Development of a New Hybrid Adsorbent Based on Polyaniline@Chitosan and Its Application to Acetaminophen Removal From Aqueous Solution

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Abstract

The polyaniline (PANI) with chitosan (CS) (PANI@CS) was synthesized using in-situ polymerization process and its preparation was assured by surface area, XPS, TPD, XRD, FTIR, TGA and SEM analysis. PANI@CS, CS and PANI were used for the removal of acetaminophen (AAP). The maximum value of adsorption capacities were found to be 385.25 mg.g⁻¹ for PANI@CS, 359.84 mg.g⁻¹ for CS and 242.49 mg.g⁻¹ for PANI which reveal that the adsorption capacity of hybrid adsorbent is major than CS and PANI respectively. Moreover, H-bonding, π - π bonding, pore-filling and chemisorption have been suggested as probable mechanism for the elimination of AAP by PANI@CS. Furthermore, AAP elimination was preferable at pH 7.0. Pseudo-second-order (PSO) and Langmuir models reported the kinetic and isotherm data acceptably. This shows that the adsorption processes of AAP are a monolayer chemical adsorption, and it was endothermic, spontaneous, and favorable for the three adsorbents. Moreover, when reused, the hybrid adsorbent remains at around 69% of their original capacities after five adsorption cycles.

1. Introduction

Pharmaceutical composites (PhCs) are renowned emerging environmental contaminants that have been widely used for human and animals' therapy [1]. These products related to irregular consuming have been discovered in the environment [2]. Although of the consumption, PhCs disposal and effluents of unutilized and expired medicine have a significant role to introduce the medicaments into the environment [3]. Today, the existence of PhCs as potential sources of water and waste water has become a significant attention [4]. In spite, the concentrations of PhCs in waste water are considerably found in $\mu\text{g.L}^{-1}$ grades, but in waste water purification plants with influent from PhCs manufacturing, the quantity of these products has been found up to several ppm [5]. Classical water and waste water purifying techniques have no fundamental impacts on the PhCs elimination and subsequently rest intact in environment [4].

Out of varied other emerging pollutants is acetaminophen (AAP), In contrast called; an paracetamol or acylated amide medicine. AAP is one of the most considerably used antipyretics, painkillers and soreness relieving medicines throughout the world as a first line medicine due to it is effective, inexpensive and comparatively has low side impacts [6–8]. AAP is widely rejected into water body via elimination of unutilized hospital wastes and processing effluent discharges. AAP is however famous for its cumulating in aquatic organisms and around 59–69% of the consumed medicine is transferred out into available water bodies in the form of urine [6, 7].

In literature various studies have reported different methods of waste water treatments, such as ultrafiltration electro-dialysis [9], reverse osmosis [10], Fenton based process [11], and adsorption [12]. Amongst these, investigators have display an growing attention in the adsorption method because it is a highly efficient process, low-cost and energy. Conversely most other methods such as that comprising advanced oxidation process, adsorption is unable of degrading pollutant and creating highest toxic species.

The use of Chitosan (CS) for the preparation of adsorbent composite, due to its increased adsorption abilities, is at its peak nowadays and many researchers worldwide focus on their synthesis. In contrast, some observable obstacle of bare CS, contain low porosity, sensitivity to pH changes, reduced surface area and difficulty in renewal post course of processing [13], undermined its industrial scale applications. One approach to exceed these disadvantages is to dope two or more appropriate polymers, which demonstrated that the doping ameliorates resistance to acidic medium and displays enhanced adsorption capacity [14].

CS is also considered as a promising material to removal pollutants. Extensive work has been performed to investigate the ability of chitosan and its derivatives for pharmaceutical compounds (PhCs) adsorption purposes. For example, the adsorption of PhCs, in three classes as anti-biotics, anti-inflammatory, non-steroidal and other PhCs, from aqueous solution using diverse CS-based adsorbents was reviewed [15]. The high adsorption capacity of chitosan adsorbent composite for diclofenac uptake using EPCS@PEI adsorbent composite has been reported by Liakos et al. [14]. A magnetic Chitosan-Fe₃O₄ composite was successfully synthesized and used for the elimination of two PhCs (diclofenac sodium (DCF) and tetracycline hydrochloride) from water [16].

The textural properties of CS can be improved in combination with other polymers such as polyaniline (PANI). Moreover, PANI finds large applications in preparing adsorbent materials and photo-catalysts through doping, assembling composites and chemical modifications. The PANI functions such as imine and amine could react efficaciously with diverse contaminants molecule in polluted water, making it promising materials for waste-water treatment [17–19]. However, its industrial applications are limited by some obstacles like little processability and reduced mechanical properties. One process to surmount this disadvantage for workable applications is to functionalize PANI into CS. After functioning, the mechanical properties and the resistance to acidic medium will be ameliorated [20]. Consequently, the active binding-sites will be completely exposed. Lately, investigators have given significant attention in formation of various PANI@biopolymeric composites, according to their large applications in environmental science [21]. These composites provided a greater adsorbent capacity for anion/oxyanion [21]. But, to our knowledge, PANI functionalized by CS (PANI@CS) as a hybrid material has never been utilized as an adsorbent for the elimination of AAP from aqueous solution.

The object of this investigation was to simple develop, low-cost and environmentally benign process for elimination of AAP from aqueous solution by PANI, CS and PANI@CS adsorbent. Those products were characterized by BET, XPS, SEM, XRD, DTP, FTIR and TGA techniques. Moreover, the experimental variables affecting optimal adsorption were studied. Different isotherm models and adsorption kinetics also tested in detail. Finally, the recyclability of adsorbents was also examined.

2. Experimental

2.1. Materials

All solutions were prepared with deionized H₂O (18.2 MΩ.cm) obtained from an “Elga Labwater Purelab” system, Acetaminophen (AAP) (Sigma Aldrich, ≥97%), Chitosan (CS) (Merck, Average molecular weight) was used as received, Aniline (ANI) (Merck, ≥99.5%), Ammoniumpersulfate (APS) (Sigma Aldrich, ≥98%), Ammonia solution (NH₄OH) (Sigma Aldrich, 25%), hydrochloric acid (HCl) (Sigma Aldrich, 70%), potassium hydroxide (KOH) (Sigma Aldrich, 37%), Ethanol (C₂H₅OH) (Merck, 96%) and Filter paper (EAPI Company, Annaba, Algeria).

2.2. Measurements

The chemical composition and structure of the materials were recorded with a Fourier transform infrared spectrometer (FT-IR, Bruker Model Alpha, Germany) in a range of 4000-500 cm⁻¹. X-ray diffraction (XRD) graphics were obtained by a diffractometer (Bruker-CCD-Apex) under Cu-K_α radiation. The surface morphology of adsorbents was obtained by scanning electron microscope (SEM; Hitachi S-4700). Thermal gravimetric analysis (TGA; STA-1500) was applied to examine the thermal stability of samples under nitrogen atmosphere with heating rate of 10°C.min⁻¹. Electron binding energies of the elements were recorded on X-ray photoelectron spectroscopy (XPS; VG-3000 Electron), with monochromatic Al-K_α X-ray radiation. The TPDs were performed at 20°C.min⁻¹ up to 900°C under a Helium flow (100 mL.min⁻¹) in SDT/2960 Simultaneous equipment (TA-Apparatus) coupled to a MSC/200 mass spectrometer (Balzers. Thermostar). The adsorbents were heated up to 950 (2°C.min⁻¹), and kept at this temperature for 60 minutes, under a Helium flow, and the type and amount of surface oxygen groups (CO and CO₂) were characterized with a microgas chromatograph (Varian/490-GC). UV-Vis spectra were performed to calculate the AAP concentrations by Hitachi (U3000). The surface structure data were determined from the N₂ adsorption-desorption isotherms at 77.2°K using instruments (ASAP-2020; Micromeritics). The Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size distribution measurements were carried out by a N₂ adsorption method applied Autosorb iQ. [18, 19].

2.3. Adsorbents preparation

The synthesis of PANI@CS adsorbent was performed according to the procedures reported by Mahi et al. [19]. 10 g of CS was dissolved into 200 mL of HCl (1M) then 5 mL of aniline monomer was added. The resulting solution was left under stirring for 30 minutes to homogenize it (Solution A). Solution B (50 ml) of APS was prepared and was poured into solution A (resulting in 250 ml). The molar ratio of ANI:APS was 1:1. The resultant solution was kept at room temperature for 24 horas under 1100 rpm stirring. Then, the precipitate was washed with C₂H₅OH and distilled H₂O to eliminate the non-reacted compounds and dried at 70°C for 24h. For comparison, PANI synthesis was performed according to Bekhoukh et al. [18]. Generally, the proposed pathway of PANI@CS preparation was illustrated in Fig. 1.

2.4. Adsorption tests in batch mode

The stock solution (S_{so1}) of 1000 mg.L⁻¹ AAP was produced with a purity of 97%. Required test concentrations were prepared by appropriate dilution of the S_{so1}. The adsorption kinetics was investigated

at pH of the solution in a thermo-stated bath at 298K, utilizing 50 mL of different AAP concentrations put in contact with 5mg of adsorbent (PANI, CS and PANI@CS). The samples were agitated for various times (10 to 2160 min), and then the solutions were filtered and tested using UV-Vis spectroscopy at a detection wavelength of 242 nm. The adsorption isotherm were examined out at pH of the solution; a 50 mL volume of different initial concentrations of AAP solution (100 – 20000mg.L⁻¹).

The pH influence was investigated using Erlen beaker that contain 50 mL of AAP solution with a concentration of 15000 mg.L⁻¹ at pH between 2 and 12. The solutions were agitated for 1440 min at 298K. The initial pH values of these solutions has been adjusted by adding (0.1N) HCl or (0.1N) KOH.

The temperature impact was studied out at 298K, 303K, 313K and 318K at same conditions as adsorption at 298K. The removal efficiency and the adsorption capacity were determined using the equations are presented in Table 1. Where; C_0 (mg.L⁻¹): initial AAP concentration and C_{eq} (mg.L⁻¹): residual AAP concentration. V (L): solution volume, m (g): adsorbent mass.

Table 1
The mathematical expressions of adsorption

Expressions	Linearized Form
Removal efficiency	$R\% = \frac{(C_0 - C_{eq})}{C_0} . 100$
Adsorption capacity	$Q_{eq} = \frac{(C_0 - C_{eq}) V}{m}$
Langmuir isotherm	$\frac{C_{eq}}{Q_{eq}} = \frac{1}{K_L C_m} + \frac{C_{eq}}{Q_m}$
Freundlich isotherm	$Ln Q_{eq} = Ln K_f + \frac{1}{n} Ln C_{eq}$
Pseudo-first order (PFO)	
Pseudo-second order (PSO)	
Van't Hoff law	$Ln \left(\frac{Q_{eq}}{C_{eq}} \right) = - \frac{\Delta H}{RT} + \frac{\Delta S}{R}$
Gibbs free energy	$\Delta G = \Delta H - T\Delta S$

Adsorption isotherm showed how adsorbate react with adsorbent and so are important in improving the usage of adsorbent materials. So, the correlation of equilibrium values by either mathematical or experimental relations is significant for empirical design and employment of adsorption processes. To develop the most favorable correlation for empirical equilibrium values, the two most common isotherm laws (Langmuir & Freundlich) were investigated [22, 23]:

The Langmuir isotherm is valid to homogeneous adsorption operations where the surface of the adsorbent are uniform, that is, all removal sites are equal, there are no interactions among adsorbed species and only mono-layer creation is probable. The linear formula of the Langmuir equation can be displayed in Table 1. Where; Q_{eq} (mg.g⁻¹): adsorbed amount, C_{eq} (mg.L⁻¹): Equilibrium concentrations of adsorbate, Q_m (mg.g⁻¹): maximum adsorption capacity and K_l (L.mg⁻¹): Langmuir constants.

Both multi-layer (physi-sorption) and monolayer (chemi-sorption) can be defined using the Freundlich isotherm. This class is founded on adsorbent surface by the heterogeneous equilibrium. The formula for Freundlich isotherm is in Table 1. Where; n and K_f (mg^{1-1/n}.L^{1/n}.g⁻¹): Freundlich constants, C_{eq} (mg.L⁻¹): equilibrium concentrations.

2.5. Adsorption kinetic

The kinetics studies was performed out with an overall contact time of 36 h for AAP adsorption taking the initial concentrations of 15000 mg.L⁻¹, adjusting the pH at 7.0. PFO and PSO models were considered to explicate the kinetics adsorption mechanisms [18, 24]. The linear using PFO and PSO equations are illustrated in Table 1. Where; Q_t (mg.g⁻¹): AAP concentration at time (t), Q_e (mg.g⁻¹): equilibrium concentration,, k_1 (min⁻¹): PFO rate constant of adsorption, k_2 (g.mg⁻¹.min): PSO rate constant, $k_2Q_e^2$ (g.mg⁻¹.min): initial rate adsorption.

2.5. Adsorbent regeneration tests

The reusability of CS, PANI and PANI@CS, the adsorbent materials that exhibited superior overall performance, was evaluated using a five cycle adsorption test. About 0.5 g of adsorbent were mixed with 50 mL of a 15000 mg.L⁻¹ AAP solution and shaken at room temperature for 24 h. The pH was adjusted to obtain a neutral range at equilibrium conditions and these tests were also done in triplicates. After the end of the adsorption cycle, the adsorbent was separated, followed by elution with C₂H₅OH and distilled water.

3. Results And Discussion

3.1. Physicochemical characterization

The surface area and also poresize distribution of adsorbents were examined by the BET way (Fig. 2-a). The three samples displayed the isotherm of type-III. The calculated S_{BET} of PANI, CS and PANI@CS are 46 m².g⁻¹, 988 m².g⁻¹ and 1008 m².g⁻¹, respectively. The S_{BET} , mesoporous volume and total pore of materials are given in Table 2. The S_{BET} value is more important for hybrid adsorbent versus to CS and PANI which confirms the existence of more activated surface sites for PANI@CS [25].

Table 2
Textural characterization and Surface composition (at%) from XPS of
adsorbents prepared before and after adsorption.

Adsorbents	Before adsorption			After adsorption		
	PANI	CS	PANI@CS	PANI	CS	PANI@CS
$S_{\text{BET}} / \text{m}^2.\text{g}^{-1}$	46	988	1008	25	51	64
$V_{\text{DR}} (\text{N}_2) / \text{cm}^3.\text{g}^{-1}$	1.82	1197	2.10	1.02	82	1.54
$V_{\text{mes}} / \text{cm}^3.\text{g}^{-1}$	0.02	0.31	0.30	0.01	0.19	0.28
$V_{\text{mic}} / \text{cm}^3.\text{g}^{-1}$	0.01	0.43	0.44	0.01	0.08	0.13
$V_{\text{tot pore}}$	0.03	0.74	0.74	0.02	0.27	0.41

To confirm the molecular structure of adsorbents, XPS analysis was carried out for three samples prepared. In Fig. 2-b, for the wide scan of the samples the peaks at 284 eV, 398 eV and 530 eV for C, N and O. Table 3 illustrates measured chemical composition of specimens. Moreover, the C1S peak of CS adsorbent is divided into three parts, at 284.59 eV, 286.06 eV and 288.30 eV (Fig. 3-a). The peaks indicate the C–C, C–OH and O–C–O bonds, respectively; and these obtained values are exactly matched with available literature [26, 27]. In addition, we can notice these peaks exist in both CS and PANI@CS. Moreover, Fig. 3-c displays the deconvoluted high resolution C1s spectrum of PANI@CS. The XPS spectrum can be deconvoluted into four components, at 284.56 eV, 285.66 eV, 286.94 eV and 290.96 eV, respectively. The main peak at 284.56 eV is assigned to the C–C/C–H groups present in polymers. The peaks at 285.66 eV and 286.94 eV are due to C–N and C–OH groups due to the hydroxyl groups which are incorporated between CS and PANI. There is shake-up satellite at 290.96 eV, due to the existence of C–N groups.

Table 3
XPS data of Binding Energy (BE) for adsorbents prepared.

Species	Adsorbents and BE (eV)			Observation
	CS	PANI	PANI@CS	
O1s	531.74	//	531.35	C=O, O=C-OH
	//	532.33	532.50	C-OH
	533.41	533.57	533.74	H ₂ O
C1s	284.59	284.60	284.56	C=C, C-H, C-C
	//	285.91	285.66	C-O, C-N
	286.06	287.73	286.94	C-OX, N-C=N
	288.30	//	290.96	O-C-O
N1s	//	399.74	399.44	=N-
	400.95	401.11	400.63	-NH-
	402.51	//	401.84	-NH _x

The N1s XPS spectrum of CS is shown in Fig. 3-d. The results indicated the peaks at 400.95 and 402.51 eV assigning to the assignments of -NH- and -NH_x groups, respectively. Further, based on the N1s values in PANI@CS (Fig. 3-f), characterized by XPS it was concluded that there peaks observed at 401.84 eV, 400.63 eV and 399.44 eV which can be attributed to -NH_x, -NH- and =N- groups, respectively. This result suggests that blending PANI with CS produced a hybrid adsorbent with more amino functional groups on surface [28].

To further investigate of the different adsorbents prepared, the overall nitrogen content was determined. The surface elemental compositions from the XPS analysis are listed in Table 4. The PANI@CS, shows a nitrogen content of 10.80% in the surface layer. Moreover, the XPS analysis of CS adsorbent reveals a significantly less total nitrogen content compared with other adsorbents prepared. The content difference is obviously due to the new structure. Further, this nitrogen content obtains indicated that the matrix PANI were well-dispersed in the CS during the polymerization.

Table 4
Surface composition of the adsorbents obtained by TPD and XPS.

Adsorbents	TPD / $\mu\text{mol.g}^{-1}$			XPS / at.%		
	CO	CO ₂	O _{tot}	O	C	N
CS	1975	513	3000	28.75	67.66	3.59
PANI@CS	1485	355	2190	16.09	73.11	10.80

The surface chemistry of those adsorbents has been also investigated by thermal programmed desorption (TPD), which presents more detailed description about the quantity and nature of surface oxygen (O) groups [29]. The quantity of O groups that transferred as CO, as CO₂ and the resulting quantity of O in adsorbents have been compiled in Table 4. The CS adsorbent possesses a large amount of oxygen functionalities that decompose mainly as CO and in lower extent as CO₂ (Fig. 2-c and Fig. 2-d). The PANI matrix produces the attachment of nitrogen to the surface of the CS by consumption of oxygen functional groups [30], as confirmed by XPS (Table 4). Thus, PANI@CS has lower oxygen content than the pristine CS adsorbent.

The FT-IR spectra of PANI@CS, CS and PANI before AAP retention are used as a reference for interpreting any possible structural changes (Fig. 4). FT-IR spectrum of CS presents adsorption bands at 1021, 1084 and 1153 cm⁻¹ are due to C-O stretching vibration of primary alcoholic groups, C-N stretching vibration and saccharide unit of CS. The vibration bands at 1021 and 1153 cm⁻¹ disappear after AAP adsorption. It can be seen also the stretching vibration at 1387 and 1456 cm⁻¹ indicating amide III (C-N stretching) and aromatic C-C stretch, respectively. These latter bands turn to a single band at 1393 cm⁻¹ after AAP adsorbed. On the other hand, a vibration bands at 1625 and 2872 cm⁻¹ characteristic of C=O stretching on the bond (-NHCO-CH₃) and C-H stretching of CH₂ groups, respectively. The -OH and -NH stretching is between 3100 and 3400 cm⁻¹ [32]. Moreover, in hybrid adsorbent typical bands of PANI were found at 806 cm⁻¹ due to C-C stretching of quinoid rings and deformation of the benzenoid rings respectively. The band at 1207 cm⁻¹ for PANI appeared due to C=N stretching vibration. The transmittance peak at 1326 cm⁻¹ owing C-N bond, 1516 cm⁻¹ due to C=C stretching vibration of benzenoid rings, 1573 cm⁻¹ due to stretching vibration of quinoid rings. The bands between the ranges 3000–3500 cm⁻¹ ascribed to secondary amines stretching (N-H) vibrations [21]. The FT-IR spectra of PANI@CS adsorbent displays the next bands at 3426, 2878, 1657, 1578, 1317 and 1078 cm⁻¹. Compared to CS, the functional groups moved to a higher frequency band. On the contrary, the peaks at 1516 and 1208 cm⁻¹ were disappeared. These modifications confirm that significant amounts of O-H and N-H at CS were grafted by PANI [21]; while most of the bands changed their positions after absorption.

The XRD patterns of all adsorbents were recorded in Fig. 5-a. The diffraction pattern of CS displays two peaks at $2\theta = 10.36^\circ$ and 20.78° indicating the ordered crystalline structure of CS. Moreover, PANI is semi-crystalline in nature as the patterns show three peaks centered at $2\theta = 7.41^\circ$ (011), 20.21° (020), and

25.91° (200) because of the presence of B with Q group in the polymer chain [31]. Moreover, the XRD pattern of PANI@CS displays different crystalline structure with small moves associating together to PANI and CS, which further confirmed the succeeded grafting of PANI backbone with CS chain [16, 18, 22], in the peaks positions. It is distinctly seen from XRD study that the hybrid material offer an amorphous in nature with a little crystalline part from $2\theta = 10^\circ$ to 30° . The CS crystallinity has been reduced after surface grafted by PANI backbone and this can be because the intermolecular forces into structure of composite formed, which is predicted for the elimination of AAP [21].

The TGA thermograms of CS, PANI and PANI@CS are present in Fig. 5-b. The TGA curve of CS displays two stages of weight loss, the first occurring in the range of 25 to 160°C attributed to loss of H₂O molecules with the weight loss approximately 3.49%. The primary degradation of CS started at 230°C and it was completely degraded at near 900°C with a weight loss of almost 13.27% [34]. TGA of PANI@CS presented three different steps of weight loss. The first step starting from 25 to 160°C, can attributed to the loss of adsorbed H₂O with a weight loss of almost 7.59%. The second decomposition step occurs between 220°C and 450°C, correspond to degradation (approximately 23.96%). The third step of the TGA curve is after 500°C to 900°C with a weight loss of almost 13.78%. These values prove the loss of the thermal stability for PANI@CS compared to the CS, confirming the formation of the hybrid adsorbent.

The SEM image of CS presents full amorphous regions as illustrated in (Fig. 6-a). The image clearly depicts the surface of CS is coarse and consisting of holes and uneven lumps that make it suitable for adsorption [35]. The SEM micrographs of PANI@CS as shown in (Fig. 6-b), reveal that the inclusion of PANI chain has great influence on morphology of the adsorbents that result in an interlocking arrangement of material. A close investigation of the surface reveals that PANI matrix is uniformly distributed on CS forming a network interconnecting each other and distributed on the entire surface during the polymerization process.

3.2. Adsorption assessments

3.2.1. Effect of pH

pH is one of the most significant parameters for adsorption process since the surface charge of molecules changes according the pH of the environment [18]. Thus, the influence of pH on the AAP adsorption by the three adsorbents was tested. The plot showing the adsorption of AAP on CS, PANI and PANI@CS is given in Fig. 7-a. The results of CS showed that adsorption efficiency increased as pH increased from 2.0 to 6.0. After increasing pH to 7.0, the adsorption percent slightly increased, and then it is quickly decreased to pH 12.0 values. However, for PANI, the adsorption percent decreased as the pH is increased. Obviously, PANI@CS has a higher affinity for AAP adsorption rather than both CS and PANI overall investigated pH range. Thereby, the deposition of PANI matrix on the CS surface is a efficacious strategy to ameliorate its AAP uptake ability. Moreover, it can be inferred that the imine and amine groups in PANI@CS hybrid adsorbent act as very helpful hosts to bind AAP from the aqueous solution. For the increase from 7.0 to 12.0, the capacity decreased for all adsorbents prepared. This behaviour is linked to

the dissociation of functional groups on the adsorbent surface at pH above 6.0 ($pK_a = 9.5$), causing adsorbate and adsorbent to be negatively charged. In this condition, electrostatic repulsion happens between the adsorbent and adsorbate molecules, causing the elimination to be disadvantaged [36]. This behaviour is in accord with other studies reporting the adsorption of AAP [36, 37]. Thereby, pH 7.0 was suggested as an optimum pH value for experiments of sorption of the studied AAP from aqueous solutions.

3.2.2. Effect of contact time

The shaking time between adsorbed and adsorbent is an essential role, as it enables us to know more in detail the characteristics, the design of the adsorption process, the mechanism as well as the adsorbate adsorption ratio and equilibrium time [38]. The influence of the time on the adsorption was studied and the equilibrium time was determined in the experiments carried out with the most suitable adsorbents with maximum adsorption capacity at pH 7.0 at 25 °C (Fig. 7-b). As can be seen from the figure, at the end of 480 min, AAP adsorption to CS and PANI@CS reached the maximum level with values 359.84 mg.g^{-1} and 383.48 mg.g^{-1} , respectively. In the adsorption processes, it is expected that equilibrium will be established between the adsorbent and the substance to be removed after a certain period of time. Because the functional groups on the adsorbent material reach fullness, the adsorption reaches equilibrium after a certain period of time [18, 19]. On the other hand, it is observed that the maximum adsorption (242.84 mg.g^{-1}) on PANI was achieved within only 360 min.

3.2.3. Adsorption kinetics

Figure 7-b. illustrates the impact of contact time on AAP adsorption by CS, PANI and PANI@CS with 15000 mg.L^{-1} initial concentration. The AAP was noted to rapidly achieve equilibrium (300 min) by PANI. However, onto CS and PANI@CS, AAP need longer contact time (480 min) to arrive equilibrium. The augmentation in equilibrium time with hybrid adsorbent is because to the increased contest for new active sites of the PANI@CS.

Adsorption kinetics of AAP on materials obtained was studied by using pseudo-1st -order (PFO) and pseudo-2nd -order (PSO) laws. The adsorption kinetics have been investigated in the initial concentration of 15000 mg.L^{-1} .

The PFO explains the adsorption happens between solid and liquid system depending to the elimination capability of adsorbent materials were expressed by the relations are presented in Table 1. Where; Q_e (mg.g^{-1}): equilibrium concentration, Q_t (mg.g^{-1}): concentration at time t , k_1 (min^{-1}) : PFO rate constant of adsorption. PFO linear regression plot of $\log(C_e - C_t)$ versus t presents a weak correlation coefficients (Table 5) displaying that the PFO kinetic was not succeed by adsorption.

Table 5

PFO and PSO kinetics for AAP elimination on adsorbents at pH:7.0, 298K and C_0 :15000mg.L⁻¹.

Adsorbents	$Q_{eq.Exp}$ (mg.g ⁻¹)	PFO			PSO		
		k_1 min ⁻¹	$Q_{eq.Cal}$ mg.g ⁻¹	R^2	$k_{2.ads}$ g.mg ⁻¹ .min ⁻¹	$Q_{eq.Cal}$ mg.g ⁻¹	R^2
PANI	242.49	0.0103	214.48	0.78	0.00015	196.08	0.94
CS	359.84	0.0066	298.26	0.57	0.00026	208.33	0.97
PANI@CS	385.25	0.0129	348.01	0.92	0.00088	344.82	0.98

The PSO kinetic shows a chemisorption phenomenon from solutions [43]. Also, the linear formula is written by the relations are presented in Table 1. Where; k_2 (g.mg⁻¹.min): PSO rate constant, Q_t (mg.g⁻¹): concentration at time t , Q_e (mg.g⁻¹): adsorption capacity, $k_2Q_e^2$ (g.mg⁻¹.min): initial adsorption rate.

The PFO and PSO kinetic data are calculated taking into account the correlation values (R^2). According to Table 5, the adsorption kinetic of AAP by three adsorbents is better defined by the PSO kinetics data than the PFO models because of the high R^2 . This shows that AAP removal by CS and PANI are dominated by chemical adsorption [43].

The adsorption rate values measured based on PSO kinetic are 88×10^{-5} , 26×10^{-5} and 15×10^{-5} g.mg⁻¹.min⁻¹ for PANI@CS, CS and PANI, respectively, reflecting a faster adsorption process by hybrid adsorbent. This is possibly because the better feasibly accessible to active sites of hybrid material compared with other adsorbents used. This augments the electrostatic attraction between PANI@CS adsorbent and AAP molecules, consequent a speed adsorption rate. Several investigators illustrated the succeeded usage of the PSO equation for the represent empirical kinetics values of AAP adsorption by several materials adsorbent (Table 6) [4, 8, 12, 36–44].

Table 6
The adsorptive capacity of several adsorbents for removal of AAP

Adsorbents	Adsorption Efficiency	pH	Ref.
AC from Oak acorn	45.45	3.0	[4]
Chemically modified Orange peel	28.09	//	[8]
SAC from Biomass waste	356.22	5.0	[12]
AC from Butia capitata	100.60	7.0	[36]
NH ₄ Cl-induced AC	233.00	7.1	[37]
ABSAC	145.40	8.0	[38]
AC from Dende coconut	70.62	2.0	[39]
AC from Babassu coconut	71.39	2.0	[39]
Rice husk ash	7.65	8.0	[40]
Chemically Modified AC	75.00	6.5	[41]
AC Pellets	105.00	7.0	[42]
Commercial AC	261.04	7.0	[43]
AC from Fly ash	270.30	7.0	[44]
PANI@CS	385.25	7.0	This work

3.3. Adsorption isotherm modeling

The monolayer adsorption capacity, the amount adsorbed was measured by the linear equation presented in Table 1, where Q_{eq} (mg.g⁻¹): amount adsorbed, C_{eq} (mg.L⁻¹): equilibrium concentration of the adsorbate, Q_m (mg.g⁻¹): maximum adsorption capacity of adsorbent and K_l (L.mg⁻¹): Langmuir constant.

Both multilayer (physisorption) and monolayer (chemisorption) can be measured using the Freundlich isotherm. This model is based on the heterogeneous equilibrium on adsorbents surface. The formula for Freundlich isotherm is illustrated in Table 1, where; n and K_f (mg^{1-1/n}.L^{1/n}.g⁻¹): Freundlich isotherm constant and C_{eq} (mg.L⁻¹): equilibrium concentration.

Basically, the adsorption phenomenon of porous adsorbent possesses three steps. First, the pollutant moved from solution to adsorbents surface by a liquid-boundary film. Secondly, this pollutant moved from adsorbents surface to intraparticle active site and finally, a strong interaction of pollutant molecules with the disposable sites on both the internal and external surfaces of adsorbents [45].

As a result of the adsorption studies carried out at the specified concentrations, the maximum AAP concentration to be adsorbed by different adsorbents was determined by plotting the amount of adsorbed AAP against the concentration values (Fig. 7-c). As display in Table 7, the fitting data of Langmuir equation for AAP adsorption were better than Freundlich equation, which exhibited the adsorption phenomenon, appertained to a chemisorption adsorption. And the n value ($n > 1$) of Freundlich equation confirmed that the three adsorbents was conducive to absorb AAP. As a result, this model is unable to justify the experimental capacity for AAP where the values of K_f obtained from this model are significantly lower than the experimental values, as shown in Table 7. Also, the R^2 values were smaller than those obtained from the Langmuir model. Thus, the Freundlich model does not fully explain the experimental results for these elements [46]. Combined with the kinetics and isotherm analysis data, the chemisorption was prevailing on adsorption of AAP by adsorbents prepared.

Table 7

Langmuir & Freundlich isotherms constants for AAP removal by adsorbents at pH:7.0 and 298K.

Adsorbents	Langmuir				Freundlich		
	Q_m (mg.g ⁻¹)	K_L (L.mg ⁻¹)	R_L	R^2	K_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	n	R^2
PANI	101.01	0.087	0.101	0.99	28.64	5.21	0.71
CS	243.90	0.539	0.007	0.99	45.84	3.27	0.75
PANI@CS	196.08	0.024	0.172	0.98	30.95	4.33	0.76

3.4. Adsorption thermodynamics.

Temperature effects on the adsorption of AAP by PANI, CS and PANI@CS adsorbed from aqueous solution with pH 7.0 were investigated at different temperatures in the range from 25 to 45 °C. In Fig. 7-d, it can be found that the AAP adsorption decreases with increasing temperature. In the adsorption process the thermodynamic parameters of enthalpy change ΔH , free energy change ΔG and entropy change ΔS can be measured by the formulas presented in Table 1, where; ΔS (kJ.mol⁻¹): entropy, ΔH (kJ.mol⁻¹): enthalpy, T (K): absolute temperature and R (8.314 J.mol⁻¹.K⁻¹): general gas constant.

The negative values ΔG displays the adsorption of AAP molecules by CS adsorbent is extremely favorable (Table 8). Furthermore, ΔG values are found to decrease with the augmentation of temperature is proved the spontaneous character of the adsorption processes at increased temperatures, this may demonstrated that the increased of adsorbents pores and more surface modification. The ΔH positive values illustrate the endothermic character of the elimination and it may also exhibit the adsorption processes physiosorption. The increasing positive values of ΔS at higher temperature may because to the increasing mobility and reducing the size of AAP which causes to increase in kinetics energy of the AAP. It favors the fast diffusion of AAP towards the adsorbents [47].The same way was followed in the case of

PANI and PANI@CS adsorbents, which confirmed that the bonding between AAP and adsorbents related to formation of PANI matrix on CS surface.

Table 8
Thermodynamic data for the AAP adsorption by the adsorbents prepared.

Adsorbents	T / K	$\Delta G / \text{kJ.mol}^{-1}$	$\Delta H / \text{kJ.mol}^{-1}$	$\Delta S / \text{kJ.mol}^{-1}$
PANI	298	-10.17	29.05	0.131
	303	-10.81		
	313	-12.16		
	318	-12.79		
CS	298	-9.18	27.86	0.123
	303	-9.46		
	313	-10.05		
	318	-12.01		
PANI@CS	298	-9.01	25.25	0.114
	303	-9.34		
	313	-10.20		
	318	-11.46		

3.5. Proposed adsorption mechanism

The proposed elimination mechanism of hybrid adsorbent preparation and adsorption of AAP on their surface are sketched in Fig. 1. According to the available functional groups on the PANI@CS surface, the adsorption mechanism of AAP by PANI@CS can be ascribed to the various interactions. Firstly, the electrostatic bonding was ruled out due to the AAP ($\text{pK}_a \approx 9.5$) was not ionized under solution pH 7.0; an analogous conclusion was reported in the literature [48]. On the other hand, the presence of the chemical bond between nitrogen species and AAP, and Van der Waals forces in the elimination was certain (Fig. 8-a), however this weak forces was recognized as a less significant contributor in adsorption mechanisms [49]. In fact, the $n-\pi$ bonding and also known as “donor–acceptor complex mechanism” (Fig. 8-b) is generally occurred where the lone pair electrons on an oxygen or nitrogen atom are delocalized into the π -orbital of an benzene ring of AAP [49, 50].

3.6. Regeneration study

The regeneration has been investigated in a specific manner for all the adsorbents since the renewability may be crucially important and significant parameters for holding the processes costs down and reduce wastes. Please refer to the experimental section above for details. Generally, the adsorption capacity of

adsorbents progressively decreases as the cycles number increases as illustrated in Fig. 9, which is fundamentally assigned to the incomplete, desorption of AAP during the renovation processes, thereby causing a decrease in adsorption active sites [51]. Moreover, the PANI@CS showed slightly diminishing in the adsorption capacity after five cycles of adsorption–desorption processes above 68%, which is because hybrid adsorbent has an additional cavity resulting from the formation of polymer matrix on the CS surface, indicating the structural stability and reusability of the optimized PANI@CS. Moreover, the adsorption capacity of PANI decreased from 75.89–25.16% after also five cycles. Nevertheless, the adsorption capacity of CS for AAP still reaches 52.82% after 5-cycles, indicating that CS also has acceptable renovability and recyclability compared to PANI.

4. Conclusions

In this study, CS supported on PANI matrix was synthesized through a simple polymerization method and its preparation was proved by surface area, XPS, TPD, XRD, FTIR, TGA and SEM analysis. The PANI@CS displays exceptional porosity, thermal stability and renewability. After the most suitable adsorbent was synthesized for adsorption, the rest of the experiments were carried out on these adsorbents. In the second stage of the study, the effect of pH, adsorption equilibrium time, temperature and AAP initial concentration on adsorption were investigated. The maximum adsorption capacity of PANI@CS, CS and PANI were found to be 385.25mg.g^{-1} , 359.84 mg.g^{-1} and 242.49mg.g^{-1} , respectively; at 25°C and optimal pH 7.0, which was best than that of other adsorbents published in literature. The kinetics and isotherm model corresponds to PSO and Langmuir formulas. This displays that the adsorption processes of AAP is chemisorption. The adsorption phenomenon can proceed spontaneously and appertain to the endothermic process according to the thermodynamic data. Moreover, the good performances adsorption is mainly due to the H-bonding, $\pi\pi$ bonding, pore filling and chemisorption as possible mechanism for the elimination of AAP by PANI@CS. Significantly, hybrid adsorbent has good selectivity towards the AAP and fabulous regeneration behaviour. With the good selectivity, elevated adsorption capacity and outstanding renewability, the PANI@CS adsorbent could be a favorable candidate to AAP adsorb from wastewater.

Declarations

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Figures

Figure 1

A graphical exemplification of the PANI@CS prepared.

Figure 2

(a) BET surface area, (b) Survey XPS spectra, (c) CO-TPD profiles and (d) CO₂-TPD profiles of adsorbents

Figure 3

XPS spectral: (a) C1s of CS, (b) C1s of PANI, (c) C1s of PANI@CS, (d) N1s of CS, (e) N1s of PANI and (f) N1s of PANI@CS.

Figure 4

FTIR analysis of adsorbents before and after adsorption.

Figure 5

(a) XRD patterns and (b) TGA analysis of adsorbents.

Figure 6

SEM images of: (a) raw CS and (b) PANI@CS.

Figure 7

(a) Influence of pH on adsorption capacity, (b) Effect of contact time on the adsorption process, (c) Adsorption isotherm and (d) Influence of temperature on adsorption capacity (adsorbents dose: 0.1g; AAP: 100mL; C_0 : 15000 $mg.L^{-1}$; T: 298K; pH 7.0).

Figure 8

Possible adsorption mechanism of various mods of interactions between AAP and PANI@CS: (a) H-bonding and (b) n- π interactions.

Figure 9

Cyclic adsorption-desorption performance of adsorbents on AAP (adsorbents dose: 0.1g; AAP: 100mL; C_0 : 15000 mg.L⁻¹; T: 298K; pH 7.0).