sorbent to remove ¹³⁷Cs and ⁹⁰Sr from the environment and lowering the danger to human health is extremely desirable [23].

Cesium (I) cations sorption was studied from a solution with the concentration of 200 mg/mL onto 0.03 g CAMW. The concentration C_e was obtained when the solution reached equilibrium. According to eq. 2 and 3, we could get q_e equilibrium sorption of CAMW. All sorption processes were tested at 25°C. Sorption of Sr (II) cations was studied in the same way at the same condition. The data obtained are shown in Figure 7.

Figure 7 explain the time-dependent behaviors of Cs(I) and Sr(II) cations removal from aqueous phase by using CAMW. Sorption of Cs (I) reached equilibrium in about 120 min and the sorption was 77 mg/g. In the case of Sr(II), the sorption reached equilibrium in about 100 min and the maximum amount of Sr(II) sorption was 120mg/g.

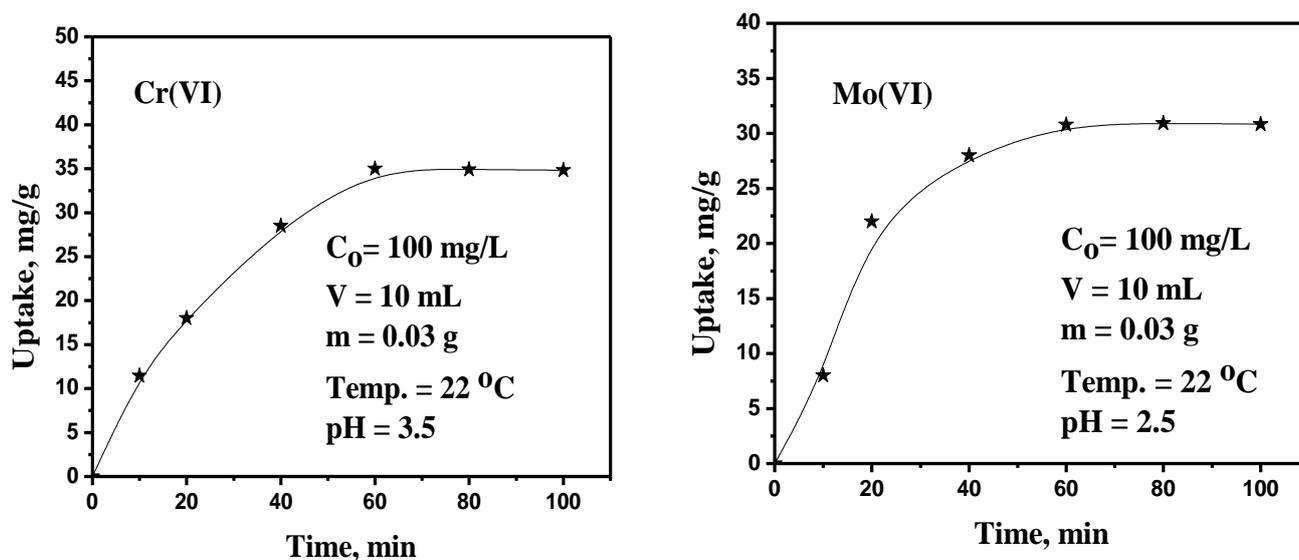


Fig. (6): Sorption curves of Cr(VI) and Mo(VI) anions

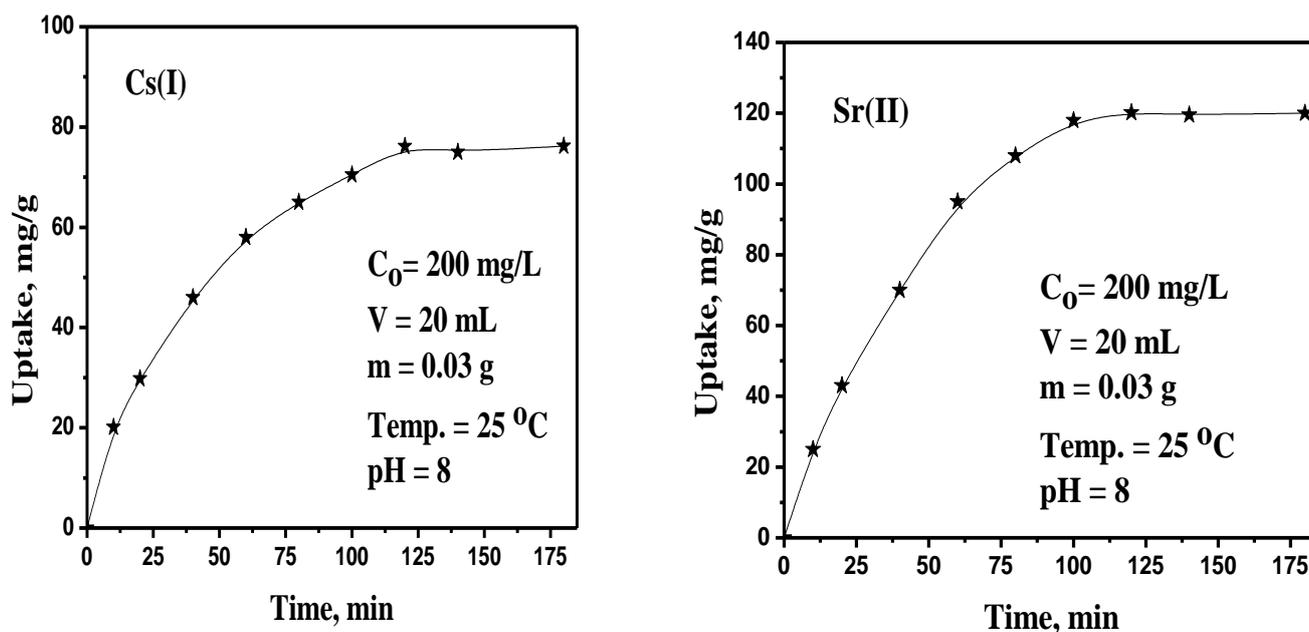


Fig. (7): Sorption curves of Cs(I) and Sr(II) cations

Sorption of Co(II) and Eu(III) Cations

^{60}Co is a widespread component in liquid radio-waste resulting from different nuclear facilities. Due to its wide employment in the area of nuclear-medicine and industry, its radioactive half-life of 5.3 y, and its gamma energy, it has a significant value to retain and to separate

it from different water streams [23]. With the frequent use, progression in atomic energy, and in the post-processing of spent fuels, massive quantities of radionuclides, especially of long-lived lanthanides (such as $^{152,154,155}\text{Eu}$) and actinides (such as $^{241, 242m, 243}\text{Am}$), are also created [23].

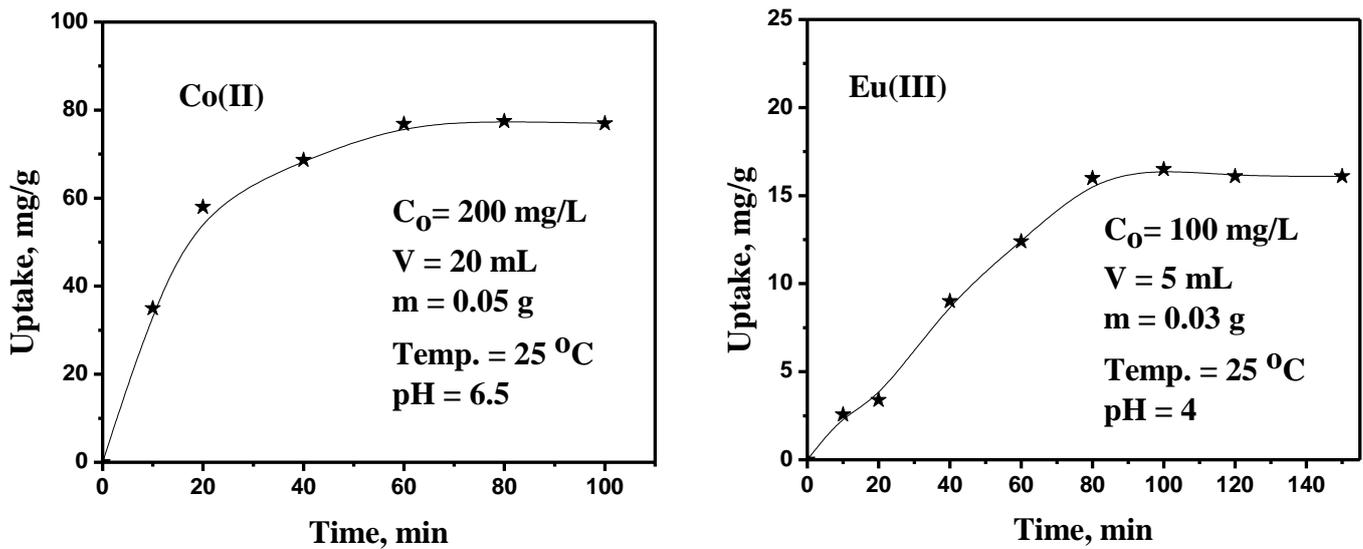


Fig. (8): Sorption curves of Co(II) and Eu(III) cations

Sorption tests were performed for Co (II) & Eu (III) cations from their aqueous phase onto CAMW. As can be shown in Fig. 8, removal of Co(II) reached the equilibrium in about 60 min and maximum amount of sorption (q_e) was 80 mg/g. As for when removing the Eu(III), it was revealed to us the sorption of Eu(III) reached equilibrium in about 80 min and the maximum amount of sorption was 15 mg/g, Fig. 8. Generally, the obtained sorption results of Cs(I), Sr(II), Co(II), and Eu(III) specified that the CAMW has also excellent sorption capacity towards all these cation species.

From all the sorption results that we obtained in the previous experiments, it becomes clear to us that this newly prepared material (CAMW) has wonderful properties that make it a suitable sorbent for both the anions and the cations. Table 2 shows all the results gained from sorption tests for anion and cation species.

Table (2): Sorption data for anions and cations species

Ion	pH	Equilibrium Time, min	Equilibrium Capacity, mg/g
Cr(VI)	3.5	60	35
Mo(VI)	2.5	50	30
Cs(I)	8.0	120	77
Sr(II)	8.0	100	120
Co(II)	6.5	60	80
Eu(III)	4.0	80	15

Application

To find out the qualifications of the new prepared (CAMW) sorbent, 0.05 grams of it was utilized to treat Nile-River water contaminated with some radioactive isotopes (spiking method) such as ^{137}Cs , ^{90}Sr , ^{60}Co , $^{152+154}\text{Eu}$, ^{131}I and ^{99}Mo . The Nile water was used with a view to know the matrix effect of this water on removing these isotopes mentioned above. The results gained are tabulated in Table 3. From the results in this table, it appeared to us that the prepared material showed a removal rate ranging from 94% to 99%, which makes this material a suitable adsorbent for various purposes unlike all adsorbents used often in such treatment processes. Another important feature of this new adsorbent is its preparation from economical material (waste material), in addition, to the employ of non-toxic chemicals in its preparation. Moreover, huge amounts quantities of this sorbent (CAMW) are prepared easily.

Table (3): Removal efficiency of some radionuclides from river water samples

Sample No.	pH	Spiked with, mg/L	Radionuclide spiked	* Removal efficiency, %
1	8.0	5	^{137}Cs	95.0
2	8.0	5	^{90}Sr	94.0
3	6.5	5	^{60}Co	96.5
4	4.0	5	$^{152+154}\text{Eu}$	99.0
6	2.5	5	^{99}Mo	98.0
7	3.5	5	^{131}I	99.0

(*) Just one treatment

CONCLUSIONS

CAMW was synthesized and evaluated as a dual-function carbonaceous material containing both micropores and meso-pores for retaining of anions and cations from solutions. The newly prepared adsorbent is found to possess an excellent sorption capacity to-Cs(I),-Sr(II),-Co(II), Eu(III), Cr(VI) and Mo(VI) ions. CAMW was successfully-utilized to the removal of ^{137}Cs , ^{90}Sr , ^{60}Co , $^{152+154}\text{Eu}$, ^{131}I and ^{99}Mo in spiked environmental water (Nile river) samples. The employment of CAMW has shown that all radionuclides can be wonderfully separated from these samples with percent removals ranging from 94% to about 99% with just one treatment. The results offered that CAMW sorbent could be counted to be exceedingly effective and helpful material for anionic and cationic radionuclides species removal from different wastewaters.

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