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### RESEARCH ARTICLE

#### DEVELOPMENT OF A LOW-COST OLEOPHILIC ADSORBENT BASED ON AMINATED CHITOSAN - POLY (BUTYL ACRYLATE) GRAFT COPOLYMER FOR MARINE OIL SPILL CLEANUP.

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#### Abstract

In the present study, a new low-cost oil adsorbent was prepared based on graft copolymerization of commercial chitosan biopolymer derivative. Aminated Chitosan (AmCS) was prepared from chitin which initially extracted from the marine waste sources, followed by amination step using p-benzoquinone (PBQ) as activation agent and ethylenediamine (EDA) as amine source. The prepared AmCS was grafted with a hydrophobic butyl acrylate (ButA) monomer via a free radical polymerization process, and the resultant grafted copolymer was characterized using FT-IR, TGA, DSC, and SEM characterization tools. The oleophilic character of the grafted copolymer was investigated using oil uptake measurements. Moreover, oil/water-contact angle measurements (wettability) displayed that the hydrophobic and oleophilic characters of the grafted copolymer were enhanced after the grafting process and recorded maximum values 115° and 28° using water and crude oil droplets respectively compared to 52° and 82° in case of the native aminated chitosan. Evaluation of the oil spill cleanup process was also optimized using crude oil- artificial seawater system under different adsorption conditions. Oil adsorption values were increased gradually from 49 to 84% for the grafted AmCS samples with increasing the oil viscosity in the following order; gasoil < mobil-1 oil < light crude oil < heavy crude oil using 0.1g of the adsorbent sample, while the native AmCS only increased from 17.5 to 37% at the same adsorption conditions. The results obtained clearly suggested that the developed AmCS-poly (ButA) graft copolymer could be applied as a new low-cost oil adsorbent material for marine oil spill cleanup technologies.

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**Introduction:-**

Commonly, more than 35 billion gallons of petroleum oil are transported across the seas every day and about 100 million gallons are spilled every year [1, 2]. This poses a great risk of pollution to the marine ecosystem, hence the petroleum oil pollution affects sea life, aquaculture, tourism, economy, and human health [3, 4]. In fact, Oily contaminants in the polluted sea water may be identified in different forms such as heavy hydrocarbons (tars, crude oils and diesel oil) and light hydrocarbons (kerosene, jet fuel and gasoline) in addition to fats, lubricants and cutting liquids [5, 6]. Numerous physical, chemical, and biological methods have been established for oil spill removal, including burning, oxidation/reduction, chemical dispersants, booms, skimmers, and biological agents [7-9]. However, the main limitations of these methods are the high cost, environmental harmfulness and their inefficiency at high water tide. Actually, sorbent materials are applied for solving these problems since this sorbent technique is the most effective and cost saving for reducing the environmental damage [10].

To date, several categories of oil sorbent materials such as natural organic sorbents, inorganic sorbents, and synthetic organic sorbents have been widely studied. Oil adsorbent materials have been stated to be one of the most highly effective sorbents from the economic and ecologic point of view such as bentonite, silica aerogels, activated carbon, and polymers [11-14]. Additionally, the development of oil adsorbent materials based on natural organic waste materials was presented to afford resources for marine oil spill clean-up with low-cost production [15]. It has been reported that adsorbents based on biopolymeric materials resultant from renewable resources are an innovating solution to replace the other conventional petroleum-based adsorbents. However, to obtain useful and inexpensive products some of their properties such as the poor mechanical properties, high water uptake, and moisture sensitivity should be improved [16].

Chitosan (CS) is the partially de-acetylated form of the naturally chitin polysaccharide (the second abundant biopolymers after cellulose) which extracted from the shrimps, crab, and other crustaceans skeleton [17]. Chitosan is a cationic biopolymer consists of a copolymer of  $\beta$ -(1 $\rightarrow$ 4)-2-acetamido-2-deoxy-D-glucopyranose and de-acetylated unite  $\beta$ -(1 $\rightarrow$ 4)-2-amino-2-deoxy-D-glucopyranose [18]. Actually, chitosan can be used in various applications such as medical, pharmaceutical, food packaging, water treatment, and other industrial applications compared to the other natural polymers [19-24]. This is due to its excellent properties such as bio-degradability, low cost production, non-toxicity, and simplicity modification [17, 23]. Moreover, chitosan has various functional groups such as hydroxyl and amino groups which induced simple chemical alteration and modifications. Physical and chemical modifications of chitosan such as amination, sulfonation, carboxymethylation, coating, and grafting allow formation of different functional derivatives with special hydrophilic and/or hydrophobic characters [25-28].

Grafting of chitosan with other polymers is an important topic in the production of functionalized materials with enhanced properties. Where, chitosan presents two types of reactive sites which can be modified by grafting the C-2 (free amino groups) on deacetylated units and the C-3 and C-6 (hydroxyl groups) in either acetylated or deacetylated units [29]. Much works have been carried out to perform grafting copolymerization of chitosan and vinyl acrylate monomers such as acrylic acid, methyl methacrylate, acrylamide, and other acrylate monomer derivatives [30-35]. The resultant graft copolymers normally have the main properties of both initial components.

In the present study, a new graft copolymer adsorbent based on aminated chitosan derivative and a hydrophobic n-butyl acrylate monomer was prepared using free radical polymerization process. The resultant aminated chitosan-poly( butyl acrylate) graft copolymer (AmCS-g-poly (ButA)) was characterized using different characterization techniques. Furthermore, the hydrophobic/hydrophilic and oleophilic characters were investigated using oil/water uptake and oil/water contact angle measurements. The evaluation study of the prepared grafted copolymer for the adsorption of oil spill was achieved under different environmental seawater conditions.

**Experimental:-****Materials:-**

Shrimp shells were collected from marine waste sources in Alexandria (Egypt), N-butyl acrylate (98%) was obtained from Sigma-Aldrich (Germany), p-Benzoquinone (PBQ; 99%) was obtained from Sigma-Aldrich (Germany), Ethylenediamine (EDA; 99%) was purchased from Alfa Aesar (Germany), Potassium persulphate (KPS; 99%) was purchased from sigma-Aldrich (Germany), Sodium hydroxide (99%), ethanol (99%), hydrochloric acid (purity 37%), and acetic acid (98%) were brought from El-Nasr Company (Alexandria). Mobile-1 oil was supplied from Exxon Mobil Co. (Egypt). Gasoil was delivered from Misr petroleum Co. (Egypt). Light and crude oils were provided from Belayem Petroleum Company, (Egypt). Viscosity values of the used oil types were listed in Table 1.

**Table 1:-** Measurement values of viscosity for the used oil types

Type of oil	Viscosity Kin. @ 40 °C (Centistokes)
Gasoil	2
Mobil-1 oil	8.1
Light crude oil	15.5
Heavy crude oil	110

**Methods:-****Extraction of chitin:-**

Extraction of chitin from shrimp shells was achieved according to the reported published method [36]. In brief; the shrimp shells were dispersed at room temperature in 5% HCl (w/v) in the ratio of 1:14 (w/v) and left overnight. The de-mineralized shells were washed using distilled water to remove the excess of acid and other impurities, then treated with 5% (w/v) NaOH at room temperature for 24hr. Pure chitin was obtained after The washing the collected residues several times with water to neutrality.

**Preparation of aminated chitosan (AmCS):-**

Aminated chitosan derivative was prepared according to author's preceding work [25]. Firstly, chitin (4g) was activated by dispersing it in 50ml of p-benzoquinone (PBQ) of a known concentration at a chosen pH with continuous stirring for 6hr at 50°C. The resulted PBQ-activated chitin was separated and washed with distilled water for removing the excess of un-reacted PBQ. Secondly, PBQ-activated chitin was dispersed in 50ml of EDA of a known concentration at 50°C for 6hr with continuous stirring. The resultant aminated chitin was separated and washed with distilled water to eliminate un-reacted EDA. Finally, the pure aminated chitin was de-acetylated using aqueous solution of 50% NaOH at 120–150°C for 6 hr. The resulted aminated chitosan was then separated and washed with distilled water to remove the excess of NaOH and followed by drying at 40°C.

**Preparation of aminated chitosan- poly (butyl acrylate) graft copolymer:-**

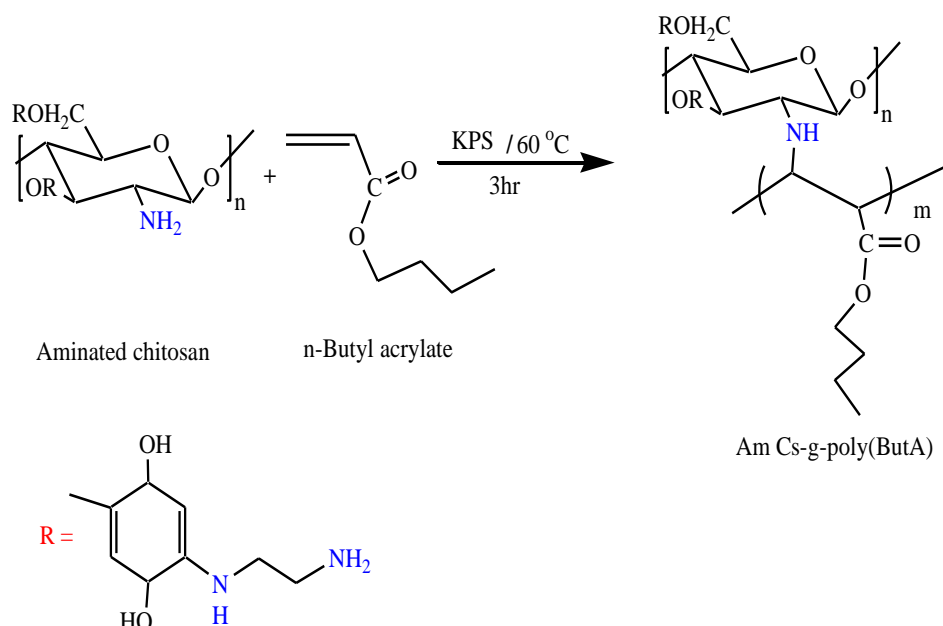
Accurately, a known amount of the prepared aminated chitosan (AmCS) was dissolved in 20ml of 2% acetic acid solution at room temperature, then ethanol (10ml) was add drop wise to the solution with continuous stirring. Potassium persulphate (KPS, 0.1g) was dissolved in 50ml distilled water and added to the aminated chitosan solution, the reaction temperature was elevated to 60°C. After 20min, butyl acrylate (10 and 20ml) was added slowly with additional amount of KPS (0.05g dissolved in 5ml). The grafting reaction was conducted for 3hr. The precipitated grafted copolymer was recovered by centrifugation followed by washing several times with acetone and pure methanol using soxhlet for 2hr to remove un-grafted butyl acrylate homopolymer and dried at 50°C. The resultant graft copolymers were coded as AmCS-g-poly (ButA 10) and AmCS-g-poly (ButA 20). Fig. 1 represents the proposed mechanism for synthesis of aminated chitosan- poly (butyl acrylate) graft copolymer.

The grafting percentage (Gp %) and grafting efficiency (GE %) were determined as follows [37, 38]:

$$GP (\%) = ((W1 - W0)/W0) \times 100$$

$$GE (\%) = ((W1 - W0)/W2) \times 100$$

Where,  $W_0$  is weight of AmCS,  $W_1$  is weight of AmCS-g-poly (ButA), and  $W_2$  is the weight of ButA monomer.



**Fig. 1:-** Synthesis of aminated chitosan- poly (butyl acrylate) graft copolymer.

#### **Physico-chemical characterization:-**

The chemical structures of the AmCS and AmCS-poly (ButA) graft copolymer were investigated by using Fourier Transform Infrared Spectrophotometer (Shimadzu FTIR - 8400 S, Japan). While, Their thermal stability were assessed using Thermal Gravimetric Analyzer (Shimadzu TGA -50, Japan) and Differential Scanning Calorimeter (Shimadzu DSC-60-A, Japan).The morphological structures of AmCS and AmCS-poly (ButA) graft copolymer were observed with the help of a Scanning Electron Microscope (SEM; Joel Jsm 6360LA, Japan).

Additionally, both hydrophobic characters of the prepared graft copolymer were examined using contact angle measurement (Rame-hart instrument Co. Model 500-F1, UK) using distilled water and light crude oil droplets.

#### **Water/oil uptake measurements:-**

For studying the water/oil uptake behaviors of both AmCS and the prepared grafted copolymers, 0.1g of each sample was immersed in 25ml of liquid (water, Gasoil, Mobil-1 oil, Light crude oil, and Heavy crude oil) under constant shaking rate (100rpm) for 2hr. The swollen samples were separated and the excess of the adherent liquid was removed using filter paper, followed by weighing in a closed electronic balance. The liquid uptake (LU) can be expressed by the following equation:

$$\text{LU (\%)} = \frac{(W_s - W_0)}{W_0} \times 100$$

Where;  $W_s$  is the weight of the swollen sample, and  $W_0$  is the initial dry weight of sample.

#### **Batch oil adsorption experiments:-**

The oil adsorption process was achieved based on the Standard Test Method for adsorbent performance (ASTM F726-99) [39] using oil-artificial seawater system with. Various amounts of oil (2.5-15g) were poured into a 500ml beaker containing 300ml of artificial sea water, then different amounts of adsorbent sample (0.1-1g) were spread on the oil-water surface under different shaking rates (50-200rpm) at different temperatures ranged from 25 to 40 °C for a known contact time (10-300min.). While, the used oils were gasoil, mobil-1 oil, light and heavy crude oil, Finally, samples were removed and weighted using electronic balance.

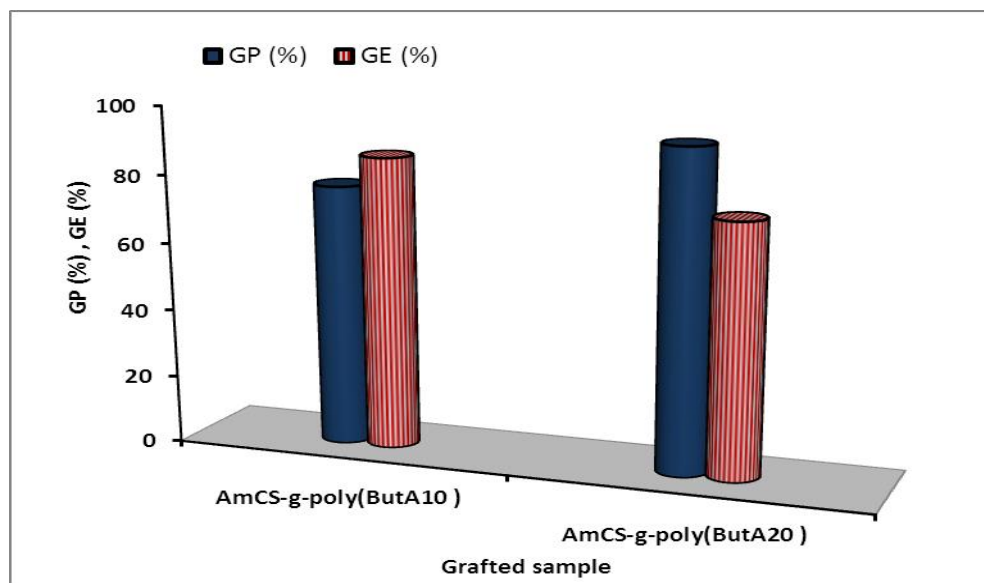
The percentage of oil adsorption (%) was calculated according to the following equations [40, 41 ]:

$$\text{Oil adsorption (\%)} = \frac{(W_a/W_b)}{W_b} \times 100$$

Where;  $W_a$  is the weight of adsorbed oil (g), and  $W_b$  is the initial weight of oil (g).

### Results and Discussion:-

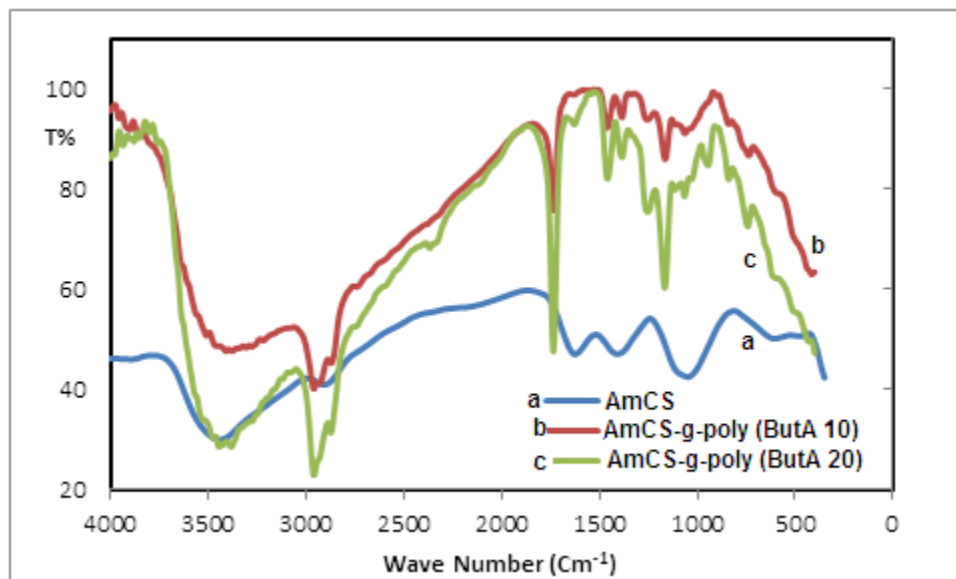
The effect of butyl acrylate concentration on the grafting parameters (GP% and GE%) was shown in Fig. 2. Results showed that the grafting percentage increased from 77 to 93.5% with increasing the amount of butyl acrylate in the feed mixture. These results could be attributed to that increasing the monomer concentration facilitates the diffusion of monomer into the active sites of aminated chitosan backbone, and subsequently increases the grafting percentage. However, increasing the concentration of ButA monomers from 10 to 20 ml decreases the grafting efficiency (GE%) from 86 to 74%, this could be due to increasing the divisor value. Generally, both GP% and GE% exhibited to be exceed than 70% for the used ButA concentrations.



**Fig. 2:-** Values of GP% and GE% for the prepared grafted copolymers.

### FT-IR

FTIR of AmCS, AmCS-g-poly (ButA 10) and AmCS-g-poly (ButA 20) were investigated and presented in Fig 3. It was clear that AmCS shows characteristic hydrophilic bands of aminated polysaccharide; a broad band between  $3200-3600\text{ cm}^{-1}$  equivalent to the stretching vibration of OH and  $\text{NH}_2$  groups that spread along the polymer structure [42]. C-H stretching of methyl and methylene groups was exhibited between  $2835-2950\text{ cm}^{-1}$ . Bands at  $1620\text{ cm}^{-1}$  result stretching vibration of C=O and NH-C=O. Bands at  $1066-1059\text{ cm}^{-1}$  corresponding to C-O-H stretching [43]. On the other hand, the grafted copolymers demonstrate a significant difference in the spectra of FT-IR. Where, the absorption bands at  $1729\text{ cm}^{-1}$  were corresponding to stretching vibration of acrylate C=O group and the characteristic absorption bands of the C-H stretching vibration and the C-H in-plane bending vibration looked at  $2876, 2930\text{ cm}^{-1}$  and  $1380, 1470\text{ cm}^{-1}$ , respectively.



**Fig. 3:-** FT-IR spectra of AmCS, AmCS-g-poly (ButA 10), and AmCS-g-poly (ButA 20).

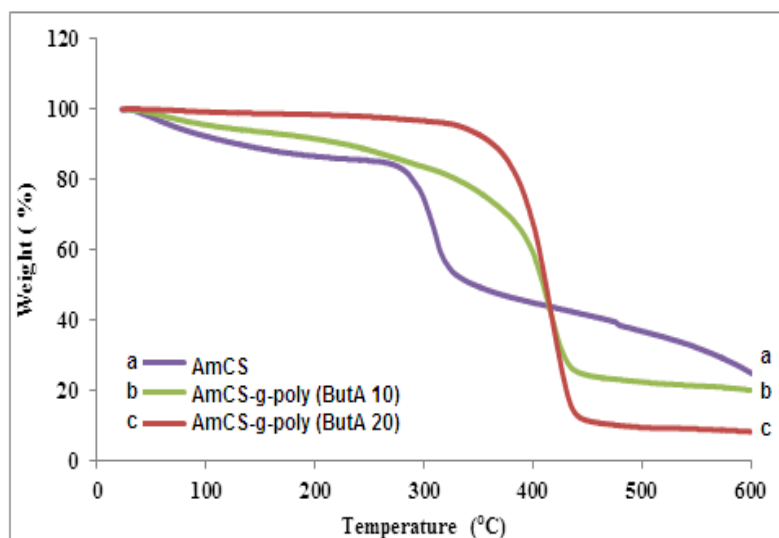
### TGA

Thermal gravimetric analysis of AmCS, AmCS-g-poly (ButA 10), and AmCS-g-poly (ButA 20) was investigated in Fig. 4. Aminated chitosan was thermally degraded via three weight loss stops. The first weight loss that initiated from ambient temperature to about 150°C was associated with loss moisture content that interrupted in the polymer chain. The presence of hydrophilic groups (hydroxyl and amine groups) can be attributed to the capability of the polymer to trap moisture from surround atmosphere.

The subsequent degradation that distinguished from 220°C to 320°C was a result of thermal oxidative decomposition of the pyranose ring along AmCS backbone. In this phase, the decline was generated from the elimination of amine groups to form cross-linked residue [44]. The final degradation step was obtained from the decomposition of a new cross-linked residue produced by thermal crosslinking reactions at a higher temperature. Table 2 describes more details about the thermal behavior of the grafted copolymers compares to AmCs. Both derivatives exhibiting less moisture content 6.35% and 1.21% respectively, this can attribute to hydrophobic nature of poly (butyl acrylate). Where, poly (ButA) exhibits a single degradation step between 380-400°C [45]. The obtained results indicated that the grafted copolymers have a great thermal stability than that of neat polymer (aminated chitosan).

**Table 2:-** Thermal gravimetric parameters of AmCS, AmCS-g-poly (ButA 10), and AmCS-g-poly (ButA 20)

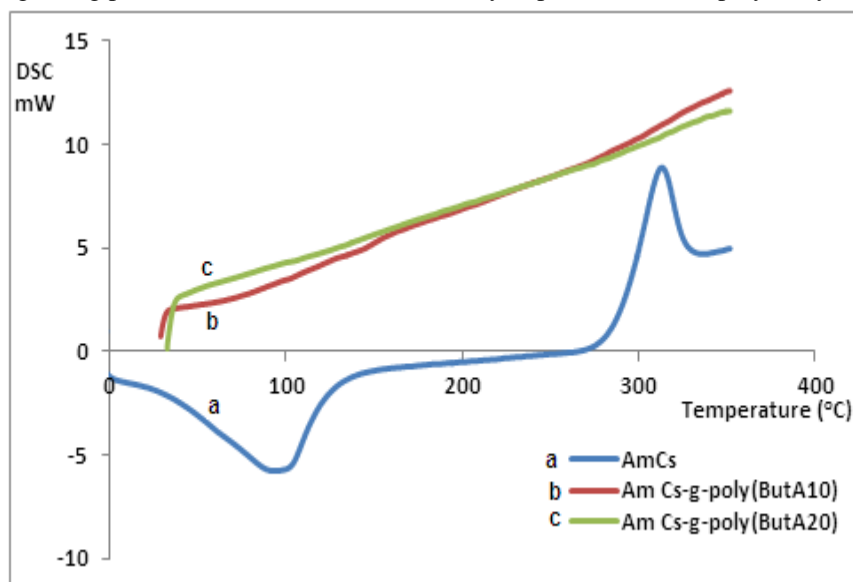
Sample	Weight loss (%) ambient – 150 °C	T <sub>50</sub> (°C)
AmCs	12.13	345.19
AmCS-g-poly (ButA 10)	6.352	409.43
AmCS-g-poly (ButA 20)	1.21	411.89



**Fig. 4:-** TGA of AmCS, AmCS-g-poly (ButA 10) and AmCS-g-poly (ButA 20) copolymers.

### DSC

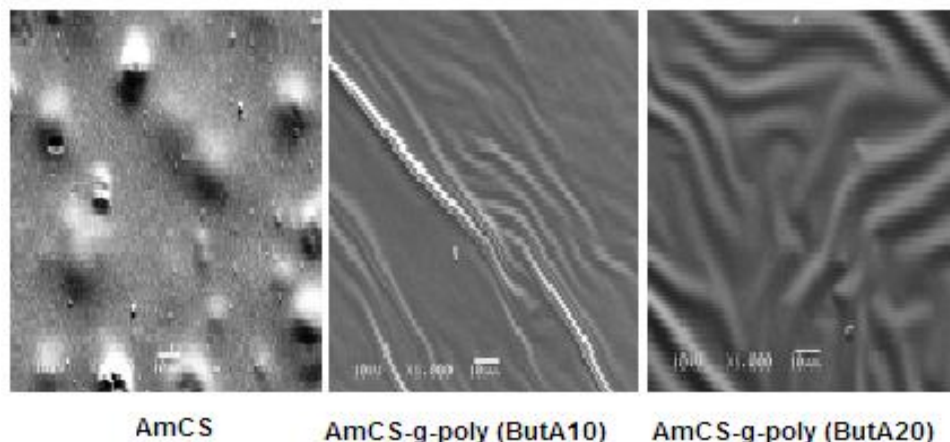
Differential scanning calorimeter of AmCS-g-poly (ButA 10) and AmCS-g-poly (ButA 20) compared to neat polymer AmCS was investigated in Fig. 5. Results demonstrate a distinct endothermic band around 100 °C that indicated to dehydration of moisture content of samples. AmCS has hydrophilic groups such as amine and hydroxyl groups, of these groups to trap moisture from surrounding or during preparation increase with increasing the hydrophilic nature of AmCS backbone. The relatively large amount of binding water in aminated chitosan was decreased after the grafting process under the influence of the hydrophobic nature of poly (butyl acrylate).



**Fig. 5:-** DSC of AmCS, AmCS-g-poly (ButA 10) and AmCS-g-poly (ButA 20) copolymers.

### SEM

The changes in the morphological structure of the developed grafted copolymers were investigated as shown in Fig. 6. It was observed from SEM images that the grafting process was affected the surface morphology of the grafted copolymers. Where, AmCS has a rough surface, while AmCS-g-poly (ButA 10) and AmCS-g-poly (ButA 20) copolymers have flat and smooth homogenous surfaces and the density of the surface increased with increasing the amount of butyl acrylate in the grafting medium. These results could be related to hydrophobic nature of poly (butyl acrylate).



**Fig. 6:-** SEM images of AmCs, AmCS-g-poly (ButA 10) and AmCS-g-poly (ButA 20) copolymers.

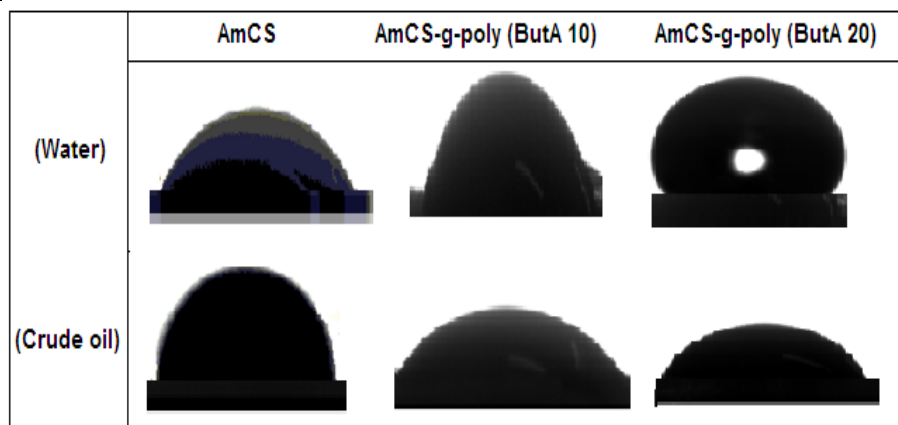
#### Contact angle

The hydrophobic/hydrophilic and oleophilic characters of AMCS and AmCS-poly (ButA) graft copolymers were investigated as shown in Fig. 7 and Table 2 using water and crude oil droplets based on wettability measurements. It was clear from the obtained results that the oleophilic character of the AmCS-g-poly (ButA) were enhanced and recorded  $45^\circ$  and  $28^\circ$  in case of CS-g-poly (ButA 10) and CS-g-poly (ButA 20) respectively compared to the native AmCS ( $82^\circ$ ) using light crude oil droplet.

Results also indicated that the hydrophobic character of the grafted copolymer increased with increasing ButA amount in the grafting medium and recorded maximum value  $115^\circ$  using water droplet compared to AmCS ( $52^\circ$ ). These behaviors could be related to the nature of the used hydrophobic ButA monomers.

**Table 2:-** Data of contact angle for aminated chitosan and its developed grafted copolymers using water and heavy crude oil droplets

Sample	$\theta$ (Water)	$\theta$ (Light crude oil)
AmCS	52	82
CS-g-poly (ButA10 )	105	45
CS-g-poly (ButA 20)	115	28



**Fig. 7:-** Contact angle images for AmCS, AmCS-g-poly (ButA10), and AmCS-g-poly (ButA20).

#### Water/oil uptake measurements:-

Fig. 8 represents the behavior of AmCS, AmCS-g-poly (ButA 10), and AmCS-g-poly (ButA 20) for water and oil uptakes (liquid uptake; LU). From the obtained results, it was clear that water uptake of AmCS increased compared



to the grafted copolymers, this is due to the available hydrophilic groups (i.e.; hydroxyl and amine groups) of AmCS which bind with water molecules resulting an increasing water uptake value. While, in case of the prepared grafted copolymers the water uptake have very little values due to the consumption of the hydrophilic groups of AmCS through the grafting process. In contrast, oil uptake increased with increasing ButA monomer in the feed mixture, and this can be explained by increasing the hydrophobic character of the resultant graft copolymers with increasing the grafted ButA molecules onto AmCS polymer. Results also showed that oil uptake values increased gradually with increasing viscosity of the used oil type, where maximum oil uptake was observed using heavy crude oil.

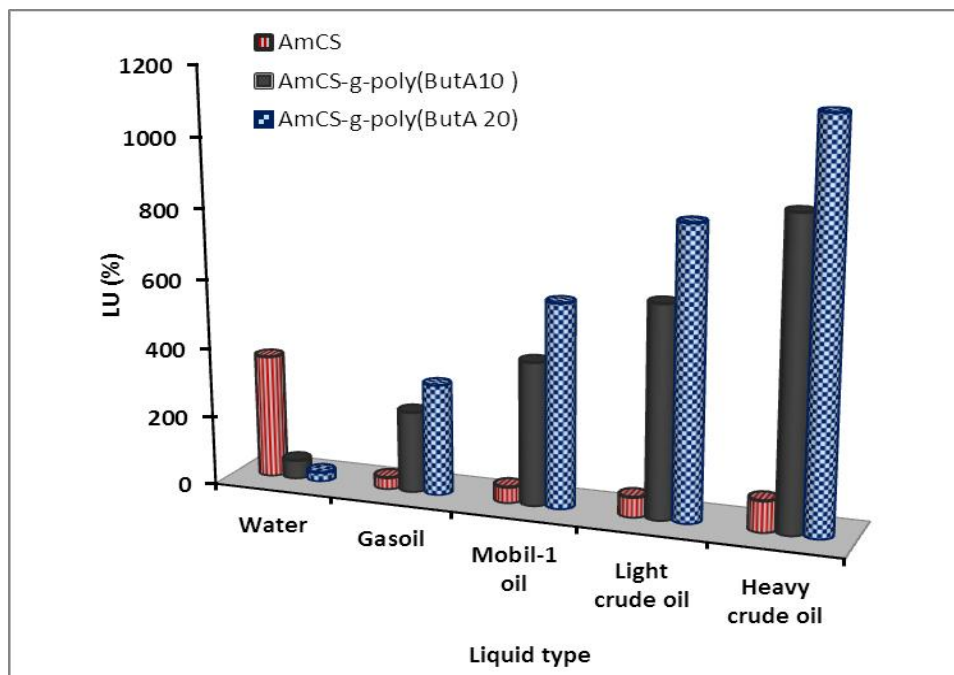


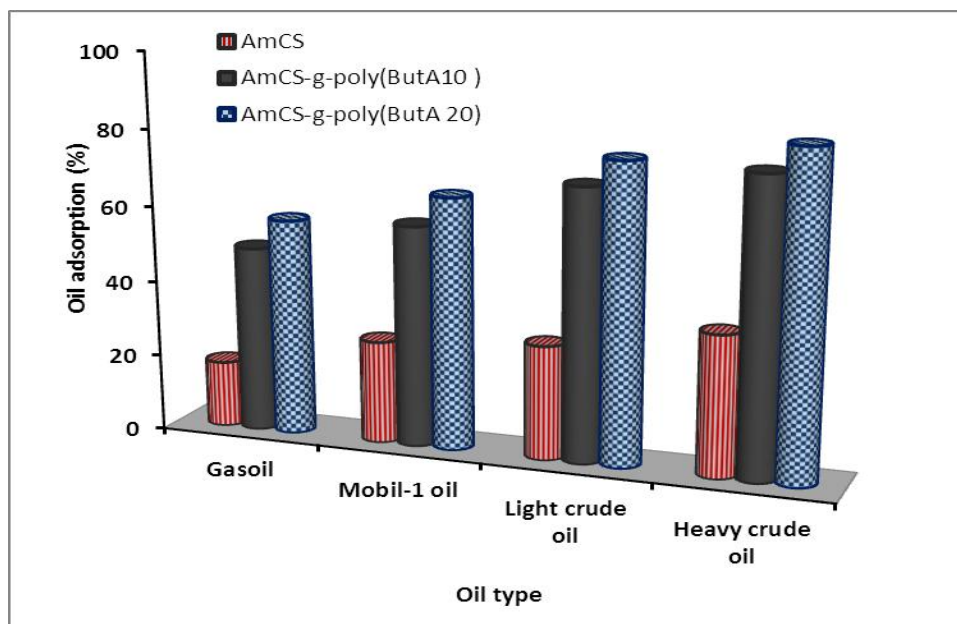
Fig. 7:- Liquid uptake behaviors of AmCS, AmCS-g-poly (ButA 10), and AmCS-g-poly (ButA 20).

#### ***Oil adsorption measurements:-***

The hydrophobic-oleophilic nature of n-butyl acrylate reflects positively on the prepared Aminated chitosan grafted poly (butyl acrylate), where the adsorption process was improved after grafting process. Basically, AmCS and the grafted copolymers were assessed their ability for oil adsorption under seawater conditions as following:

#### ***Effect of oil type:-***

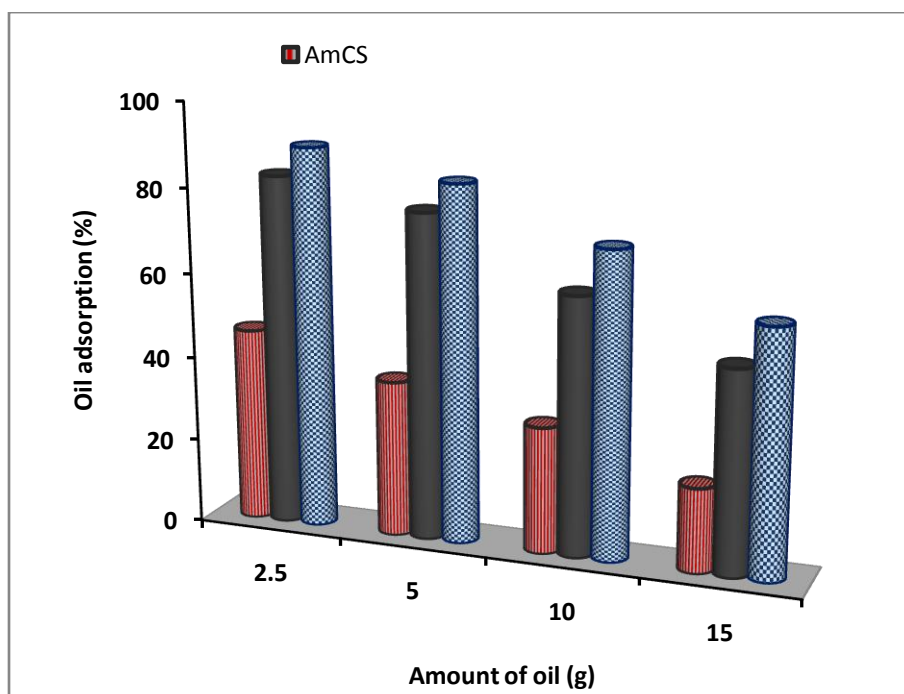
The effect of oil type on the oil adsorption percentage was explored using four oil types with different viscosity values as shown in Fig.8A. It was observed that the oil adsorption values increased gradually with the following order; Gasoil < Mobil-1 oil < Light crude oil < Heavy crude oil. Where, maximum values for adsorption were recorded using the heavy crude oil. These results can be explained by increasing the adherent forces between the adsorbent and oil surface with increasing oil viscosity, and consequently the oil adsorption increases. On the other hand, it was observed that the oil adsorption values of the grafted copolymers were increased with increasing the amount of butyl acrylate in the grafting medium (77% and 84%) compared to the AmCS (37%) using heavy crude oil.



**Fig. 8A:-** Effect of oil type on the oil adsorption (%) for AmCS, AmCS-g-poly (ButA 10), and AmCS-g-poly (ButA 20) at constant contact time (180min), adsorbent amount (0.1g), oil amount (5g), agitation rate (100 rpm), and adsorption temperature medium (30°C).

**Effect of initial oil amount:-**

Fig. 8B shows the effect of the initial amount of oil on the oil adsorption process was studied and investigated as shown in Fig. 8B. It was clear from results that oil adsorption decreased with increasing the initial amount of oil from 2.5 to 15g. Commonly, it well known that oil adsorption (%) is defined as the ratio of the adsorbed oil amount to the initial amount of oil. Accordingly, the oil adsorption values take adverse trend with increasing the initial amount of oil.

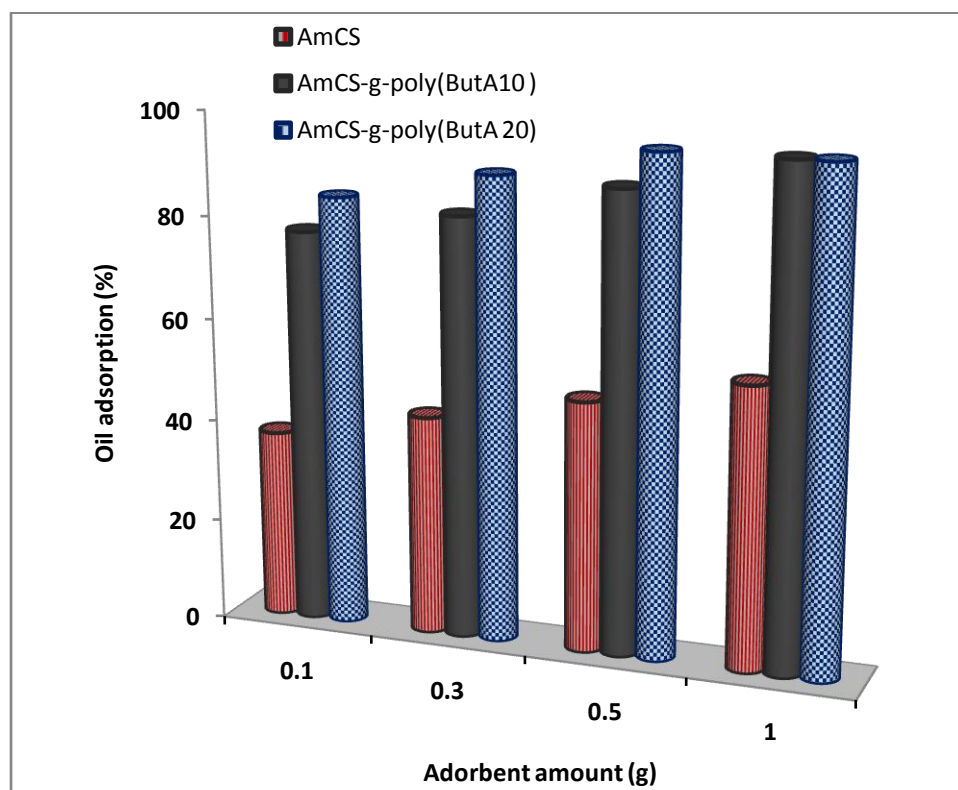


**Fig. 8b.** Effect of initial amount of oil on the oil adsorption (%)AmCS, AmCS-g-poly (ButA 10), and AmCS-g-poly (ButA 20) at constant contact time (180 min), adsorbent amount (0.1g), agitation rate (100 rpm), and adsorption temperature medium (30°C) using heavy crude oil.

**Effect of adsorbent amount:-**

The effect of the adsorbent amount on the oil adsorption (%) was investigated as shown in Fig. 8C. In all cases, results indicated that the oil adsorption (%) increased gradually with increasing the adsorbent amount up to 1g. Also, it was noted that only 0.5g of AmCS-g-poly (ButA 20) sample was needed to reach the maximum oil adsorption value (96%), while 1g was required for AmCS and AmCS-g-poly (ButA 10) to reaches the maximum adsorption values (55% and 96%). Increasing the adsorbent amount increases the exposed sites for adsorption of oil molecules. Moreover, increasing the hydrophobic ButA amount in the adsorbent sample decreases the required amount of adsorbent.

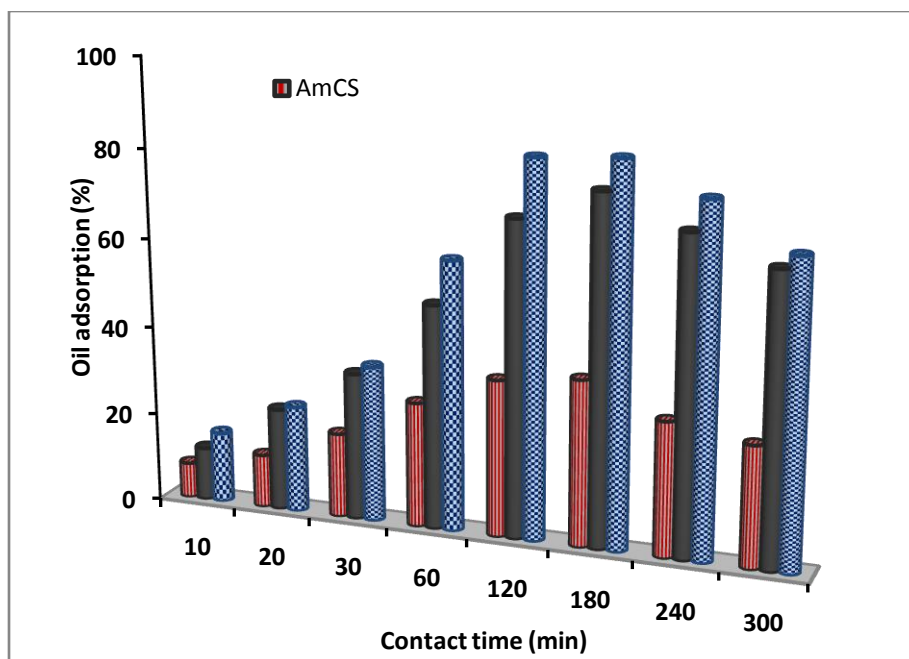
Where, only 0.1g of the grafted copolymers can adsorb more than 75% of heavy crude oil compared to AmCS (37%) at the same adsorption conditions and this is due to increasing the oleophilic properties after grafting with ButA monomer.



**Fig. 8:-** Effect of initial amount of adsorbent on the oil adsorption (%) for AmCS, AmCS-g-poly (ButA 10), and AmCS-g-poly (ButA 20) at constant contact time (180 min), oil amount (5g), agitation rate (100 rpm), and adsorption temperature medium (30°C) using heavy crude oil.

**Effect of contact time:-**

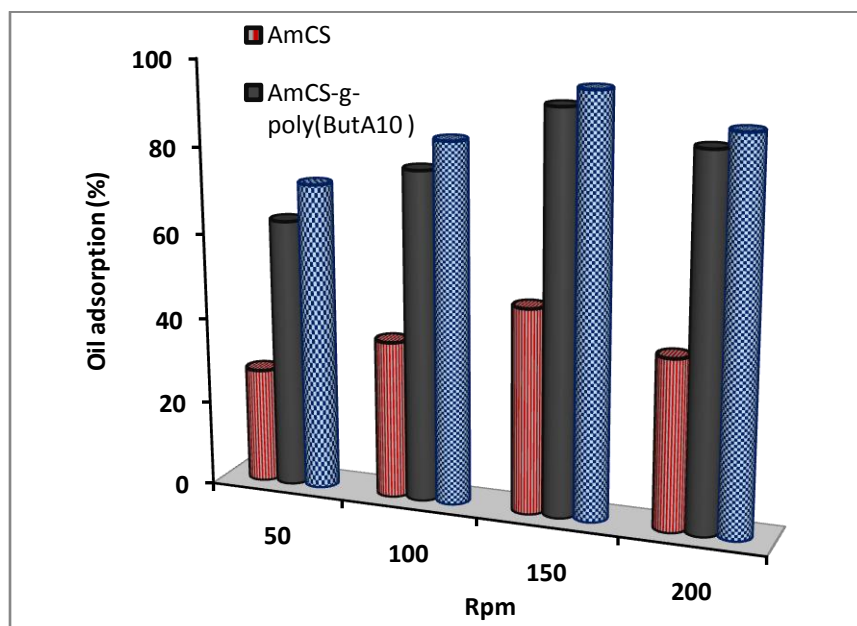
Fig. 8C represents the effect of variation contact time from 10 min to 300 min on the oil adsorption (%) of AmCS and the grafted copolymers (10-300 min). Results investigated that that with increasing the contact time up to 180 min the oil adsorption (%) increased and reached maximum values 37%, 77%, and 84% for AmCS, AmCS-g-poly (ButA 10), and AmCS-g-poly (ButA 20) respectively. While, further increasing in the contact time beyond 180 min decreases the oil adsorption values. These results could be attributed to that increasing contact time from 10 min to 180 min enhances the available adsorbent sites to attract large number of oil molecules resulting increase in the oil adsorption values. However, with increasing contact time beyond 180 min (the equilibrium contact time), no further oil molecules can be adsorbed and the affinity of adsorbent sample towards oil molecules decreased, then oil desorption process occurred followed by decreasing oil adsorption (%).



**Fig. 8D:-** Effect contact time on the oil adsorption (%) for CS, CS-g-poly (ButA10), and CS-g-poly (ButA20), adsorbent amount (0.1g), oil amount (5g), agitation rate (100 rpm), and adsorption temperature medium (30°C) using heavy crude oil.

#### **Effect of rpm:-**

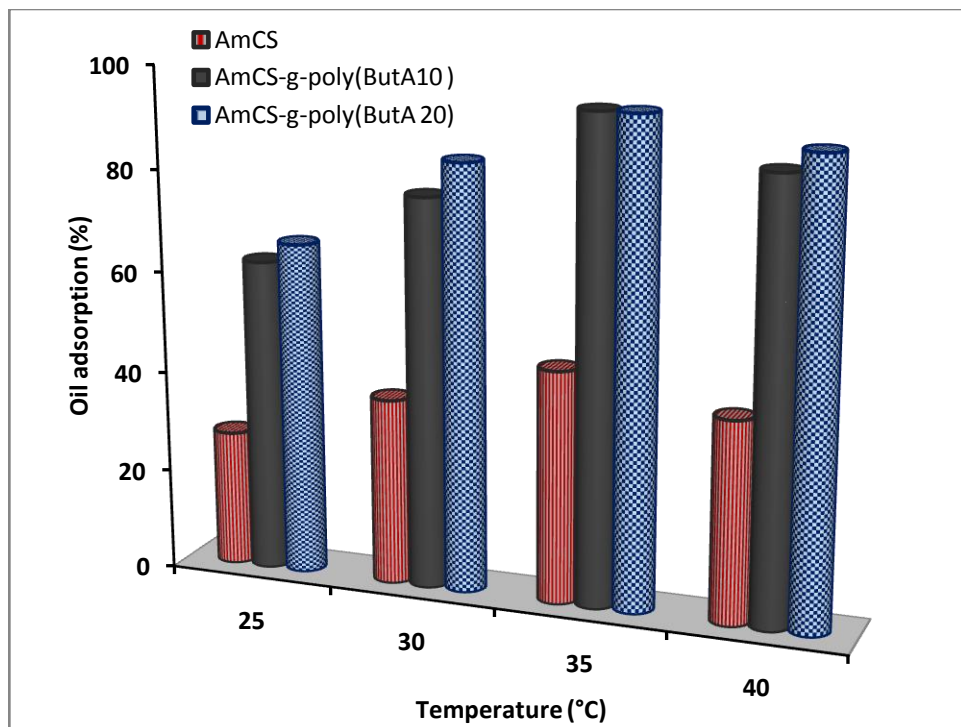
Fig. 8E shows the effect of variation shaking speed on the oil adsorption (%). The obtained results indicated that the oil adsorption values increased gradually with increasing the shaking speed up to 150 rpm. These results could be attributed to that with increasing the rate from 50 to 150 rpm, the dispersion of oil spill increases and enhances the diffusion of oil spills towards the surface of adsorbent samples resulting an increasing in oil adsorption (%). However, further increase up to 200 rpm causes decreasing in the oil adsorption (%) could decrease the attraction forces between oil molecules and the available sites of adsorbent surface, followed by oil desorption process.



**Fig. 8E:-** Effect of agitation rate (rpm) on the oil adsorption (%) for CS, CS-g-poly (ButA10), and CS-g-poly (ButA20) at constant contact time (180 min), adsorbent amount (0.1g), oil amount (5g), and adsorption temperature medium (30°C) using heavy crude oil.

**Effect of adsorption temperature:-**

The effect of variation adsorption medium temperature oil the adsorption process was investigated as shown in Fig. 8F. It was clear from results that oil adsorption (%) was greatly improved and reached maximum values with increasing adsorption temperature up to 35°C. These results could be due to increasing the diffusion rate of oil molecules into the adsorbent surface sites with increasing temperature from 25 to 35°C. However, increasing temperature beyond 35°C decreases the oil adsorption values, which causes less probability of oil attachment on the adsorbent surface and the desorption process occur.



**Fig. 8F:-** Effect of adsorption medium temperature on the oil adsorption (%) for CS, CS-g-poly (ButA10), and CS-g-poly (ButA20) at constant contact time (180 min), adsorbent amount (0.1g), oil amount (5g), and agitation rate (100 rpm) using heavy crude oil.

**Conclusion:-**

Aminated chitosan-poly (butyl acrylate) graft copolymers were developed and characterized. The effect of butyl acrylate amount on the grafting percentage and grafting efficiency was studied. Both hydrophobic and oleophilic characters of the resultant graft copolymers were significantly enhanced through oil/water- contact angle measurements and oil/water uptake studies. The oil adsorption process was evaluated using different oil types. The oil adsorption (%) was found more than 95% in case of the grafted aminated chitosan- poly (butyl acrylate) copolymers compared to the native aminated chitosan ( about 37%) at constant contact time (180 min), adsorbent amount (0.1g), oil amount (5g), agitation rate (100 rpm), and adsorption temperature medium (30°C) using heavy crude oil. The developed adsorbent could be applied as a low-cost oleophilic adsorbent material for oil spill cleanup.

**Conflicts of Interest:-**

The authors have no conflict of interest to declare.

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