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College of Science
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Preparation Nanocellulose-Graphene Oxide Composite for Removal Cadmium (II) ions in Aqueous Solutions

A graduation research project submitted to the Department of Chemistry in partial fulfilment of the requirements for the completion of the degree of
Bachelor of Science in ***Chemistry***.

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under supervision
of

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Abstract

Residual heavy metals in water are often became harmful inorganic pollutants. The purpose of this project was to prepare a composite of graphene oxide (GO)/nanocellulose (NC) for the removal of the cadmium ions from aqueous solutions by adsorption. The prepared composite was characterized using scanning electron microscope, Fourier transform infrared (FT-IR), X-ray diffraction, and other characterization methods to study the physical structure and chemical properties of the GO-NC. Its adsorption capacity of the GO-NC for the Cd(II) was investigated using equilibrium study. The composite material exhibited good metal adsorption capacity, with a removal percentage exceeding 85% at pH of … Consequently, the as-synthesized CNCs-GO demonstrates good potential for the effective removal of cd from aqueous media.

الملخص باللغة العربية

غالبًا ما تصبح المعادن الثقيلة المتبقية في الماء ملوثات غير عضوية ضارة. كان الغرض من هذا المشروع هو تحضير مركب من أكسيد الجرافين (GO)/ النانوسليلوز (NC) لإزالة أيونات الكادميوم من المحاليل المائية عن طريق الامتزاز. تم تشخيص المركب المحضر باستخدام المجهر الإلكتروني الماسح، وتحويل فورييه للأشعة تحت الحمراء (FT-IR)، وحيود الأشعة السينية، وطرق التوصيف الأخرى لدراسة التركيب الفيزيائي والخصائص الكيميائية لـ GO-NC. تمت دراسة قدرتها على الامتزاز لـ GO-NC لـ Cd (II) باستخدام دراسة التوازن. أظهرت المادة المركبة قدرة جيدة على امتصاص المعدن، مع نسبة إزالة تتجاوز ٨٥% عند درجة حموضة قدرها ... وبالتالي، تُظهر CNCs-GO المُصنّعة إمكانات جيدة للإزالة الفعالة للقرص المضغوط من الوسائط المائية.

1. Introduction:

There is a huge harmful material such heavy metals used in industry in Saudi Arabia [1]. In the Kingdom of Saudi Arabia, the industrial revolution has led to a notable surge in the production of extremely polluted industrial wastewater including a variety of heavy metals. Metal plating, mining, tanning, chlor-alkali, ceramic coating, paint manufacturing, catalysts, alloy industries, wire conduction, iron galvanizing, polymer stabilizers, storage battery manufacturing, semiconductors, pesticides, wood preservation, and dye factories are among the various factory wastes that contain heavy metal contamination [2].

Graphene oxide:

A C60 product was created by Robert Curl et al. in 1985 using graphene, a substance composed of carbon. But Krätschmer verified the cage structure of C60-fullerene four years later. The first report of carbon nanotubes and the expansion of the family of carbon materials was made by Nippon Electric Company (NEC) Ltd. in 1991. Using a micro-computer peeling technique, Novoselov et al. effectively removed graphene from the monolithic state in 2004, challenging the status of science about two-dimensional crystals. Fig.1 depicts the structure of graphene, which is made up of a layer of separate sp2 hybrid carbon atoms. It is a two-dimensional carbonaceous substance with a crystal structure resembling a hexagon honeycomb. With a sheet thickness of 0.34 nm, graphene is currently the strongest and thinnest nanomaterial available [3].

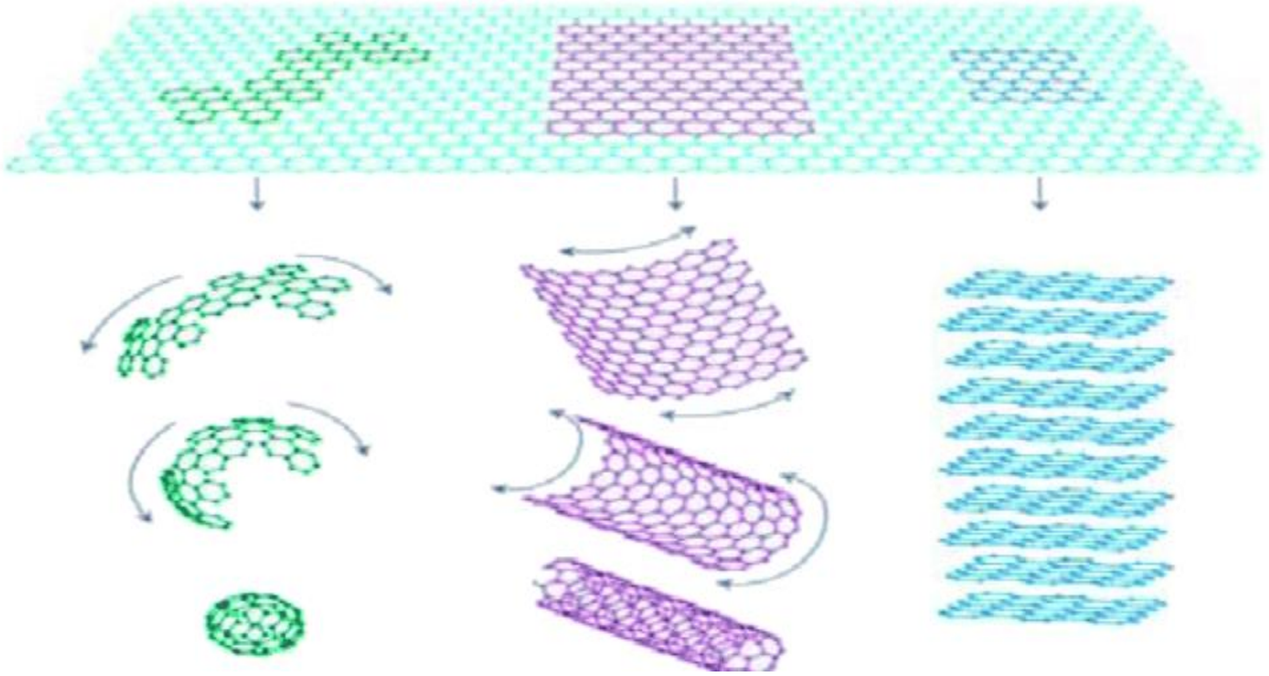

Figure 1. Structure of graphene different types [3].

Preparation of Graphene Oxide

The preparation of graphene oxide is generally carried out *via* two steps of oxidant intercalation oxidation and sheet peeling, as shown in Fig 2. 150 years ago, Brodie prepared graphite oxide for the first time, but it was not noticed at that time. With the development of the graphene oxide. Graphene oxide (GO) is a derivative of graphene, easy and has excellent solubility in water. Therefore, there are many researchers interested in developing methods to produce GO efficiently. Although the traditional chemical oxidation method is widely used for GO synthesis, it has problems, such as long time consumption, explosion risk, and easy to pollute the environment. Recent research on the use of electrochemical methods for GO synthesis has made significant progress, namely achieving a pollution-free, safe, and efficient large-scale preparation of high-quality GO within a few hours. This article introduces the principle of electrochemical GO synthesis and summarizes the research progress on the preparation of GO via two-electrode, three-electrode, and electrolyte exfoliation with emphasis on product quality and quantity. Challenges in producing high-quality electrochemical GO and future research directions are also presented [4]. GO can be functionalized by chemical bonds, compounded with other materials and assembled into various large-scale graphene architectures (transparent conductive films, strong and stiff papers, multifunctional separation membranes, conductive and strong fibers, ultralight super-elastic aerogels, etc) through electrostatic interactions, van der Waals forces and hydrogen bonds [5].

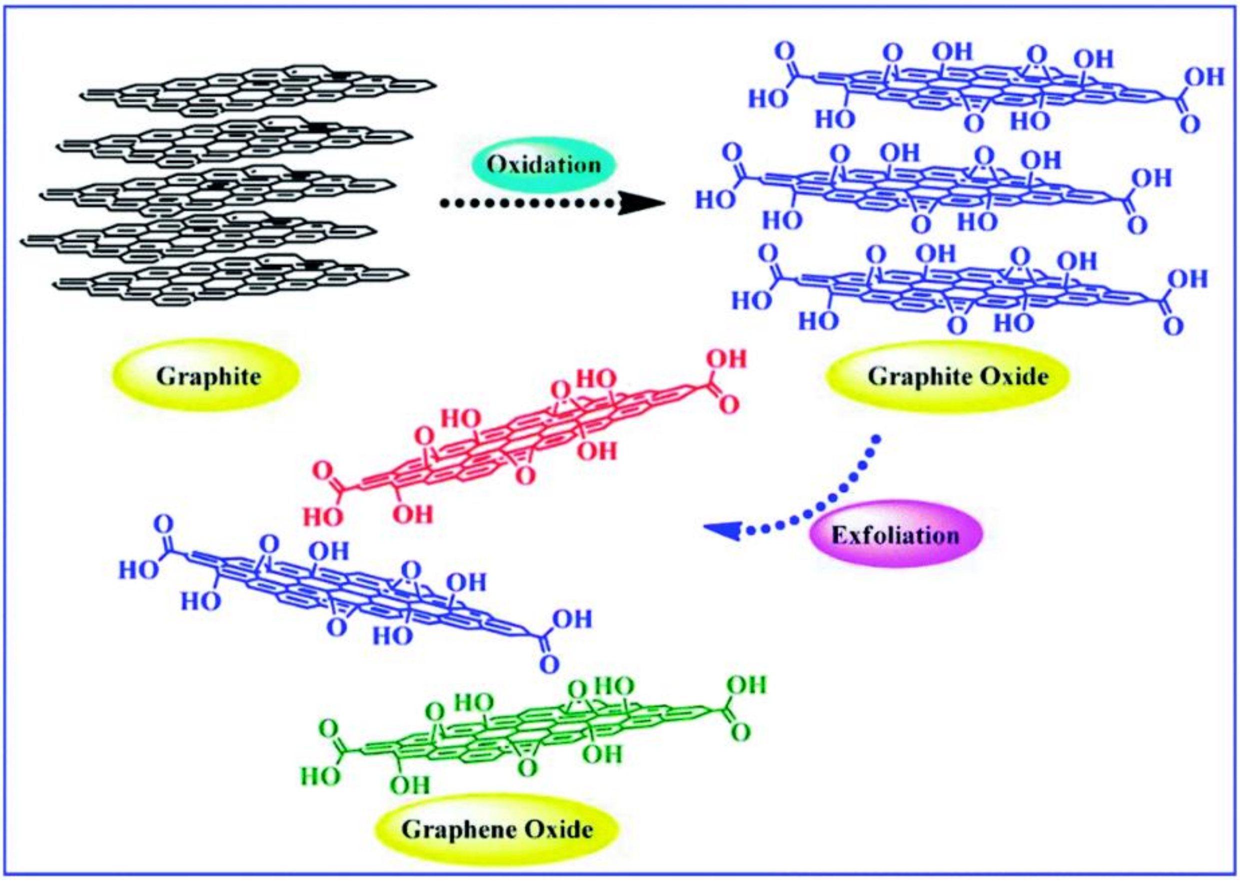

Figure 2. Preparation of Graphene Oxide [4]

Researchers have made extensive improvements to the three methods by fixating on enhancing the oxidation and exfoliation of graphite. However, these chemical oxidation approaches consume hours and even days and produce various toxic gases (e.g. NOx and ClO_2). Moreover, the most broadly applied Hummers method entails a danger of explosion because of the production of intermediate Mn_2O_7, and the use of $KMnO_4$

causes permanent defects that cannot be repaired after GO reduction [6-7]. What's more, extra decontamination operations are needed to wipe off residuary acids and impurity metal ions in GO, and these steps produce a large volume of wastewater. Compared with graphene, GO has received considerably less attention in the investigation new synthetic methods. New methods of GO synthesis, such as electrochemical stripping of graphite, [7] ball milling [8] and ultrasonic treatment, [9] have been widely used in recent years. Electrochemical exfoliation is regarded as a pollution-free, safe, efficient method of synthesising GO, and it has the following advantages:

(1) no strong chemical oxidants are involved because the current is a pollution-free oxidant functionalized by graphene.
(2) the process is usually completed within hours or even minutes.
(3) the quality and yield of GO, such as the degree of oxidation and defect density, can be easily regulated by adjusting the electrochemical reaction conditions.

Also, agricultural residue usually disposed of through open burning, which has a good potential as an alternative material to synthesize into nanomaterials. The production of carbon from natural sources can overcome the hazardous effect and reduce the risk of pollution. Researchers have developed a method by using coconut shell due to renewable waste product to produce new natural carbon source. This review has focused on research carried out on coconut shell powder (CSP) turn to natural graphite or activated carbon with high carbon content from various region worldwide [10].

Nanocellulose:

Lignocellulosic biomass (LB) is an abundant and renewable resource from plants mainly composed of polysaccharides (cellulose and hemicelluloses) and an aromatic polymer (lignin). LB has a high potential as an alternative to fossil resources to produce secondgeneration biofuels and BioSource chemicals and materials without compromising global food security. One of the major limitations to LB valorisation is its recalcitrance to enzymatic hydrolysis caused by the heterogeneous multi-scale structure of plant cell walls. Factors affecting LB recalcitrance are strongly interconnected and difficult to dissociate. They can be divided into structural factors (cellulose specific surface area, cellulose crystallinity, degree of polymerization, pore size and volume) and chemical factors (composition and content in lignin, hemicelluloses, acetyl groups). Goal of this review is to propose an up-to-date survey of the relative impact of chemical and structural factors on biomass recalcitrance and of the most advanced techniques to evaluate these factors. Also, recent spectral and water-related measurements accurately predicting hydrolysis are presented. Overall, combination of relevant factors and specific measurements gathering simultaneously structural and chemical information should help to develop robust and efficient LB conversion processes into bioproducts [11]. Local biomass like date-palm tree consist of wood components (Cellulose, hemicellulose, and lignin). The following figure 4 Shows the structure of plants units.

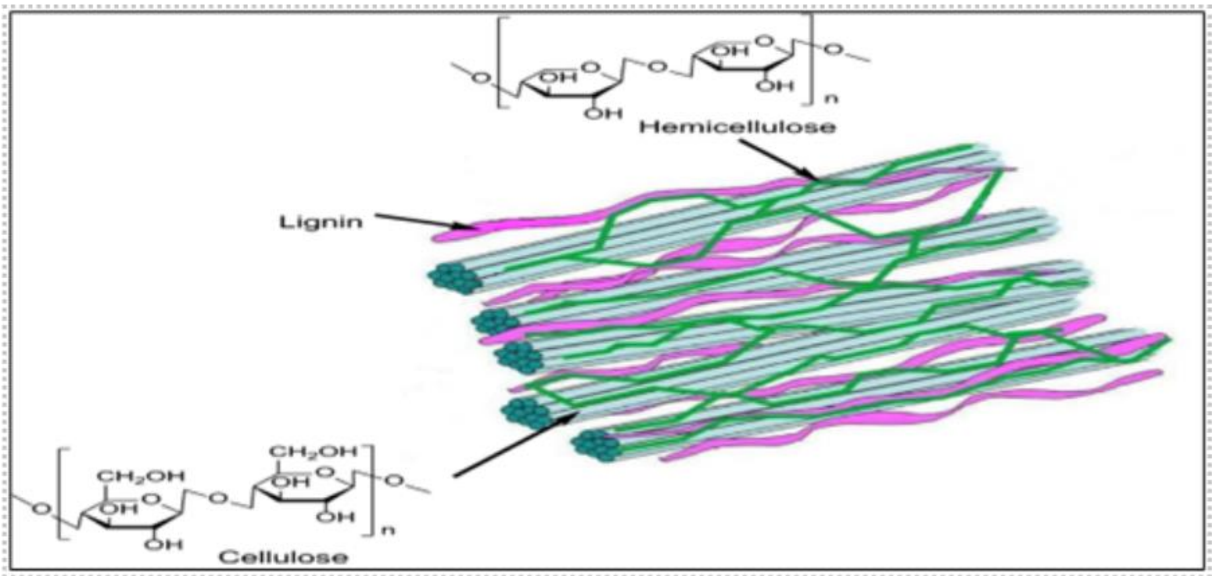

Figure 3. Components of wood from plant [12].

Nanocellulose-Graphene oxide composite:

Cellulose is known as a natural polymer that is renewable, low-cost, biodegradable, and naturally abundant [13].28 The structure of cellulose contains many hydroxyl groups. Consequently, it is easy to create internal and intermolecular hydrogen bonds with water, creating favourable conditions for this material to exist in the form of hydrogels, especially when they are at a nanometre size. The nanocellulose aerogels can be fabricated for many applications by many different methods, of which the vacuum freeze-drying technique is the simplest and most popular technique. The nanocellulose aerogel has a highly porous structure, light weight, and a large surface area, making it very suitable for adsorption applications [14].29 The surface of the nanocellulose aerogel has good polarity, so it has good interactions with polar organic dyes. However, the nanocellulose aerogels have a limited sub-resolution [15] and often have to be latticed or reinforced with other materials in adsorption applications. In the water environment, the research to improve the adsorption capacity of dye wastewater for this type of adsorbent is very interesting to expand its applicability.

Other carbon materials almost all have high adsorption capacity due to the characteristics of the graphite lattice structure and high surface areas, such as graphene, [16] , carbon nanotubes,,[17] and graphene oxide (GO).[18] Graphene/matrix composites have been shown to have excellent mechanical properties, including high compressive and flexural strength, [19] Young's modulus and compressive strength, [20] and controllable pores and mechanical flexibility [21]. GO nanosheets have a special 2D structure with a high surface area, and when in the aerogel form, the GO aerogel has a highly porous 3D structure with a low density. Also, these two structures of GO should be applied as direct adsorbents for heavy metals and MB [22]. The GO aerogel material shows a high adsorption efficiency for MB with a maximum adsorption capacity of

416.6667 mg/g. However, GO disperses very well in the natural aquatic environment due to the abundant oxygen surface that reduced the reusability of the GO aerogel in wastewater treatment. Moreover, this process has a hidden risk of secondary pollution [23] if the adsorbents are not recovered completely after adsorption. When GO was reinforced by agar in the agar/GO aerogel through hydrogen bonds combined with dehydration in the interaction between oxygen-containing functional groups on agar and GO during hydrogel preparation, the adsorption efficiency of the agar/GO composite aerogel (AGO) was increased to 578 mg/g according to Chen et al [24].
Nanocrystalline cellulose (CNC)/graphene oxide (GO) composite films were prepared by drop casting water dispersion of GO in the presence of CNC and their nanostructures, surface and electrical properties were investigated. It was found that pristine hydrophilic GO presents a good dispersion when mixed with CNC along with a decrease of the composite electrical resistivity. The surface properties of the composite film indicated a poorer wettability with respect to that measured for separated materials. By applying an electric current through the CNC/GO composite a transition from an electrically insulating material to a conductive one was observed along with an improved wettability. The obtained results open an easy route for paper electronic based on the integration of nanocrystalline cellulose onto graphene devices. (25)

2. Literature Review:

Yong Zhang et al reported that When graphene is used as an electrode material for supercapacitors, it tends to have minor volumetric specific capacitance (<200 F cm–3) and low volumetric energy density (<10 Wh L–1) due to its small packing density and poor pseudocapacitive properties. Herein, nanocellulose/reduced graphene oxide composite hydrogels (NCGHs) with a dense porous structure and large packing density are prepared via a simple hydrothermal method using graphene oxide (GO) and nanocellulose (NC) as a reacting substance. In the reaction system, the high-concentration GO solution provides the driving force for the formation of the dense porous structure of NCGHs through the strong π–π stacking interaction between graphene sheets (27) .

Other study by Haibiao et al. prepared nanocellulose/graphene oxide composites (NCC/GO) by dissolving NCC with AmimCl ionic liquid, and covalently modifying NCC with functionalized GO via esterification reaction, which weakened the hydrogen bonding of molecules and reduced chemical inertness. The morphology of modified NCC was characterized by SEM. The structure between NCC and GO was analyzed by FTIR. The crystalline phase of NCC and NCC/GO composites was investigated by XRD. The results revealed that NCC/GO composites were successfully prepared, and GO was uniformly dispersed in the NCC matrix. Because of the introduction of GO, it greatly increased the proportion of functional groups in composites. In addition, taking heavy metal ions-Ni^{2+} as an example, the adsorption rate of NCC and NCC/GO composites on Ni^{2+} was studied, and the adsorption mechanism also was explored. The experimental results showed that the adsorption rate of Ni^{2+} by NCC/GO composites was 95.8% higher than that of pure NCC (28) . Radhakrishnan presented a study that the preparation of the novel adsorbent, multi-carboxyl-functionalized Nanocellulose/Graphene Oxide-Zinc Oxide composite for the removal of Uranium. In this work the Nanocellulose/Graphene Oxide-Zinc Oxide composite were synthesized to compare the selective adsorption behavior for hazardous metal ion such as Uranium ions. From the adsorption studies, it would be clear that Nanocellulose/Graphene Oxide-Zinc Oxide composite exhibited much higher adsorption performance than individual NC and Graphene Oxide-Zinc Oxide (ZnO-GO). `The kinetic data followed the pseudo-second-order model. The equilibrium attained at 120 min and isotherm follows the order Sips > Langmuir > Freundlich. The adsorbed Uranium is desorbed using 0.1 M HCl. The adsorption–desorption studies conducted over 6 cycles illustrate the viability and repeated use of the adsorbent for the removal of Uranium from aqueous solutions. (29) Numerous techniques are reportedly established to eliminate these toxins and undesirable microorganisms. Adsorptive treatment and/or exclusion of water toxins and microbial sanitization through different nanocellulose (NC)-graphene oxide (GO) nanocomposite (NGON) materials (adsorbents) are introduced in this chapter. As per available literature, these adsorbent materials have shown extraordinary outcomes for the adsorptive exclusion of water contaminants such as poisonous metal ions and colors/dyes along with the removal of aquatic germs, insecticides, etc. Besides, they have numerous other necessities, including ease of preparation, cheap, and eco-friendly, as green composite blends are handily worked, energy-economical, and fit for multifaceted uses. This chapter also focuses on discussing the technologies embraced to fabricate the aforementioned adsorbents, their performance-based response with regards to adsorption capacity (Q). (30)

In other hand, aerogel materials such as the low density and large surface area enable them to adsorb large amounts of substances, so they show great potential for application in industrial wastewater treatment. Some researcher used a combination of completely environmentally friendly materials such as cellulose nanofibers (CNFs) extracted from the petioles of the nipa palm tree and graphene oxide (GO) fabricated by simple solvent evaporation, a composite aerogel was prepared by a freeze-drying method. The obtained aerogel possessed a light density of 0.0264 g/cm3 and a porosity of more than 98.2%. It was able to withstand a weight as much as 2500 times with the maximum force (1479.5 N) to break up 0.2 g of an aerogel by compression strength testing and was stable in the aquatic environment, enabling it to be reused five times with an adsorption capacity over 90%. The CNF/GO aerogel can recover higher than 85% after 30 consecutive compression recovery cycles, which is convenient for the reusability of this material in wastewater treatments. The obtained aerogel also showed a good interaction between the component phases, a high thermal stability, a 3D network structure combined with thin walls and pores with a large specific surface area. In addition, the aerogel also exhibited a fast adsorption rate for methylene blue (MB) adsorption, a type of waste from the textile industry that pollutes water sources, and it can adsorb more than 99% MB in water in less than 20 min. The excellent adsorption of MB onto the CNF/GO aerogel was driven by electrostatic interactions, which agreed with the pseudo-second-order kinetic model with a correlation coefficient R2 = 0.9978. The initial results show that the CNF/GO aerogel is a highly durable "green" light material that might be applied in the treatment of domestic organic waste water and is completely recoverable and reusable. (31)

Rijith Sreenivasan, S Suma Mahesh & V S Sumi , A series of batch adsorption experiments under optimized conditions were performed and also to evaluate the reliability and feasibility of prepared adsorbent, carboxylate functionalized ethylene glycol dimethacrylate (EGDMA) crosslinked nanocellulose/graphene oxide polymer composite (EGDMA-g-nCell/GO) for Th(IV) recovery from aqueous media. The material was well characterized by using FTIR, XRD, XPS, SEM-EDS, TG-DTA and zeta potential analysis. The equilibrium adsorption capacity (Q0) among the various models was 141.21 mg/g at 30 °C and was well correlated with Langmuir isotherm model with reduced χ2 and R2 values. The spent adsorbent was undergone four cycles of regeneration process without any significant loss in adsorption capacity using 0.1 M HNO3 as desorbing agent, with up to 98.0 % recovery. (32). Da Silva , M. et al. reported an instantaneous adsorption of a mixture of complex dyes by nanocomposites of non-toxic cellulose nanocrystals (CNC) and graphene oxide (GO). Despite advances in adsorption, the removal of complex dye with four or more aromatic rings is the least reported in the literature. Herein, we prepared and characterized three novel CNC:GO composites and applied them for removing complex dyes basic blue 7 (BB7), reactive orange 122 (RO) and rhodamine B (RhB) in a binary systems with the non-complex dyes methyl orange (MO) and basic brown 4 (BB4). The adsorption capacity of nanocomposite increased with the amount of aromatic ring in dyes' structure. The CNC:GO 70:30 composite was the most efficient for removing BB7, showing incredible instantaneous adsorption capacity of 1943 mg g−1 (0.1 g.L-1 CNC:GO and 100 mg.L-1 BB7). Under real conditions, the BB7 removal rate from river water sample was 77%. Also, a complex dye (RO) and MO were not adsorbed in single systems, however in the presence of BB7 the qmax was 681 and 516 mg g−1 (0.1 g.L-1 CNC:GO and 100 mg.L-1 of dye), respectively, indicating a synergic effect. In the presence of a complex (RhB) and BB4 cationic dyes, BB7 was preferentially adsorbed. BB7 adsorption was also studied in a dynamic fixed-bed process, whose 80% breakthrough time occurred after 13.5 h (qmax of 213 mg g−1). XPS and FTIR analyses confirmed that electrostatic and ion exchange are the main adsorption mechanism. CNC:GO composite has potential for removing mixtures of complex and ordinary dyes.(33)

- Luis Valencia , The deposition of a thin layer of graphene oxide onto cellulose nanofibril membranes, to form CNF–GO layered-composite membranes, dramatically enhances their wet-mechanical stability, water flux and capacity to adsorb water pollutants (P. Liu, C. Zhu and A. P. Mathew, J. Hazard. Mater., 2019, 371, 484–493). In this work, we studied in real time the behavior of these layered membranes during filtration of water and metal ion solutions by means of in situ SAXS and reactive molecular dynamics (ReaxFF) computational simulations. SAXS confirms that the GO layers limit the swelling and structural deformations of CNFs during filtration of aqueous solutions. Moreover, during filtration of metal ion solutions, the connection of the CNF–GO network becomes highly complex mass-fractal like, with an increment in the correlation length. In addition, after ion adsorption, the SAXS data revealed apparent formation of nanoparticles during the drying stage and particle size increase as a function of time during drying. The molecular dynamics simulations, on the other hand, provide a deep insight into the assembly of both components, as well as elucidating the motion of the metal ions that potentially lead to the formation of metal clusters during adsorption, confirming the synergistic behavior of GO and CNFs for water purification applications.(34)

- Zhongguo Wang , A composite graphene oxide (GO)/nanocellulose aerogel was prepared by dispersing cellulose nanofibrils (CNFs) into GO nanosheets. CNFs with high aspect ratios and negative potential helped the exfoliation of GO flakes without the need of a chemical linker via steric hindrance and electrostatic repulsion. Water purification tests were performed using methylene blue (MB) and tetracycline (TC) as model pollutants. The composite aerogel obeyed a pseudo-second-order model and Langmuir adsorption isotherm. The composite aerogel possesses a maximum adsorption capacity of 111.2 mg/g for MB and 47.3 mg/g for TC. Meanwhile, the aerogel can be easily recycled and regenerated using ethanol. After three cycles, the aerogel can maintain a high removal efficiency for MB (98%) and TC (97%). The adsorption mechanism was mainly ascribed to electrostatic attraction and π-π interactions. (35)

3. Experimental Section:

3.1. Material:

Graphite powder (Code: G/0900/60) , Sodium Nitrate, Cadmium sulphate hydrate 98% extra pure, (LOBA CHEMIE PVT.LTD.),Nanocellulose, Eriochrome black-t C.I14645 , Ethylenediaminetetraacetic acid tetrasodium salt , Sulfuric acids 98% , Hydrogen peroxide 30% w/v (100vol.) stabilized pure , potassium permanganate , Sulfuric Acid 95-98% (USP,NF,Ph,Eur.) pure.

3.2. Procedure

3.2.1 Preparation of reduced graphene oxide (GO)

We took 5.0 g of graphite powder and added to 120 ml of 98% of (H2SO4) in an ice bath with continuous stirring and temperature didn't exceed 20°C. Then 2.5 g ($NaNO_3$), followed by 20 g of ($KMnO_4$) were added gradually to avoid a sudden increase in temperature. The mixture was stirred for 2 h in an ice bath and 1 h at 35°C. After that sample would be like a paste, then 250 ml of distilled (H_2O) was added drop by drop in an ice bath, which causes effervescence and temperature suddenly increased to 98°C then cooled after 10 min. Next, 50 ml of (H_2O_2) was added, lead to convert sample into oily color. The mixture was heated at 90°C for 30 min. The mixture was centrifuged and washed by boiling distilled water until the mixture becomes neutral. The product was dried at 65°C for 24 h to get (GO).

3.2.2 Preparation Graphene oxide/nanocellulose composite:

Nanocellulose was previously prepared in the research lab. 1.3 grams of graphene oxide (GO) was suspended with distilled water under stirring for 30 min, and 122 grams of nanocellulose (NC) also was suspended in distilled water for 30 min, as well. The two suspensions (GO and NC) were mixed in one beaker to 100 mL. Then it was placed in a device (ULTRASONS H-D) for sonication (15 min and the temperature was 30°C). The mixture was stirred for 24 hours at room temperature. Then, the gel-like composite was collected by evaporation the water.

3.2.3 Adsorption experiment:

We use the contact method for adsorption experiment. First, we prepared a standard Cd (II) solution from cadmium sulfate tetrahydrates ($CdSO_4.4H_2O$) by dissolving 15.19 grams in 250-mL volumetric flask, (1515.9 $mg . L^{-1}$). Then Cd (II) solutions ranging from 100 to 500 $mg . L^{-1}$ were prepared by dilution from the standard solution.

The (100, 200, 400, and 500 $mg . L^{-1}$) solution of Cd^{2+} were mixed with the GO, NC, and GO/NC composite, subsequently, as follow;

2 mL of Cd^{2+} was mixed with 2 mL of 0.25 wt% suspensions of for GO, NC, and GO/NC composite separately. Then, they were placed in shaker for 1 hours at 1000 rpm. After shaking they were left for 24 hours for equilibrium. adsorption study. After 24 hours, each solution was filtered using syringe-filter (microfiltration).

The adsorption efficiency of each sample (GO, NC, GO/NC) against Cd were determined based on difference in Cd2+ concentration before and after the mixing with the samples (GO, NC, GO/NC). Removal percentage (R%) were calculated using the following equation:

$$\%\boldsymbol{R} = \frac{\boldsymbol{C_0 - C_f}}{\boldsymbol{C_0}} \times \mathbf{100}$$

Where $\boldsymbol{C_0}$ is the Cd^{2+} ions concentration before adsorption; $\boldsymbol{C_f}$ is the Cd^{2+} ions concentration after adsorption.

4. Results and Discussion:

The FT-IR patterns of the GO, NC, and GO/NCs are shown in figure (1). The peaks at 1100 cm^{-1} are due to the to the C−O−C stretching vibration of the pyranose ring skeleton in cellulose molecules [26].

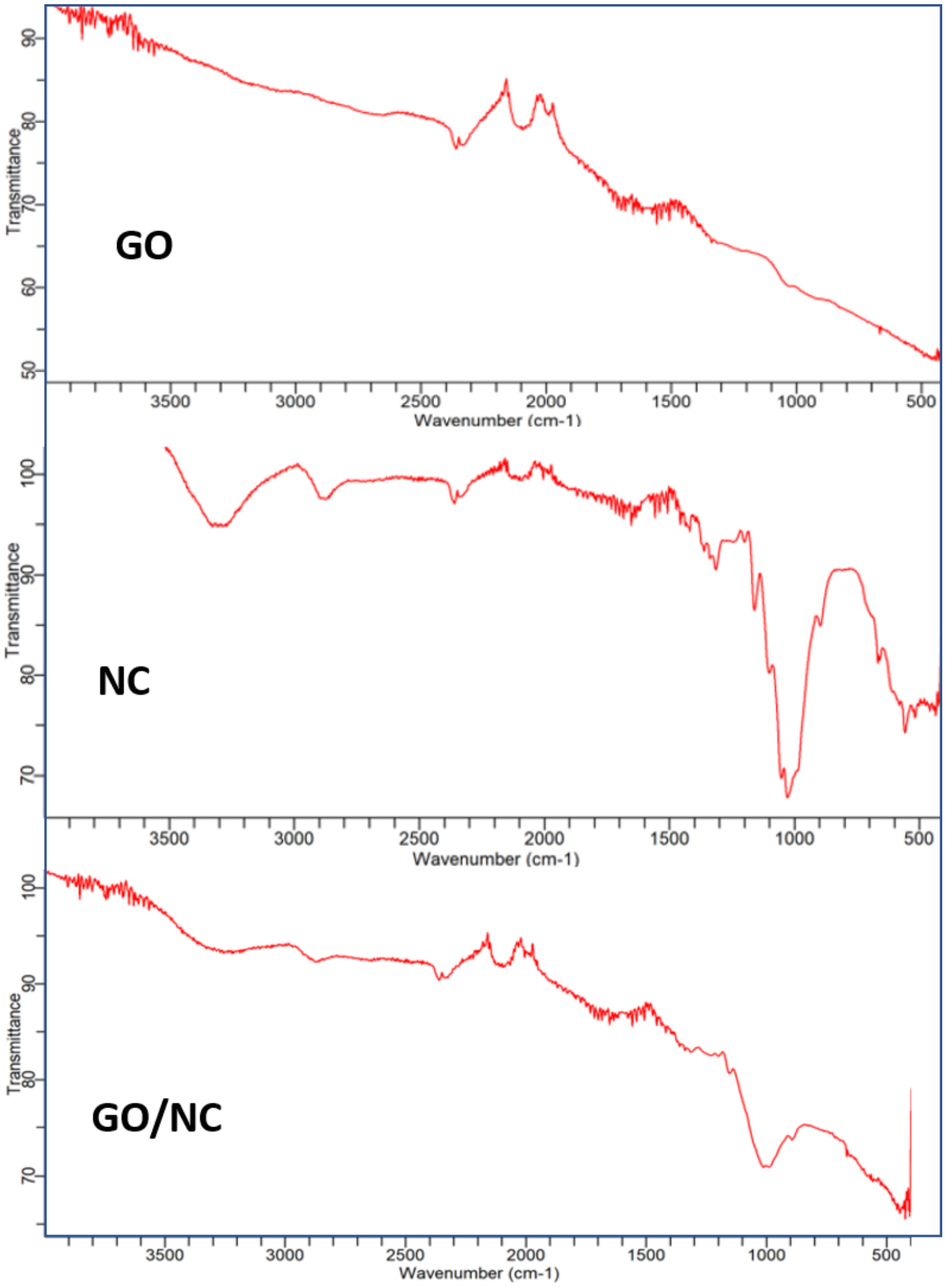

Figure (1) FTIR of the prepared samples

The bands around 1600 to 1700 cm^{-1} are for the O−H bending vibration of absorbed water due to absorbed water in the cellulose molecules. [35] The peaks at 3400 cm^{-1} are due to OH stretching (appeared on NC and GO/NC spectra). It was a broader band in NC than GO/NC due to the increase of the free stretching vibration of OH groups in the structure of the cellulose during the extracting process. The GO spectrum reveals absorption peaks at 2350, 1700 and 1621, 1218 and 1100 cm−1 , corresponding to –OH stretching motions, C=O stretching vibrations in –COOH groups, C=C stretching vibrations of sp2 hybridized carbon chains, C–OH stretching vibrations in –COOH groups and C–O–C stretching vibrations. The absorption peak at 864 cm−1 is due to C–H bending vibrations.

Adsorption experiment: showed us that high removal percentage with NC and GO/NC samples. The following table shows the data of contact method for adsorption:

Table (1). Removal percentage for the cadmium ions solutions

Cd ions solution	(R %)			
	GO	NC	GO/NC	
100 ppm	80 %	95 %	98 %	
200 ppm	83 %	92 %	98 %	
400 ppm	81 %	93 %	97 %	
500 ppm	81 %	93 %	98 %	
Average				

5. Conclusion:

GO was successfully synthesized from graphite by the modified Hummer method. The GO/CNF was also prepared and obtained. After investigating the ability to remove cadmium ions from aqueous solution, GO/NC showed an excellent adsorption with %R around 99% in 24 hours contact time. When comparing with GO and NC separately, we conclude that the composite of GO/NC has enhanced the removal efficiency.

References:

(1) Al-Jlil, S. A. Removal of Heavy Metals from Industrial Wastewater by Adsorption using Local Bentonite Clay and Roasted Date Pits in Saudi Arabia. Trends. Appl. Sci. Res. (2010), 5 (2), P. 138-145.

(2) Kadirvelu, K., 1998. Preparation and characterization of coirpith carbon and its utilization in the treatment of metal bearing wastewaters. Ph.D. Thesis, Bharathiar University, India.

(3) Geim, A., Novoselov, K. The rise of graphene. Nature Mater 6, 183–191 (2007). https://doi.org/10.1038/nmat1849

(4) B. C. Brodie, On the Atomic Weight of Graphite, Philos. Trans. R. Soc. London, 2009, 149(1), 249–259.

[4] Le Li, Dan Zhang, Jianping Deng, Qin Kang, Zhifeng Liu, Junfei Fang and Yuchun Gou, 2020 J. Electrochem. Soc. 167 155519. DOI 10.1149/1945-7111/abbbc0

[5] Chen, Shaohua, Ling Qiu, and Hui-Ming Cheng. "Carbon-based fibers for advanced electrochemical energy storage devices." Chemical Reviews 120, no. 5 (2020): 2811-2878. https://doi.org/10.1021/acs.chemrev.9b00466

[6] Pei, Songfeng, Qinwei Wei, Kun Huang, Hui-Ming Cheng, and Wencai Ren. "Green synthesis of graphene oxide by seconds timescale water electrolytic oxidation." Nature communications 9, no. 1 (2018): 145.

[7] Abdelkader, A. M., A. J. Cooper, Robert AW Dryfe, and I. A. Kinloch. "How to get between the sheets: a review of recent works on the electrochemical exfoliation of graphene materials from bulk graphite." Nanoscale 7, no. 16 (2015): 6944-6956.

[8] Mahmoud, Alaa El Din, Achim Stolle, and Michael Stelter. "Sustainable synthesis of high-surface-area graphite oxide via dry ball milling." ACS Sustainable Chemistry & Engineering 6, no. 5 (2018): 6358-6369.

[9] Muthoosamy, Kasturi, and Sivakumar Manickam. "State of the art and recent advances in the ultrasound-assisted synthesis, exfoliation and functionalization of graphene derivatives." Ultrasonics sonochemistry 39 (2017): 478-493.

[10] H. Omar, N.S.A. Malek, M.Z. Nurfazianawatie, N.F. Rosman, I. Bunyamin, S. Abdullah, Z. Khusaimi, M. Rusop, N.A. Asli, A review of synthesis graphene oxide from natural carbon based coconut waste by Hummer's method, Materials Today: Proceedings, Vol. 75, Part 1, (2023), Pages 188-192, ISSN 2214-7853, https://doi.org/10.1016/j.matpr.2022.11.427

(11) Zoghlami, A. and Paës, G. (2019), Lignocellulosic Biomass: Understanding Recalcitrance and Predicting Hydrolysis. Front. Chem. 7:874.

(12) Vy T. Nguyen, Lam Q. Ha, Tu D. L. Nguyen, Phuong H. Ly, Dang Mao Nguyen, and DongQuy Hoang.

(13) Mahfoudhi, N.; Boufi, S. Nanocellulose as A novel Nanostructured Adsorbent for Environmental Remediation: A Review. Cellulose 2017, 24, 1171−1197.

(14) Wang, C.; Ma, R.; Huang, Z.; Liu, X.; Wang, T.; Chen, K. Preparation and Characterization of Carboxymethylcellulose Based Citric Acid Cross-Linked Magnetic Aerogel as An Efficient Dye Adsorbent. Int. J. Biol. Macromol. 2021, 181, 1030−1038.

(15) Liu, T.; Li, Y.; Du, Q.; Sun, J.; Jiao, Y.; Yang, G.; Wang, Z.; Xia, Y.; Zhang, W.; Wang, K.; Zhu, H.; Wu, D. Adsorption of Methylene Blue From Aqueous Solution by Graphene. Colloids Surf., B 2012, 90, 197−203.

(16) Arias, F.; Guevara, M.; Tene, T.; Angamarca, P.; Molina, R.; Valarezo, A.; Salguero, O.; Vacacela Gomez, C.; Arias, M.; Caputi, L. S. **The Adsorption of Methylene Blue on Eco-Friendly Reduced Graphene Oxide.** *Nanomaterials* 2020, 10, 681.

(17) Bhanjana, G.; Dilbaghi, N.; Kim, K.-H.; Kumar, S. Carbon Nanotubes as Sorbent Material for Removal of Cadmium. J. Mol. Liq. 2017, 242, 966−970.

(18) Zamani, S.; Tabrizi, N. S. Removal of Methylene Blue from Water by Graphene Oxide Aerogel: Thermodynamic, Kinetic, and Equilibrium Modeling. Res. Chem. Intermed. 2015, 41, 7945−7963.

(19) Teng, K.; Ni, Y.; Wang, W.; Wang, H.; Xu, Z.; Chen, L.; Kuang, L.; Ma, M.; Fu, H.; Li, J. Adjustable Micro-structure, Higher-Level Mechanical Behavior and Conductivities of Preformed Graphene Architecture/Epoxy Composites Via RTM Route. Composites, Part A 2017, 94, 178−188.

(20) Zhu, T.; Teng, K.; Shi, J.; Chen, L.; Xu, Z. A facile assembly of 3D robust double network graphene/polyacrylamide architectures via γ-ray irradiation. Compos. Sci. Technol. 2016, 123, 276−285.

(21) Gao, Y.; Zhang, Y.; Zhang, Y.; Xie, L.; Li, X.; Su, F.; Wei, X.; Xu, Z.; Chen, C.; Cai, R. Three-dimensional paper-like graphene framework with highly orientated laminar structure as binder-free supercapacitor electrode. J. Energy Chem. 2016, 25, 49−54.

(22) Wang, Q.; Lei, L.; Kang, X.; Su, X.; Wang, F.; Wang, C.; Zhao, J.; Chen, Z. Preparation of the Crosslinked Go/Paa Aerogel and Its Adsorption Properties for Pb(Ii) Ions. Mater. Res. Express 2020, 7, 025514.

(23) Wei, M.-p.; Chai, H.; Cao, Y.-l.; Jia, D.-Z. Sulfonated graphene oxide as an adsorbent for removal of Pb2+ and methylene blue. J. Colloid Interface Sci. 2018, 524, 297−305.

(24) Chen, L.; Li, Y.; Du, Q.; Wang, Z.; Xia, Y.; Yedinak, E.; Lou, J.; Ci, L. High Performance Agar/Graphene Oxide Composite Aerogel for Methylene Blue Removal. Carbohydr. Polym. 2017, 155, 345−353

(25) Valentini, Luca, Marta Cardinali, Elena Fortunati, Luigi Torre and José María Kenny. “A novel method to prepare conductive nanocrystalline cellulose/graphene oxide composite films.” *Materials Letters,* 105 (2013): 4-7.

(26) Vy T. Nguyen, Lam Q. Ha, Tu D. L. Nguyen, Phuong H. Ly, Dang Mao Nguyen, and DongQuy Hoang *, ACS Omega* 2022 7 (1), 1003-1013 ,DOI: 10.1021/acsomega.1c05586

(27) ZHANG, Yong, et al. Nanocellulose/Reduced Graphene Oxide Composite Hydrogels for High-Volumetric Performance Symmetric Supercapacitors. Energy & Fuels, 2022, 36.15: 8506-8514.

(28) Haibiao Yu, Shaobo Zhang, Yu Wang, Dingwen Yin & Jintian Huang (2021) Covalent modification of Nanocellulose (NCC) by functionalized Graphene oxide (GO) and the study of adsorption mechanism, *Composite Interfaces*, 28:2, 145-158, https://doi.org/10.1080/09276440.2020.1731276

(29) Asha Radhakrishnan, J. Nahi, B. Beena, Synthesis and characterization of multi-carboxyl functionalized nanocellulose/graphene oxide-zinc oxide composite for the adsorption of uranium (VI) from aqueous solutions: Kinetic and equilibrium profiles,*Materials Today*: Proceedings, Volume 41, Part 3, 2021, Pages 557-563, ISSN 2214-7853

(30) Part of the Springer Series in Materials Science book series (SSMATERIALS,volume 323).

(31) Vy T. Nguyen, Lam Q. Ha, Tu D. L. Nguyen, Phuong H. Ly, Dang Mao Nguyen, and DongQuy Hoang
ACS Omega 2022 7 (1), 1003-1013

(32) Rijith Sreenivasan, S Suma Mahesh & V S Sumi (2019) Synthesis and application of polymer-grafted nanocellulose/graphene oxide nano composite for the selective recovery of radionuclides from aqueous media, *Separation Science and Technology*,54:9, 1453-1468, DOI: 10.1080/01496395.2018.1534868

(33) Environmental Nanotechnology, Monitoring & Management,
DOI: 10.1039/C9NR07116D (Paper) *Nanoscale*, 2019, **11**, 22413-22422

(34) VALENCIA, Luis, et al. Nanocellulose/graphene oxide layered membranes: elucidating their behaviour during filtration of water and metal ions in real time. *Nanoscale*, 2019, 11.46: 22413-22422

(35) Zhongguo Wang, Lian Song, Yaquan Wang, Xiong-Fei Zhang, Jianfeng Yao, Construction of a hybrid graphene oxide/nanofibrillated cellulose aerogel used for the efficient removal of methylene blue and tetracycline, Journal of Physics and Chemistry of Solids, Volume 150, 2021, 109839, ISSN 0022-3697