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RESEARCH ARTICLE

Preparation of Montmorillonite Modified with Long Hydrocarbon Tail-Bearing CTA$^+$ Ions-Polystyrene Nanocomposites (MMPS) and Investigation of Their Thermal and Mechanical Properties

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HIGHLIGHTS

- Polystyrene (PS)/organo-clay nanocomposites have been prepared via the melt intercalation by using two different organo-clays synthesized with the simple and the long-tailed CTA$^+$ ions.
- The glass transition temperature and thermal stability of the synthesized composites by using long-tailed CTA$^+$ ions are higher than those of the virgin polymer and other composites.
- The effective adhesion behavior between the organo-clay surface and the polymer chains led to the development of the exfoliated dispersion.

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ABSTRACT

Polymer nanocomposites have significantly taken lots of attention over the last decade. The reason for this attention is thanks to the substantial improvements in thermal and mechanical properties of these composites which are obtained even with a small addition of clay, compared to conventional composites. This study aims to prepare nanocomposites of organo-clay and polystyrene by melt intercalation method and to investigate their mechanical and thermal properties. Organo-clay was synthesized by solution intercalation method using aqueous dispersions of a long-chain hydrocarbon dispersed in aqueous medium by cetyltrimethylammonium bromide (CTAB) as a surfactant, with montmorillonite clay. The structural, thermal and mechanical characteristics of the nanocomposites were also investigated as a function of the content of the organo-clay. The organo-clay and the PCNs synthesized were characterized via XRD, HRTEM, FTIR and DSC techniques. The XRD patterns and HRTEM images show that in both cases, the organo-clay platelets have predominantly dispersed as tactoids (stacks of parallel clay platelets at about 100 nm separation) and also partially exfoliated into the polymer matrix. It was also found that the mechanical and thermal properties of the nanocomposites were significantly improved compared with pure polymer. The presence of the infrared bands of CTAB-montmorillonite in the PS/montmorillonite nanocomposite signifies that the clay tactoids were turned into fine particles and homogeneously dispersed in the PS matrix. DSC results also show that glass transition temperature and the thermal stability of the synthesized composites are higher than those of the pure polymer and other composites.

1. Introduction

Polymer nanocomposites have significantly taken lots of attention over the last decade. The reason for this attention is thanks to the substantial improvements in thermal, and mechanical features of these composites which are obtained even with a small addition of clay when compared to conventional composites [1]. As the clay platelets are exfoliated and dispersed randomly in the polymer matrix, the enhancements of the properties such as higher modulus, increased thermal stability and flame resistance, and more

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efficient gas barrier are maximized [2]. Interfacial interactions between polymer molecules and the ultrafine individual clay platelets causes such improvements [3,4]. The thermal stability of the organo-clay is an important issue, especially if the nanocomposite is prepared via melt compounding, because the polymer is exposed to high temperatures in melt processing. Surfactant molecules can decompose thermally or exude from the organo-clay galleries, under melt processing conditions. By products obtained during thermal decomposition can catalyze polymer decomposition and thus cause deterioration of polymer properties [5,6]. Furthermore, thermal decomposition/exudation of surfactant molecules could reduce the interlayer spacing and cause an increase in the hydrophilicity of the organo-clay. The overall result is the reduction of the probability of polymer diffusion into the clay galleries. Moreover, free surfactant molecules (usually with low molecular weight) could cause undesirable plasticization effects, the production of smoke during processing or odors in the products [7,8]. In these types of composites, polymers have been used as a matrix; and clay minerals act like reinforcement material. Different types of clay are available in nature which is able to be used in the preparation of a polymer-clay nanocomposite. Generally, montmorillonite (MMT)-type mineral found in bentonite clay is used for the preparation of a nanocomposite [9,10].

MMT is a 2:1 sheet-layered silicate, which contains two- dimensional layers with around 1 nm layer thickness and lateral dimension ranging from 300 Å to several microns [11–14]. A large-scale work has been done in the field of polymer-clay nanocomposites over the past ten years with microns [15–18]. Remarkable studies focused on synthesizing PS-clay nanocomposites have been reported, which includes the synthesis of both exfoliated and intercalated polystyrene-clay nanocomposites microns [19,20]. Polystyrene (PS) is a commodity polymer that is used in a number of commercial products microns [21]. It is a very appropriate and functional manufacturing material and, a strong plastic which can be easily injected, blow-molded, or extruded. Polystyrene-clay nanocomposites have been produced in different ways: direct melt intercalation [22], in-situ polymerization [23], and solution blending method [24].

In this study, it is aimed to prepare nanocomposites of organo-clay and polystyrene by melt intercalation method and to investigate their mechanical and thermal properties

2. Material and method

2.1. Materials

For the synthesis of composites and organo-clay were mainly used a layered clay, Bentonite, polystyrene (PS), and Cetyltrimethylammonium bromide (CTAB). Cationic surfactant, CTAB, was used for synthesizing organophilic clay and for preparing the aqueous dispersion of a long chain hydrocarbon agent which will be used to produce the long-tailed CTA$^+$ ions. The layered clay including the minerals, such as 26 percent of smectite, 20 percent of chlorite, 17 percent of illite, 14 percent of kaolinite, 11 percent of analcime, 7 percent of calcite, 3 percent of feldspar, and 3 percent of quartz was provided from Erzurum in Turkey. The chemical composition of the clay used is shown in Table 1.

Table 1. The chemical composition of the layered clay used

SiO_2	45.12
Al_2O_3	13.70
CaO	7.48
MgO	7.29
Fe_2O_3	5.63
K_2O	2.62
Na_2O	2.37
TiO_2	0.53
SO_3	0.44
P_2O_5	0.25

The methylene blue test was used for determining the cation exchange capacity (CEC) of the clay (ANSI/ASTM C837-76) [25]. Tables 2 and 3 also show the several features of the layered clay and long-chain hydrocarbon agent, respectively. Merck is the supplier for all chemicals used in the study.

Table 2. Some physical properties for the layered clay used

CEC (meg/100g)	48.9
d (g/cm^3)	2.61
OMC (%)	5.10
Liquid limit, w_L (%)	102.00
Plastic limit, w_P (%)	35.00
Plasticity index, I_p	67.00
a (m^2/g)	64.20

(CEC) Cation exchange capacity, (d) Specific gravity, (OMC) Organic matter content, (a) Specific surface area

Table 3. Some physical and chemical properties for the long-chain hydrocarbon agent used in this study

Density (15 °C), kg/m^3	990.7
Calorific value MJ/kg	42.74
Flash point °C	105.8
Water by distillation, wt %	0.1
C	83.4
H	11.9
N	0.8
S	1.5
Ash	0.03

2.2. Preparation of Nanocomposites

2.2.1. Preparation of long hydrocarbon tail-bearing CTA$^+$ ions and organo-clay modified with them

The layered clay, which was purified by washing method [26] was dried at a vacuum oven and sieved to obtain a 38-85 µm size fraction using sieves of ASTM. 12.5 g of the long chain hydrocarbon agent was dispersed in 25 L of CTAB aqueous solution (160 mg/L) and mechanically stirred at a rate of 50 min^{-1} for 30 min. Then, 50 g of raw clay was added to the prepared dispersion, and mixing was continued for 30 minutes at a speed of 200 min^{-1}. In the end, the filtered mixture was dried for 2 hours in a vacuum oven at 110 °C. The CTAB concentration and the adsorbed amount of the corresponding CTA$^+$ ions were determined, allowing the surface potential of the clay to approach 0 mV.

For this, we determined CTA^+ concentrations in the supernatant after the adsorption via a double-beam UV spectrophotometer at 375 nm along with 0.40 mL of 1,2-dichloroethane added per 1.0 ml of the supernatant and 0.02 mL of 0.1% picric acid in 0.002 M NaOH [27]. The concentrations in solution before and after adsorption were used to compute the amount of adsorbed CTAB. The measurements of the zeta potential of the modified clay were made by using Zeta meter 3+ instruments.

2.3. *Preparation of Polystyrene/Organo-Clay Nanocomposites*

2.3.1. Melt Intercalation Method

A given amount of the synthesized organo-clays via two different ions, using the simple CTA^+ and long hydrocarbon tail-bearing CTA^+ Ions, was evenly mixed with PS, and then the mixture was put into the single-screw extruder for additional melt blending at a temperature range of 190–210 °C and a screw speed of 145 rpm. In the end, the strands, which are obtained from the extruder, were mechanically pressed. The ratios of organo-clay of the nanocomposites were determined as 5.0, 10.0, 15.0 and 20.0 % wt., respectively.

2.4. *Characterization of Polystyrene (PS)/organo-clay nanocomposites*

A lot of techniques of characterization, such as XRD, HRTEM, FT-IR, and DSC were used to determine characteristics of the nanocomposites and to evaluate their thermal stabilities in this research. For XRD measurements of the organo-clay samples, Rigaku 2200D/max (Rigaku Corporation, Tokyo, Japan) powder diffractometer equipment with a CuKα radiation source was used a Perkin–Elmer Spectrum-One and KBr pelleting method for a range of 4000–400 cm^{-1} at a scanning rate of 2°/min was used for FTIR spectra for the composites. An average of 100 scans and a resolution of 1 cm^{-1} were chosen for all measurements. In order to forecast the framework rearrangement of nanocomposites, a JEOL 2100 high-resolution transmission electron microscope (HRTEM) LaB 6 flament operated at 200 kV was used for examining the specimens taken from the samples.

A differential scanning calorimeter (DSC7020) under nitrogen atmosphere was used to observe the curing behaviors of nanocomposites. The typical weight of the sample was about 10 mg and the scan rate was 200 °C/min.

For mechanical characterization of the composites, their Shore hardness which is a measurement method of the resistance a material has by penetrating a needle under a determined spring force was measured. It is defined with a number ranging from 0 to 100 on the scales A or D. If the number is high, this means the higher hardness. Flexible types are shown with the letter A and the letter D means rigid types. Measurements were carried out at room temperature. We used the Shore D hardness scale and the average of 10 hardness values was calculated.

3. Results and Discussion

3.1. *XRD Analysis*

XRD patterns for the composites, which were prepared using two different organo-clays: the simple and the long-tailed CTA^+ ions, have been shown in Fig. 1.

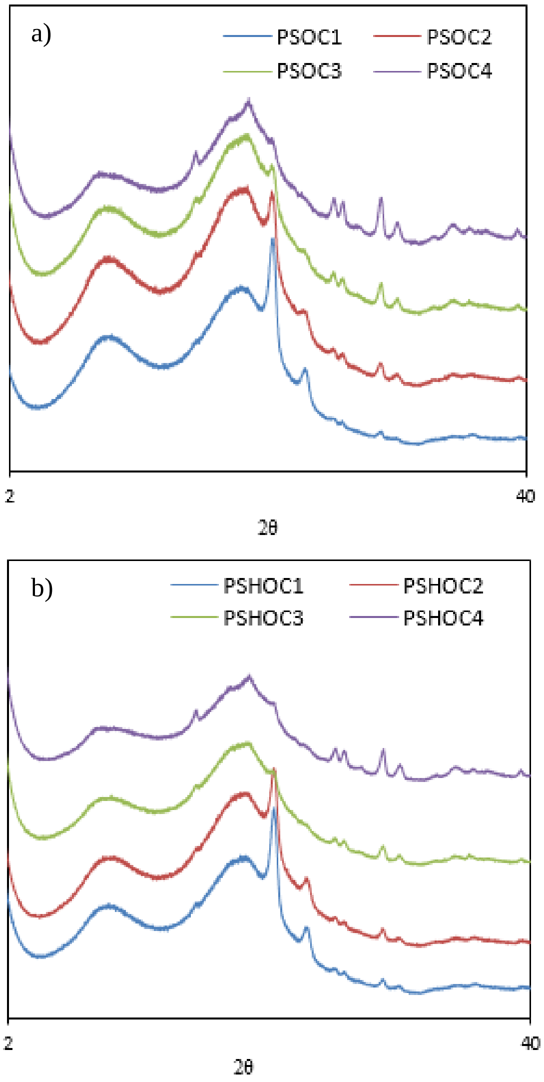

Figure 1.XRD patterns for the composites, which were prepared at the different ratios of the organo-clays, (a) (PSOC1:5.0%; PSOC2:10.0%; PSOC3:15.0% and PSOC4:20.0%, (b) PSHOC1:5.0%; PSHOC2:10.0%; PSHOC3:15.0% and PSHOC4:20.0%), using two different organo-clays, the simple and the long-tailed CTA^+ ions.

From these figures, it can be seen that in both cases, the organo-clay platelets have predominantly dispersed as tactoids (stacks of parallel clay platelets at about 100 nm separation) and also partially exfoliated into the polymer matrix. The fact that the clay platelets may be dispersed in the PS matrix, even at very high ratios, has been shown by this result. In contrast to the expected behavior, it is monitored that the exfoliation or dispersion degree of the organo-clay platelets increased with increasing clay content. The increase in the exfoliation degree took place because of facilitating diffusion of PS chains to interlayer regions along with increasing clay content facilitates, which can be concluded.

3.2. FTIR Analysis

FTIR spectra for the composites, which were prepared at the different ratios of the organo-clays, using two different organo-clays synthesized with the simple and the long-tailed CTA$^+$ ions, are given in Fig 2.

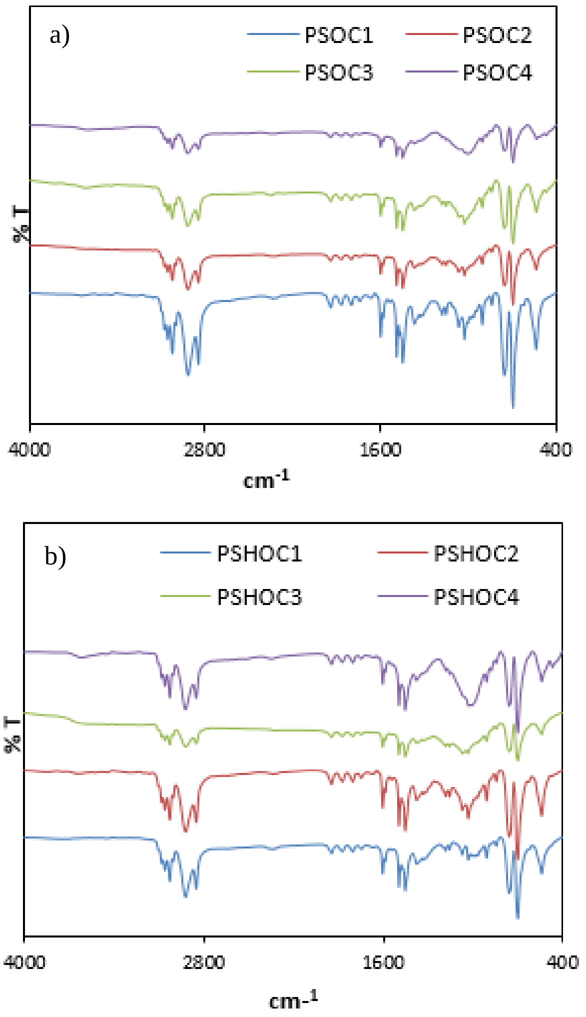

Figure 2. FTIR spectra for the composites, which were prepared at the different ratios of the organo-clays, (a) (PSOC1:5.0%; PSOC2:10.0%; PSOC3:15.0% and PSOC4:20.0%, (b) PSHOC1:5.0%; PSHOC2:10.0%; PSHOC3:15.0% and PSHOC4:20.0%), using two different organo-clays synthesized with the simple and the long-tailed CTA+ ions.

Figure 2 shows that in both cases, the peaks at 3600 cm^{-1} that are associated with OH stretching vibrations only appear at the high organo-clay ratios of 15.0 and 20.0%. Also, all composites exhibit the peaks associated with C–H asymmetric and symmetric stretching vibrations in the alkyl chains of the ammonium salt at 2924 and 2850 cm^{-1}, respectively and also the peaks at 1600 cm^{-1} and 466 cm^{-1} that are associated with the aromatic stretching vibration of C=C and Si-O bending vibrations, respectively [28]. The bands at 3062, 3033 cm^{-1} are assigned to C-H stretching of the aromatic ring in benzyl groups [29]. As can be seen from Fig. 2, in the case of the prepared composites by using the organo-clay modified with the long-tailed CTA$^+$ ions, the intensity of peaks at 2849 cm^{-1} that is associated with aliphatic stretching vibration decreases with the increasing clay content. These results clearly indicate.

3.3. DSC Analysis

Differential scanning calorimetric measurements have been extensively applied in the study of a variety of phenomena which occurs throughout the heating of organo-clays and polymer/clay nanocomposites or nanotubes, involving glass transition (Tg), crystallization, melting and, curing [30]. Thermal behaviors of the prepared PS/the organo-clay composites were evaluated via DSC analysis Fig. 3 shows the thermograms belonging to the prepared composites. As organo-clay platelets do not experience any transitions in the temperature range of the experiment, only thermal transitions polystyrene is observed. Firstly, samples are heated from room temperature to 190°C and this is performed for removing their thermal history. Then, they are heated to higher temperatures to analyze other irreversible thermal behaviors the phase conversion. There is a clear inflection in the heating path attributed to the glass transition temperature of the samples and, there is no exothermic peak in the higher temperatures, which indicates that the structure of polystyrene and its nanocomposites are chiefly amorphous and polystyrene chains are not crystallized [31]. DSC results also show that the glass transition temperature and thermal stability of the synthesized composites by using long-tailed CTA$^+$ ions are higher than those of the virgin polymer and other composites.

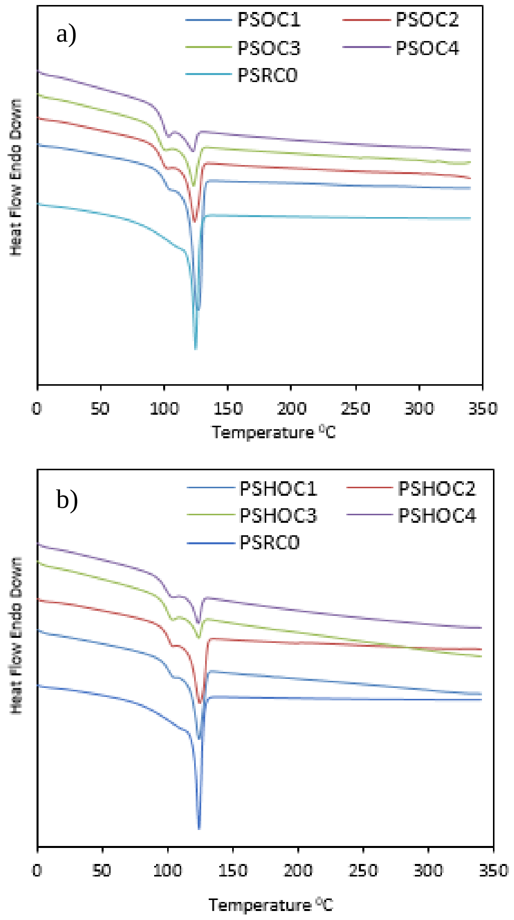

Figure 3. DSC thermograms for the composites, which were prepared at the different ratios of the organo-clays, (a) (PSOC1:5.0%; PSOC2:10.0%; PSOC3:15.0% and PSOC4:20.0%, (b) PSHOC1:5.0%; PSHOC2:10.0%; PSHOC3:15.0% and PSHOC4:20.0%), using two different organo-clays synthesized with the simple and the long-tailed CTA$^+$ ions.

3.4. HRTEM Analysis

HRTEM was used for the exfoliation or dispersion behaviors of the clay platelets in the nanocomposites, as Fig. 4 showed. The dark lines coincide with the silicate platelets in the polymer matrix [4]. Dispersion and delamination of individual silicate layers in the polymer matrix are available in the literature; however, as seen in the HRTEM micrographs, commonly intercalated stacks with a range of gallery distances are obtained [32]. As stated in the HRTEM image, some individual tactoids, and more stacks with a small number of platelets, can be monitored. Again, this from figures, it could be understood that random dispersion of partially exfoliated clay stacks, as well as predominantly, tactoidal dispersion of organo-clay platelets, in the polymer matrix has emerged.

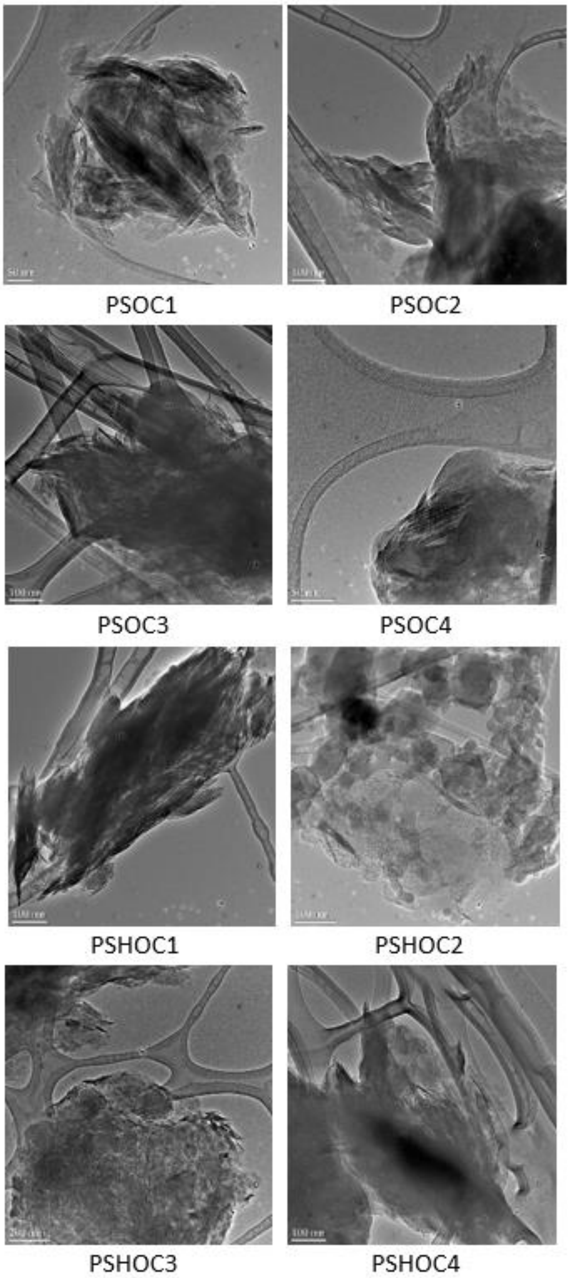
PSOC1 PSOC2
PSOC3 PSOC4
PSHOC1 PSHOC2
PSHOC3 PSHOC4

Figure 4. HRTEM images for the composites, which were prepared at the different ratios of the organo-clays, (PSOC1:5.0%; PSOC2:10.0%; PSOC3:15.0% and PSOC4:20.0%, and PSHOC1:5.0%; PSHOC2:10.0%; PSHOC3:15.0% and PSHOC4:20.0%), using two different organo-clays synthesized with the simple and the long-tailed CTA$^+$ ions.

3.5. Hardness Measurements

Mechanical properties (Fig. 5) depend in great measure on the dispersion degree of clay plates [33] and the development of adhesion between clay surface and the polymer chains [34].

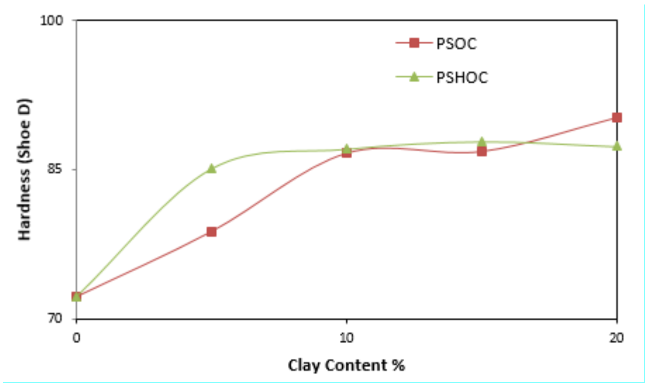

Figure 5. The variation of Hardness (Shore D) values belonging to the composites prepared by using two different organo-clays synthesized with the simple and the long-tailed CTA$^+$ ions, with clay content.

As seen from the figure, the hardness values of the composite, with increasing clay content, increased first and then remained constant. Extremely high hardness values indicate that the inclusion of organo-clay into the polymer matrix, the formation of a quite durable and relatively rigid structure provides.

3.6. Conclusion

The main findings of the study can be summarized as follows:

- The XRD patterns and HRTEM images show that in both cases, the organo-clay platelets have predominantly dispersed as tactoids (stacks of parallel clay platelets at about 100 nm separation) and also partially exfoliated into the polymer matrix. It was also found that the mechanical and thermal features of the nanocomposites were significantly improved compared with pure polymer.
- The presence of the infrared bands of CTAB-montmorillonite in the PS/montmorillonite nanocomposite signifies that the clay tactoids were turned into fine particles and homogeneously dispersed in the PS matrix
- DSC results also show that glass transition temperature and the thermal stability of the synthesized composites are higher than those of the pure polymer and other composites.
- Hardness measurement shows that the adhesion between the clay surface and the polymer chains was developed.

Compliance with Ethical Standards

There is no conflict of interest to disclose.

Conflict of Interest

The author(s) declares no known competing financial interests or personal relationships.

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REVIEW ARTICLE

A Comparative Evaluation on the Spontaneity at the Ambient Conditions of the Evaporation and Condensation in the Context of Temperature and Entropy Change of the Surroundings

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HIGHLIGHTS

> Evaporation is an endothermic process that can occur spontaneously in entropy-controlled atmospheric conditions at any temperature at the expense of the entropy decrease of the environment.

> Condensation is an exothermic process that can occur spontaneously, at the expense of a decrease in the entropy of the system, but with an increase in the entropy of the environment and with temperature control under atmospheric conditions.

> The spontaneity of condensation is dependent on the increase in entropy that can occur with the heat flow to the environment at low temperature to compensate for the decrease in the entropy of the system so that the total entropy can be positive.

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ABSTRACT

Evaporation and condensation are thermodynamic events that occur under the influence of temperature and pressure variables. Gases tend to condense at high pressure and low temperature. However, evaporation can occur at any temperature. This suggests that the temperature variable is more effective in condensation. For a system in equilibrium, the chemical potentials of the liquid and gas phases are equal to each other. The chemical potential, which encompasses the change in entropy of the particles and the effect caused by the change in enthalpy separately, corresponds to the molar Gibbs energy for a pure substance. In this context, the spontaneity of evaporation and condensation must be directly related to entropy change and temperature in order to fully conceptualize them. The aim of this study is to compare the spontaneities of evaporation and condensation at atmospheric pressure, considering the temperature and entropy change of the environment, and also to correct common misconceptions about these two processes.

1. Introduction

Condensation is defined into two main types, drop by drop and film condensation. Condensation occurs as drops on hydrophobic surfaces and as a film layer that can wet the surface on hydrophilic surfaces [1,2]. Evaporation is an endothermic process taking place by heat transfer from the environment into any liquid system [3]. There are three main mechanisms for surface evaporation by mass and energy transfer: convective and diffusive convection in two phases, temperature discontinuity at the interface, and chemical potential discontinuity at the interface. It is easier to explain evaporation via chemical potential, which is a function of enthalpy and entropy, as the simultaneous evaluation of these mechanisms makes theoretical and experimental analysis difficult [4]. The spontaneity of evaporation in the liquid systems at all temperatures and atmospheric pressure is due to a huge increase emerging in the entropy of the system during the phase change. A very higher translational freedom degree of the particles in the gas phase in the entropy context means that a much larger disorderliness could be created or much more micro-states could be generated. Moreover, the reduction of entropy in

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the surroundings is also decreased with increasing of the phase transition temperature. Therefore, an increasing tendency to evaporation with increasing temperature at atmospheric pressure and hence a higher vapor pressure of the liquid can be expected [5]. The evaporation entropy at temperature T is equal to ΔH_{vap} / T. Clapeyron equation is given in Eq 1.

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V} \qquad (1)$$

In Eq.1, $\Delta_{vap}V$ is the molar volume of vapor and $\Delta_{vap}H$ is the enthalpy of evaporation the greater the $\Delta_{vap}V$ in the Clapeyron equation, the greater the d_T / d_P ratio, indicating a greater dependence of the boiling temperature on the pressure.

Whereas, the condensation to the liquid of any vapor is the exothermic process and it can occur by a significant decrease in entropy of the system. The spontaneity of this process is controlled by the increase in entropy of the surroundings as well as the phase transition temperature. According to the second law of thermodynamics, the spontaneity of any process is assessed by considering the total entropy change including the system and the surroundings, and its value must be positive. In the light of these discussions, we aim to make a useful comparison that evaporation occurs spontaneously at every temperature, unlike condensation. On the other hand, according to the gas kinetics theory used in modeling evaporation and condensation, a phase transition occurs only under non-equilibrium conditions and therefore it is not possible to ensure the continuity of thermodynamic variables such as temperature and pressure [6,7]. The Gibbs free energy, which corresponds to the maximum amount of energy that can be obtained from a chemical reaction to do a useful job, is also the energy available to do useful work after any energy transfer occurs so that the total entropy change (ΔS_{system} + $\Delta S_{surroundings}$) is not negative. There are three restrictions in the application of phase equilibrium solutions: maintaining of matter equilibrium, the absence of a driving force from any phase to the next phase for equilibrium phase systems, and having the smallest possible Gibbs energy of the system in equilibrium phase systems [8].

Free Gibbs energy is used to determine whether a process occurs spontaneously under constant pressure and temperature conditions, and it is not necessary to know the entropy change of the environment directly in the case of use of this function, because as can be seen from Eq. 2, all quantities in the equation are related to the system.

$$\Delta G = \Delta H_{(system)} - T\Delta S_{(system)} \qquad (2)$$

From this equation, it is understood that if G <0, the change will occur spontaneously under certain conditions. Since the entropy change of the system will decrease in the condensation, the compensation of the decrease with the entropy change of the environment will be directly related to the temperature. On the other hand, again from Eq. 2, it can be clearly seen that temperature is a much more critical variable in the condensation process than evaporation since $\Delta S_{(system)} > 0$ in any case for evaporation.

The spontaneity of condensation is dependent on the transferred temperature of heat as well as the size of the surrounding entropy change. To increase the entropy, change in the environment, the only way is to use the enthalpy changes of condensation to produce a larger entropy change. The solution to this requirement can be found in Eq.3 based on the second law.

$$\Delta S = \frac{q_{rev}}{T} \qquad (3)$$

In Eq.3, q_{rew} and T, respectively reversible heat, and corresponds to the temperature at which heat is transferred. As can be seen from this equation, a significant increase in the entropy may be achieved by the higher enthalpy change or decreasing the temperature at which the heat is transferred. In the exothermic process, the surroundings in the context of spontaneity are responsible for the increase of entropy. It can be concluded that if a process takes place with the entropy decrease, its spontaneity primarily depended on temperature. Consequently, it can be said that in the condensation process, the temperature is a much more crucial variable, compared to the evaporation. On the other hand, it has been suggested that learners have many misconceptions about the concept of condensation and it may be more effective to explain the macro-micro relationship between particles in condensation to avoid these misconceptions [9]. A study conducted with second-year chemical engineering students revealed that students have a misconception that a temperature gradient is required for evaporation and condensation to occur [10]. However, it has also been reported that students who do not realize that condensation occurs in a dynamic equilibrium process and that evaporation and condensation are reversible claims that condensation only occurs on low temperature surfaces [11]. Undoubtedly, this argument is valid for the closed system and equilibrium situation, and it cannot be generalized that if there is evaporation at all temperatures, there will be condensation. A study conducted with university students, it was determined that when it was questioned that evaporation occurs at every temperature, students have the misconception that water should be heated to evaporate and that water placed in a cold environment cannot evaporate because water gives energy to the environment [12]. In another study conducted with 6th, 8th and 11th grade students, misconceptions about the condensation of water vapor were examined and it was concluded that most of the students had difficulty understanding this issue and had misconceptions about condensation [13].

Concluding Comment

As a result, the following concise results can be presented about the nature of two easily observable critical processes such as evaporation and condensation and their spontaneity under atmospheric conditions:

Evaporation is an endothermic process, and although entropy decreases in the environment, it can occur spontaneously at any temperature under atmospheric conditions, since it is an entropy-controlled process. The decrease in the entropy of the environment is compensated by the enormous disorder or entropy increase that occurs in the system due to the gas transition and so the total entropy is positive.

The endothermicity of the evaporation should also be conceived as heat flow from the environment as a result of the relative decrease in the temperature of the system itself parallel to the transition to the highly disordered gas phase, otherwise, the heat flow from the environment to the system may create a paradoxical situation, especially at low temperatures.

The fact that heat can only flow spontaneously from the high-temperature zone to the low-temperature zone is a consequence of the second law of thermodynamics.

Condensation is an exothermic process that can occur spontaneously, at the expense of a decrease in the entropy of the system, but with an increase in the entropy of the environment and with temperature control under atmospheric conditions. The spontaneity of the process is dependent on the increase in entropy that can occur with the heat flow to the environment at low temperature to compensate for the decrease in the entropy of the system so that the total entropy can be positive.

Experience and observations show that learners generally think that "-since evaporation happens spontaneously at every temperature, so condensation must occur spontaneously at every temperature”. The emergence of this misconception is the result of overgeneralization in relation to the fact that in equilibrium, the system's tendencies and velocities of evaporation and condensation will be equal so that the chemical potentials are equal.

The correction of this misconception is undoubtedly dependent on the clarification of the realization conditions of both processes by the correct use of thermodynamic principles and related functions.

It can be argued that the approach developed in this study can be useful as a complementary or auxiliary tool or conceptual change material in the teaching of thermodynamic concepts such as enthalpy, entropy, chemical potential heat, and the concept of spontaneity, as well as providing solutions to this specific conceptual learning problem.

Compliance with Ethical Standards

There is no conflict of interest to disclose.

Conflict of Interest

The author(s) declares no known competing financial interests or personal relationships.

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REVIEW ARTICLE

Using of Nanotechnology for Photovoltaic Solar Energy Systems

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HIGHLIGHTS

- > Nanomaterials used in photovoltaic cells are discussed.
- > Increasing the efficiency of photovoltaic cells has a very important effect on reducing carbon emissions.
- > The development and use of photovoltaic cells producing electrical energy from the sun and the effect of nanomaterials were investigated.

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ABSTRACT

It is very important to obtain energy from renewable energy sources at this time when energy consumption is increasing rapidly and environmental pollution has reached significant dimensions. Solar energy is one of these sources. Recently used photovoltaic systems are very important in the supply of electrical energy. The low efficiency of photovoltaic panels used to generate electricity is one of the most important disadvantages of these systems. The efficiency of photovoltaic cells is greatly affected by both the materials used to convert the incoming solar energy into electrical energy and the surface pollution. The use of nanomaterials has recently increased considerably to increase efficiency. Studies are carried out on self-cleaning materials in order to reduce the reflection of incoming rays and to ensure that the energy is selectively absorbed by the surface and prevent surface pollution. Nanotechnology makes very important contributions to the design and production of thin-film PV cells. PV cells developed using nanomaterials will continue to reduce the cost of commercial solar cells using cheaper raw materials. Nanomaterials have some desirable properties such as high catalytic activity, better stability in aqueous media, relatively easier preparation techniques, and material economy. In this study, information is given about nanomaterials used in photovoltaic cells and efficiency-enhancing studies in PV technology.

1. Introduction

The rapid increase in the world population and the rapid development of the industry are increasing the need for energy. Fossil fuels are generally used to meet the world's energy needs. Consumption of fossil fuels both causes the depletion of these limited resources and increases environmental pollution due to harmful gas emissions to the environment. Fossil fuels cause an increase in the temperature of the earth's atmosphere and climate change due to greenhouse gas emissions.

Due to the rapid increase in the world's atmospheric temperature, the Paris Agreement [1], which was accepted with the approval of 195 countries at the United Nations Framework Convention on Climate Change Conference of Parties in December 2015, is a historical turning point in terms of fighting against climate change on a global scale. The long-term temperature target of the Paris Agreement, to which our country is also a party, is to limit the global average temperature increase to 2 °C above pre-industrial levels and even to strive for 1.5 °C. It is assumed that limiting the temperature increase to 1.5 °C will significantly reduce the risks and impacts of climate change. To achieve this, it is aimed to reduce emissions as soon as possible and to balance greenhouse gases. This agreement guides the whole world in the transition to renewable energy on a global scale [2]. Fossil fuel consumption causes countries to be dependent on foreign sources. In addition, the rapid depletion of fossil fuels, the increase in harmful emissions

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in the atmosphere, the introduction of a low carbon economy by developed countries have started to cause all countries in the world to limit fossil fuel consumption. Renewable energy sources, whose investment costs are significantly reduced in order to limit fossil fuel consumption, are the most important alternative energy sources [3].

Our country has a high solar energy potential due to its geographical location. According to the Turkey Solar Energy Potential Atlas (GEPA) [4], the average annual total sunshine duration is 2741.07 hours, and the average annual total radiation value is 1527.46 kWh/m^2. As of the end of 2020, solar energy-based electricity installed power is 6,667 MW, and its share in total electricity generation is 3.66% [5]. Moreover, as of October 29, 2021, 34% of electricity production in Turkey is obtained from renewable energy. The share of solar energy in this rate is 8% [6].

Photovoltaic panels are the most used product in the conversion of solar energy into electricity. These panels work on a semiconductor basis. The structure of the materials that make up these panels affects the yields. Kalyon PV, one of the PV panel manufacturers in our country, predicts the efficiency rate of the panels, which are processed into advanced technology by processing the silicon mine, as 21.8% [7].

The low efficiency of photovoltaic panels used to generate electricity from the sun in our country and in the world, which has very important values in terms of sunshine duration, causes an increase in the unit cost of energy and a long recovery period for the investments made. For this reason, various studies are carried out in the world to increase the efficiency of PV panels. One of the most studied subjects for this purpose is nanomaterials. In order to understand the contribution of nanomaterials to PV cells, it is necessary to have knowledge about how photovoltaic cells work.

2. Material and method

2.1. Photovoltaic Cells

Photovoltaic cells are structures that convert incoming sunlight into electrical energy, and the development of these cells from the first production to the present can be classified into 3 categories.

First-generation PV cells are divided into three categories as monocrystalline, polycrystalline silicon and Gallium Arsenic cells.

Second-generation PV cells focused on thin- film technologies to reduce the high costs associated with the first generation. Amorphous silicon contains cadmium telluride/cadmium sulfide cells [8].

Third-generation PV cells are dye-sensitive solar cells. By changing the size of nanoparticles in PV cells, the energy band gap of various layers can be made to the desired value. Integrating a high-quality film of silicon nanoparticles into a silicon solar cell increases the conversion efficiency by 50-60% in the ultraviolet range of the spectrum. This results in less material usage and lowers costs. The essential components of a pigmented solar cell are a photoelectrode consisting of a pigment-sensitive film of titanium dioxide (TiO_2). In these cells, when photons come to Dye Sensitive Solar Cells, they are absorbed by the pigment and produce electrons and holes [9]. Electrons in the dye are passed to nanoparticles of TiO_2. Here, TiO_2 nanoparticles serve as carriers. Examples of 3rd generation photovoltaic cells are given in Table 1.

Table 1. Third-generation PV cells are paint-sensitive solar cells.

Technology	Efficiency	Benefits	Limitations
DSSC (Dye-sensitized solar cell)	5-20%	Low cost. Operate in low light and wider angle, work at lower internal temperature condition, robustness and long life	Temperature stability issues, toxic and volatile compound
QDS (quantum dot cell)	11-17%	Low production cost, low power consumption	Highly toxic in nature. Degradation
OPSC (Organic and polymeric solar cell)	9-11%	Low processing cost, light weight, flexible, thermally stable	Low efficiency
PVSC (Perovskite cell)	21%	Cheap and simple construction, light weight, flexible, high efficiency, low production cost	Unstable
MJ (Multi junction cell)	36%	High efficiency	Complex, costly

Last generation PV cells are flexible and cost-effective. These cells consist of organic-based nanomaterials such as carbon nanotubes, graphene, and derivatives of metallic nanoparticles and new inorganic nanostructures such as metal oxides. The carbon used here, its nanoparticles, and allotrope forms such as fullerenes, carbon nanotubes, and graphene have been used as energy materials in many different fields due to their extraordinary mechanical, chemical, electrical and thermal properties. In addition, its light-weight, flexibility, printable inks, low temperature, and ambient pressure manufacturing facilities provide a significant reduction in production costs. Organic solar cell devices based on carbon nanostructures and electrochemical capacitors, also called super capacitors, may enable the production of devices that may be more efficient and cheaper than conventional batteries in the near future [10–12].

2.2. Nanotechnology used in PV cells

Nanoparticles are a modern engineering material consisting of solid particles with sizes typically ranging from 1 to 100 nm. These materials have advanced thermo-physical properties such as viscosity, thermal conductivity, convective heat transfer coefficients, and optical properties. Nanofluids, on the other hand, are the process of obtaining a new heat transfer fluid by adding nanoparticles to heat transfer fluids. Nanofluids are widely used in various applications as a coolant with their improved thermal properties. Each nanoparticle type has unique thermo-physical properties represented by thermal conductivity and thermal diffusivity in addition to viscosity. The thermal values of the most commonly used nanofluids are shown in Table 2 [13]. In Figure 1, the types of nanoparticles are seen [14].

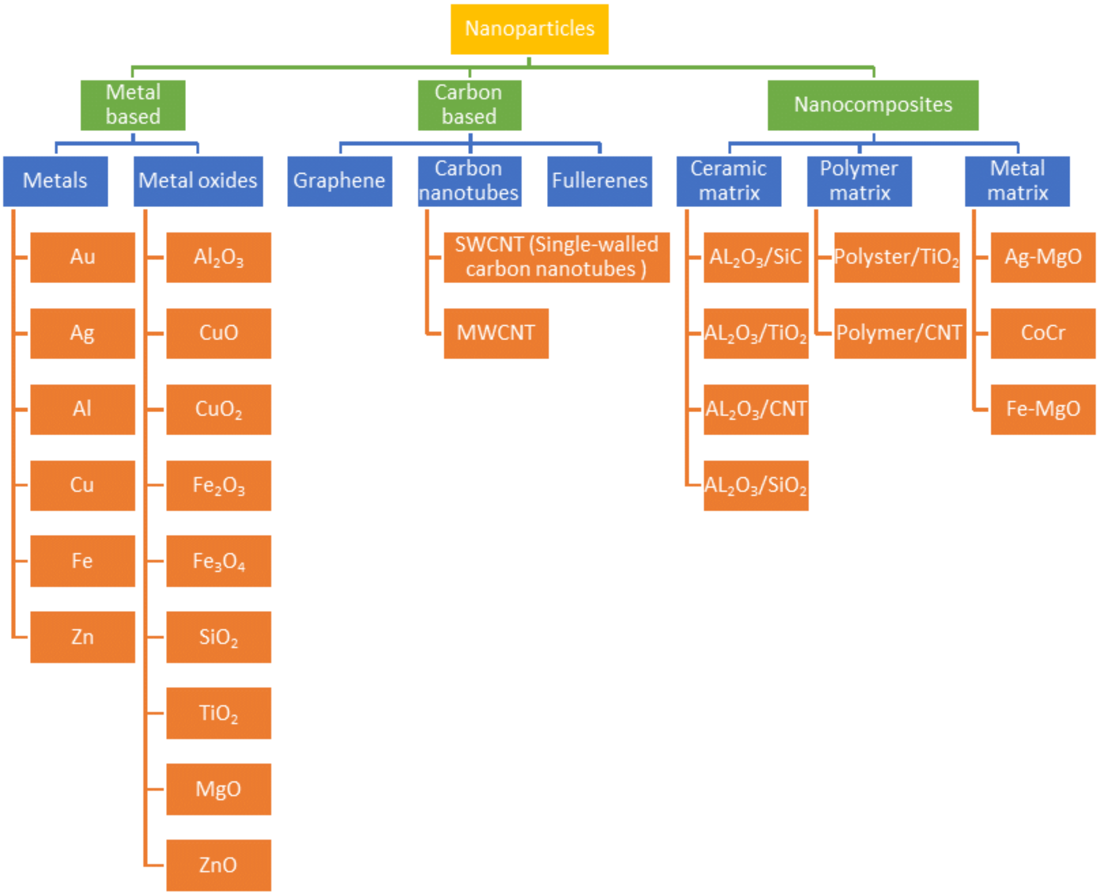

Figure 1. Types of nanoparticles

The use of nanotechnology in PV cells is very diverse. Firstly, nanoparticles are added to solar cells as a superficial layer and used to increase their efficiency and to convert incoming sunlight into electrical energy without being reflected back. Secondly, PV cells are the process of cooling these cells as a solution to the decrease in their efficiency with the increase in air temperature. Many studies are carried out to cool PV cells using nano liquids. The third is the coatings made to prevent the accumulation of dust on the solar panels by using nanoparticles, which causes a significant decrease in inefficiency.

Table 2. Thermal values of commonly used nanoparticles

Solids	$k_{c(p)}$(W/mK)	Liquids	$k_{c(f)}$(W/mK)
Silver	427	Water	0.613
Copper	395	Ethylene glycol	0.253
Aluminum	237	Engine oil	0.145
Carbon nanotubes	3200-3500	Alcohol	0.115
Brass	120	Glycerol	0.285
Nickel	91		
Alumina	39		

2.3. Use of Nanoparticles in PV Cells

Conventional solar cells have two main disadvantages. First, low efficiency is almost inevitable in silicon cells. This is because incoming photons of light must have the right energy, called band-gap energy, to hit an electron. If the photon has less energy than the band-gap energy, then it will pass. If it has more energy than the band-gap, that extra energy will be wasted as heat. These two effects alone constitute the loss of approximately 70% of the radiation energy incident in the cell. The second is the high production cost.

Because nanoparticles are so small, most of the nanoparticle atoms are usually on the surface. This means that the surface interactions nanoparticle property dominates the material behavior and therefore they often have different properties and properties from larger pieces of the same material. Nanostructured layers in thin-film solar cells have three important advantages. First, due to multiple reflections, the effective optical path for absorption is much larger than the actual film thickness. Second, the electrons and holes produced by the light have to travel a much shorter path, thereby greatly reducing recombination losses. As a result, the absorber layer thickness in nanostructured solar cells can be as thin as 150 nm instead of a few micrometers in conventional thin-film solar cells. Third, by varying the size of the nanoparticles, the energy band-gap of the various layers can be made to the desired design value. Being able to use thin films requires much less material and reduces costs. Most such cells use amorphous silicon, which does not have a crystalline structure and consequently has a much lower efficiency (8%), but is much cheaper to manufacture [15].

In conventional solar cells, ultraviolet light is filtered or absorbed by silicon and converted into heat, not electricity. Integrating silicon nanoparticles in 1-nanometer size directly into silicon solar cells increased power performance by 60% in the ultraviolet range of the spectrum. Another potential feature of solar cells is that the nanorods can be 'tuned' to absorb various wavelengths of light. This can significantly improve the efficiency of the solar cell, as more of the incident light can be used on a film made of titanium dioxide nanoparticles, and double-walled carbon nanotubes can be used, doubling the efficiency of converting ultraviolet light into electrons compared to the performance of nanoparticles alone.

Another starting point for increasing the conversion efficiency of solar cells is the use of semiconductor quantum dots (QD). Thanks to the quantum dots, the band gaps can be tuned specifically to convert the longer wave light and thus increase the efficiency of the solar cells. These cells, called quantum dot solar cells, are used in combinations of other materials such as Si/Ge or Si/Be Te/Se.

2.4. Nanofluid Applications in PV Cells

Conventional cooling systems are not sufficient to increase the efficiency of the PV system. Various studies have been carried out with different nanofluids in order to increase the efficiency more and to increase the amount of electrical energy to be obtained. The good heat transfer properties of nanofluids and the use of hybrid systems used for this purpose have become quite common. In the hybrid system, both electricity is produced and the heat obtained is used according to the need for hot water. These hybrid systems not only generate a significant amount of electrical energy but also provide thermal energy. The thermal energy produced by these systems can meet the needs of the building and limit the fuel consumption in the heating system. Thus, nanofluid-based PV thermal systems can significantly reduce emissions of various greenhouse gases such as CO_2, SO_2, CO, NO_x kg/m^2 and particulate matter. For example, the photovoltaic/thermal nanofluid-based collector system is shown in Figure 2 [16].

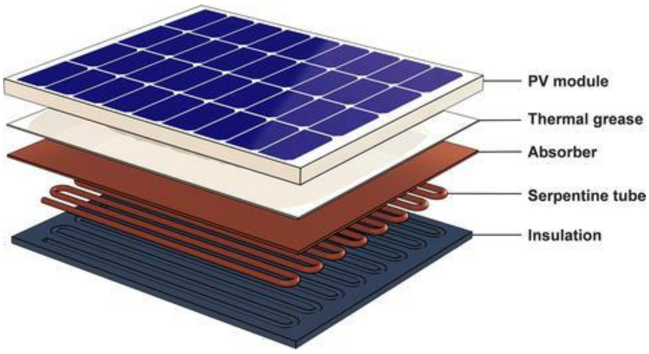

Figure 2. Photovoltaic/Thermal Nanofluid-Based Collector Systems

Many different designs are made in the hybrid system. In general, it is to increase efficiency thanks to the cooling process made with pipes placed under the PV panels. Various studies are carried out by changing the shape, diameter, material, type, and amount of nanofluid passing through the cooling pipes. Different design shapes and purposes are shown in Figure 3. In some studies, studies have been carried out to allow more sunlight to pass through the nanofluid cell to the PV cell.

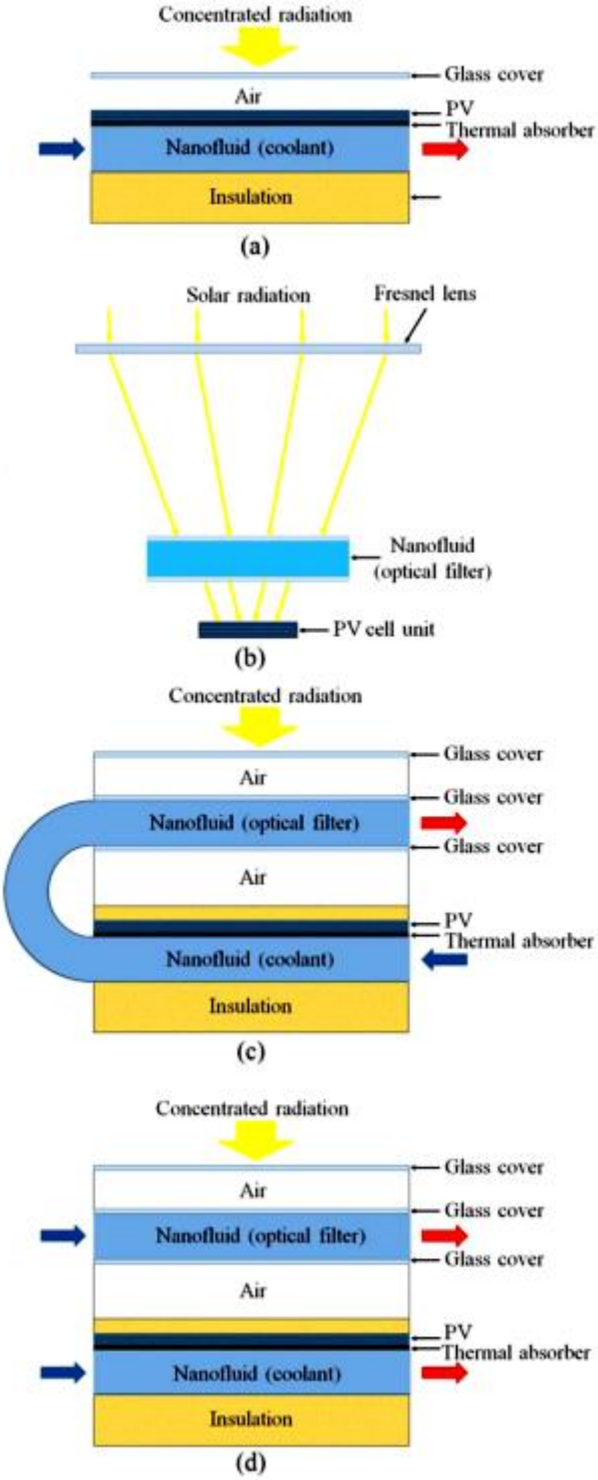

Figure 3. Schematic diagram [17], a) cooling the PV cell with nanofluid [18], b) using nanofluid as an optical filter [19], c) using nanofluid as both optical filter and coolant [20], d) using nanofluid as both optical filter and coolant with separate channels [21].

2.5. Self-cleaning and anti-reflective nano-coatings

One of the most important factors affecting the efficiency of PV cells is rainy weather and sedimentary deposits on the surface of solar cells [22]. Advances in technology and the creation of nanometer layers with self-cleaning and anti-reflective properties are crucial. Titanium oxide nanoparticles, which can trap organic compounds such as hydrocarbons by blocking the ultraviolet wavelengths of sunlight, can keep solar cell surfaces clean by reducing fossil fuel emissions and preventing contamination. In this way, sunlight enters the cell surface, the reaction becomes more effective, and the efficiency increases. Using nanotechnology, the hydrophilic and hydrophobic properties of the glass surface can be altered so that the water does not appear to moisten the surface and the sedimentary effects of the salts in the water remain on the glass surface [23]. Since the amount of electron-hole output in semiconductor cells is proportional to the strength of sunlight, the elimination of the reflective part of sunlight by the protective glass of the solar cell surface and its transition to the semiconductor surface is one of the ways to increase. In this direction, anti-reflective nano-coatings consisting of nanostructures made of silica nanometer pores made of Polydimethylsiloxane (PDMS) or titanium oxide nanoparticles are important.

3. Results and Discussion

The low efficiency of the photovoltaic panels used to generate electricity from the sun in our country and in the world, which has very important values in terms of sunshine duration, causes the energy unit cost to increase and the recovery period of the investments made to belong.

Investigations of PV/T systems with nanofluids are predominantly experimental. Most investigations have used empirical models of thermal conductivity and viscosity that only agree with their own experimental data. Future investigations should extend the developed models to greater data sets and/or develop theoretical models that explain the observed enhancements.

4. Conclusion

Studies have shown that nanomaterials will both increase material efficiency and decrease production costs. For this reason, studies should be continued and increased in order to produce different environmentally friendly, inexpensive, and commercially usable materials and systems.

Compliance with Ethical Standards

There is no conflict of interest to disclose.

Conflict of Interest

The author(s) declares no known competing financial interests or personal relationships.

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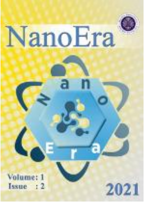

RESEARCH ARTICLE

Synthesis of Polymer-Coated Magnetic Nanoparticles to the Surface of Activated Carbon and Kinetic Studies

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HIGHLIGHTS

> The effect of polymer-coated magnetic nanomaterials.
> Recycling of adsorbents after use and their usability in wastewater treatment.
> Gaining magnetic properties of FeO, Fe_2O_3 or Fe_3O_4 and metal oxides to the activated carbon surface with polymeric materials.

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ABSTRACT

In the presented study, it was investigated the synthesis of activated carbon (AC), magnetic activated carbon (MagAC), styrene-butadiene styrene magnetic activated carbon (SBS/MagAC) and poly charbonat magnetic activated carbon (PC/MagAC) samples. Thermogravimetric Analyzer (TGA), Differential Scanning Calorimeter (DSC), Scanning Electron Microscope (SEM), X-Ray Diffractometer (XRD), Fourier Transform Infrared Spectrophotometer (FTIR analysis), Brunauer-Emmett-Teller **(**BET) analysis were used for characterization studies. Adsorbent type, temperature, solid-liquid ratio, initial concentrations and solution pH were selected as parameters in experiments. The experimental study was carried out at low pH yields were higher and performance was 98-99% in AC and Mag/AC samples. It was found that the polymer coated magnetic materials did not perform very well at high pH. It was also seen that MagAC and SBS/MagAC are more effective than AC and PC/MagAC to remove phenol.

1. Introduction

Phenol (C_6H_5OH), an aromatic compound, is one of the 126 most toxic chemicals and is very dangerous, harmful, and causes excretion of dark urine, impaired vision, diarrhea and sour mouth. Marine life additionally tends to be disturbed by the chemical phenol due to its toxic nature.

The effective removal of these pollutants from wastewater is a problem of great importance and interest. Great research efforts on adsorption processes and adsorbent materials for separating organic pollutants from waste streams have been developed. Phenol is obtained from coal tar or benzene. It is a common pollutant in wastewater as a result of its widespread use in different industrial fields (pharmaceutical, steel, textile industry, plastics, dyestuff, paper, epoxy, phenolic resin, pesticide, insecticide, petroleum refinery, coal gasification, olive water, etc.) [1,2].

The simple and effective way can be used to remove organic pollutant and also recycling, recover and reuse adsorbent materials. When the literature studies are examined, it is seen that the adsorption method is mostly

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preferred and used for phenol removal. However, it is stated that new methods, especially by using activated carbon-based materials, can provide different results and selectivity for phenol with nano-based materials. The application of magnetic particle technology to solve environmental problems has received considerable attention. Magnetic particles can be used to adsorb contaminants from aqueous or gaseous effluents and after adsorption, can be separated from the medium by a simple magnetic process. Examples of this technology are the use of magnetite particles to accelerate the coagula of sewage [3,4]. The samples of activated carbon (AC) coated with magnetically iron-containing iron components (FeO. γ-Fe_2O_3 or Fe_3O_4) have recently been used to remove toxic organic [5,6]. Cr(VI) [7], different heavy metals [8], antibiotics [9] and As (V) [10] to purify effluent streams using adsorption method. These new adsorbent materials can be used for different purposes after being coated with certain polymeric materials. In the literature, it has been stated that the chemical bond with mercury on the activated carbon surface may be the result of Hg-Cl and Hg-S interactions [11]. In the presented study, especially the phenol with toxic pollution was tried to be removed, taking into account that magnetic nanomaterials can be easily removed from the aqueous environment. The reason for using activated carbon material is better loading of the magnetic material, the height of the surface area and then the easy feasibility of recovering the adsorbent in the magnetic field. In addition, their characterization and other structural properties were investigated.

2. Materials and method

Commercially available Activated carbon samples were used in all experimental studies. These examples were provided as "Sigma-Aldrich 242276". The Iron salts were commercially available (ZAG, ZK.100380.1000) and were prepared according to literature studies [12]. In the presented experimental study, three different adsorbents were prepared and used. $FeCl_3$ (1.08 g) and $FeCl_2$ (2.40 g) and 150 ml distilled water were added as the first adsorbent. For the second sample, SBS (1 g) + THF/DMF 50ml (30:20) samples were prepared. The third sample was PC (1 g) and THF/DMF 50ml (30:20) samples. Then, after these samples were stirred at 60-65°C for 2 hours, $FeCl_3$ (1.08 g) and $FeCl_2$ (2.40 g) were added to them. Then, 5 g of NaOH was added and mixed for 1 hour and left overnight. It was washed several times with distilled water and then filtered and dried in an oven to constant weight. These examples are called Mag/AC, SBS/MagAC, and PC/MagC.

2.1. Characterization of nanoparticle material

Perkin-Elmer Lambda 35 UV-Vis Spectrophotometer for UV-Vis absorbance, Perkin-Elmer Pyris 1 Thermogravimetric Analyzer for TGA analysis, Perkin-Elmer Diamond Differential Scanning Calorimeter for DSC analysis, Scanning Electron Microscope for SEM images (JSM 7600). Rigaku-Smart-Lab-X-Ray Diffractometer for XRD analysis, Thermo Scientific. Nicolet Is10. Fourier Transform Infrared Spectrophotometer for FTIR analysis and Micromeritics TriStar II PLUS for Brunauer-Emmett-Teller **(**BET) analysis were used for characterization studies.

3. Results and Discussion

Characterization of materials synthesized by using different polymer materials constitutes an important part of the study. Considering this situation, the samples of all three nanomaterials (AC, MagAC, SBS/MagAC and PC/MagAC) Structural and characterization were investigated by various analytical techniques such as FTIR, SEM, EDS, XRD, TGA, DSC and BET. The obtained data were tried to be evaluated by considering similar studies. the results are given below in order.

3.1. SEM/EDS images and BET Analysis

SEM and EDS results have an important place in order to see closely the surface topography, morphological structures of the prepared materials and the general states of the atoms or molecules in the structure formed when coated with polymeric material. These data are given in Figure 1 below.

SEM images of activated carbon samples show a porous structure with a clear porosity. The porous structure here is evident with many cavities, recessed and protruding forms on the outer surface. On the other hand, in MagAC and PC/MagAC, it is observed that there may be more dull and clear aggregation. This suggests that the magnetic material adheres to the porous surfaces and the pores of the adsorbent. SEM images of the SBS/MagAC material are shown in figure 1c. Here, it is seen that the polymeric material leads to more aggregation. More agglomeration, especially in the surface topography, can be associated with significant diffusion of polymers into the pores of the activated carbon. When the EDS analyzes of the adsorbent materials are examined, too much Ca, Fe, C and O elements are observed here, not only on the AC surface. A very limited situation is seen on the AC surface. it is seen that it contains small amounts of Na and Mg elements. In addition, trace amounts of Cu and Si elements are observed in SBS/MagAC material. In the BET surface area measurement, the surface areas of AC and synthesized materials are generally as AC (687.751 m^2g^{-1}) > MagAC (636.86 m^2g^{-1}) > PC/MagAC (304.56 m^2g^{-1}) > SBS/MagAC (251.31m^2g^{-1}) distribution.

3.2. XRD Images

Figure 2 shows the XRD pattern of the polymeric materials with activated carbon support.

As seen from the Figure 2, the 2-theta degree of no treated activated carbon with sharply 20.82°, 26.42°, 29.37°, 42.82° and 62.26° peaks are seen in the sample confirming the homogeneous and regular crystal structure. The peaks at 26.42° and 42.82° presented the (002) and (100) planes respectively. Also, the 26.42° diffraction peak displays the growing of AC on the direction of the (002) surface [13]. In addition, the XRD pattern of other samples were examined, the peak intensity and some crystallite changings were observed suggesting the transforming of crystal structure to amorphous timely. In a word, the FWHM values were wider than that of other AC support samples. It can be concluded that particle size and amorphous phenomenon decrease [14].

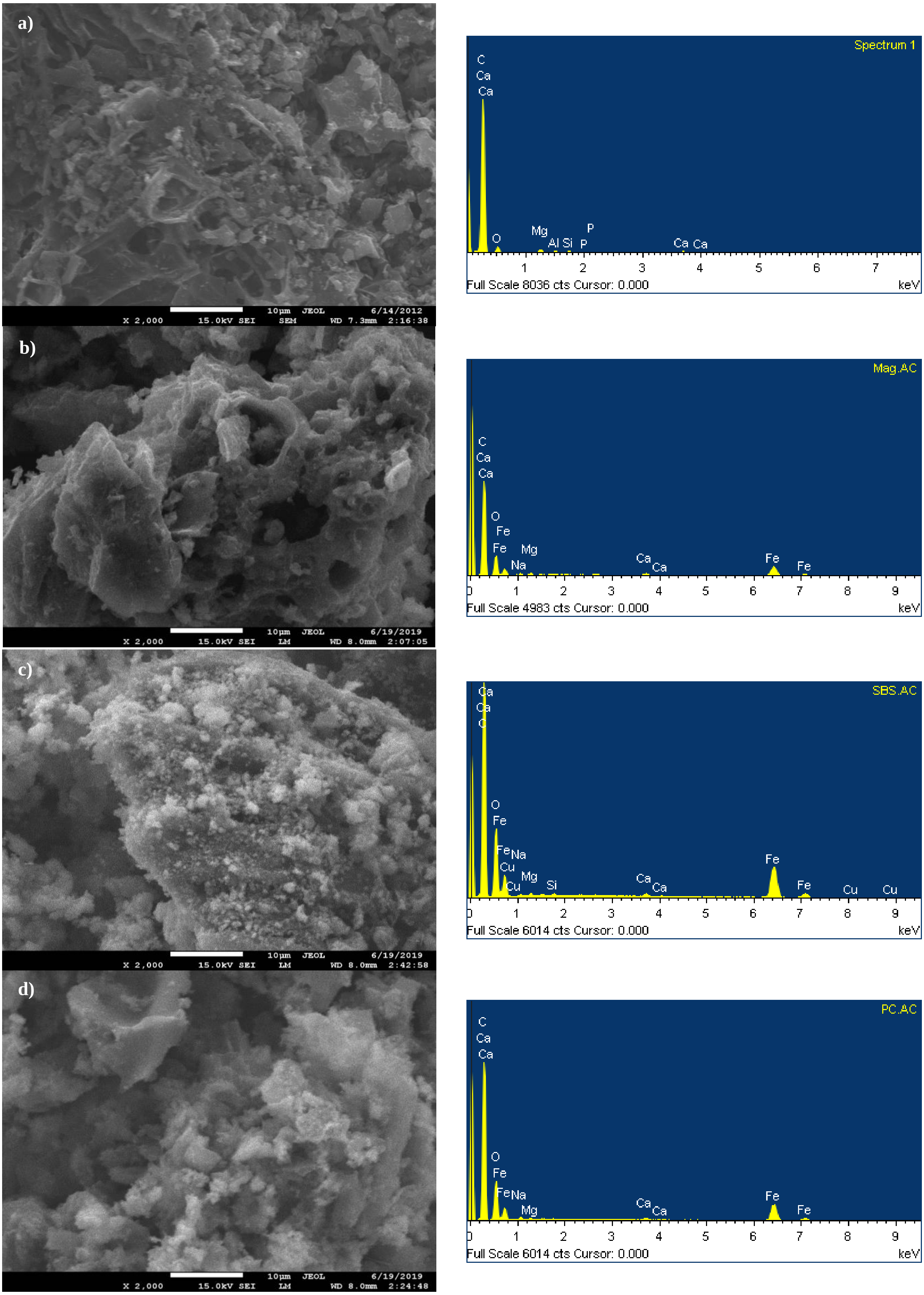

Fig. 1. SEM and EDS images of adsorbent materials a) AC, b) MagAC, c) SBS/MagAC, d) PC/MagAC

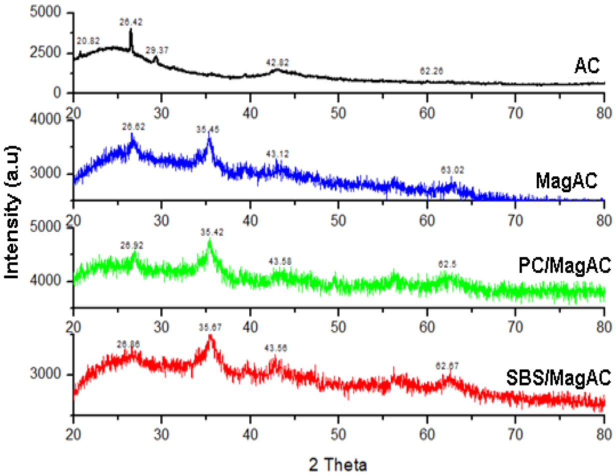

Fig. 2. XRD images of different adsorbent materials

In MagAC, the diffraction peak at 35.45° with iron components was observed with together AC diffraction peaks. These results strongly show that iron components during the synthase with treatment of strong base participated of all iron ions. The crystallite structure of PC and SBS was not changing on iron based components. As seen in SBS/MagAC diffraction peaks, FWHM values increased with decreasing of peak intensity indicating an effective size distribution of SBS on AC support. All XRD pattern presented that AC support polymeric materials were synthesized efficiently and effective dispersion of magnetic/polymeric components on AC support.

3.3. TGA analysis

TGA analysis of the samples prepared using activated carbon-based and different polymeric materials and the relationship between temperature and mass loss was investigated. Obtained results are given in Figure 3.

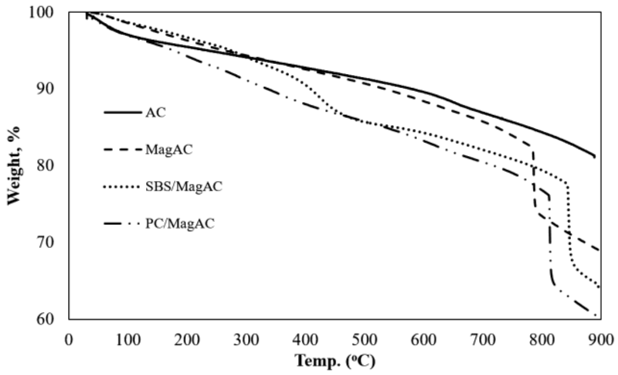

Fig 3. TGA results of AC, MagAC, BS/MagAC, and PC/MagAC adsorbents

In short, TGA is a method studied to examine the ability of a substance to maintain its mass (thermal stability) under different conditions. In an other saying, it is the continuous monitoring of the changes in the mass of the substance depending on as function of the temperature. As seen from Fig 3, it is seen that the TGA values of AC generally lose mass with increasing temperature and a significant peak change occurs. Here, a significant peak change was appeared at MagAC and PC/MagAC samples at approximately 800°C and at the other SBS/MagAC samples at 850°C. This can be explained that the thermogravimetric method is dynamic that the system will never reach equilibrium and that changes in the amorphous and crystalline structure can occur with increasing temperature [15]. It can be said in general from all the data that mass loss was evident and sharp in all adsorbents starting from 800 °C. This is particularly explained to the decomposition and change of the carbon skeleton found in polymer-coated materials [16].

3.4. DSC analysis

DSC analysis of the samples prepared using activated carbon-based and different polymeric materials, the relationship between temperature and mass loss was investigated. Obtained results are given in Figure 4.

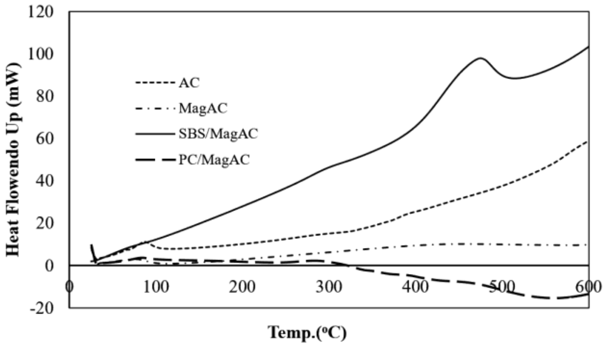

Fig. 4. DSC results of AC, MagAC, SBS/MagAC and PC/MagAC adsorbents

The DSC method is widely used in the research and development, process optimization and quality monitoring of plastics, rubber, coatings, pharmaceuticals, catalysts, inorganic materials, metal materials and composite materials**.** DSC analyses are preferred for thermal stability and oxidative stability of the material in different atmospheres, physical and chemical processes such as decomposition, adsorption, desorption, oxidation and reduction, and further reaction kinetics. Here are the experimental factors that affect the analysis and measurement. Factors such as temperature increase, sample dosage, particle size, convection, turbulence and sample tightness have significant effects. In the DSC process, the temperature of all sample and reference is increased at a regular rate by measuring the amount of energy absorbed or released while the sample is heated and cooled or kept at a constant temperature. When endothermic heat is applied to the sample simultaneously, on the other hand, there is heat transfer to the outside at the same time, where an esothermic drum is observed. In this process, the losses and gains in the sample are realized. Here, the heating of the sample appears as a function of temperature. When examined in Figure 4, it is observed that endothermic peaks occur around 100°C in AC samples. An exothermic peak of the MagAC sample was formed and increased by being affected by the temperature. Exothermic peaks are observed at 500°C in SBS/MagAC samples, and endothermic peaks are observed in PC/MagAC samples at 100°C and 300°C. Significant changes were observed specially in SBS/MagAC samples. in others, very significant changes were observed to be limited.

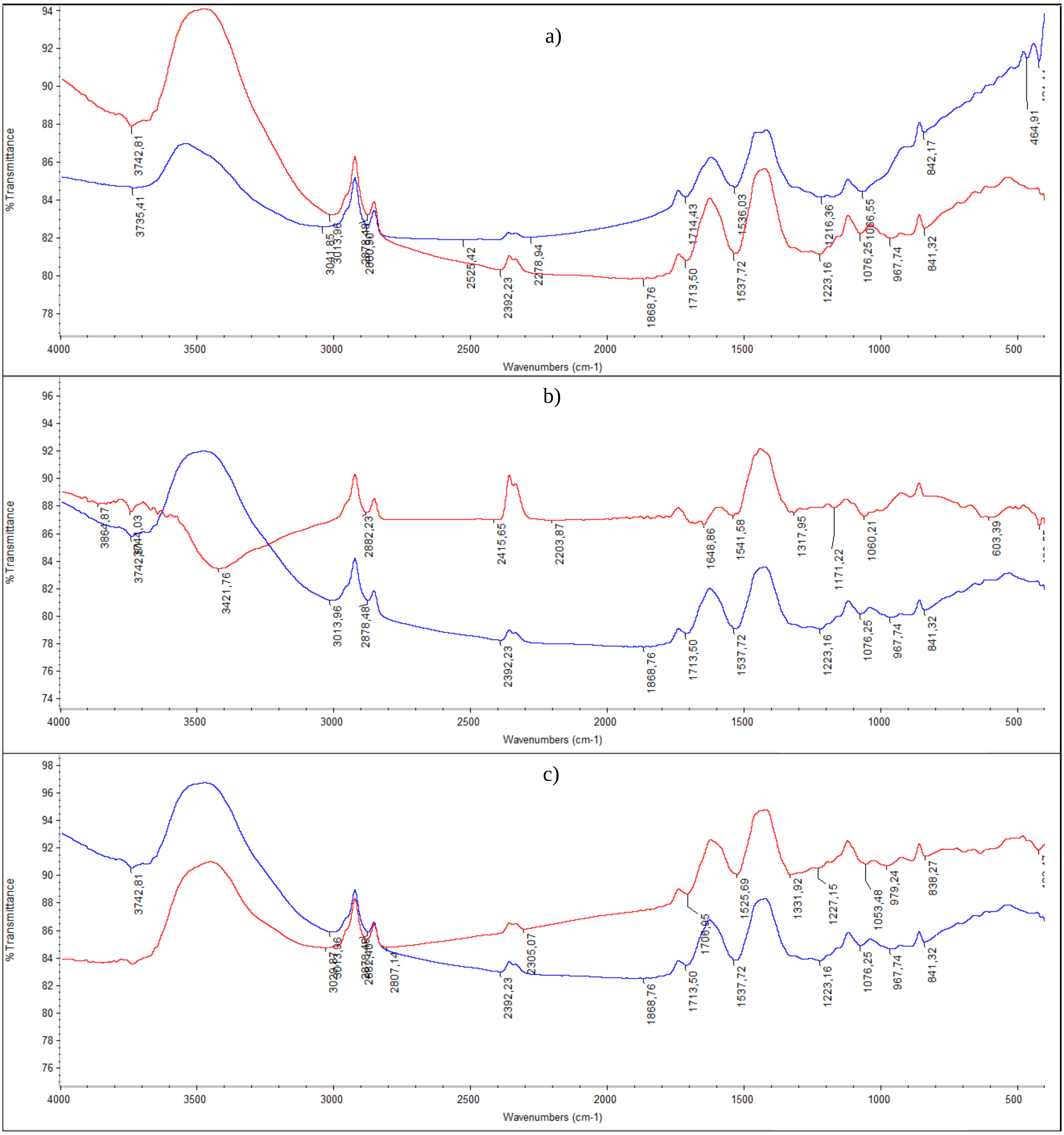

Fig. 5. FT-IR results a) AC vs MagAC, b) AC vs PC/MagAC, c) AC vs SBS/MagAC adsorbents

3.5. FT-IR Images

FT-IR spectra of polymeric coated magnetic materials using activated carbon samples are given in Fig.5.

Figure 5, shows the FTIR spectra of the adsorbent samples. As seen from the Figure 5, the –OH peak at 3041.85 cm^{-1} of AC presented the interactions of Fe_3O_4 confirming a shifting to 3013.96 cm^{-1}. This is indicating an effective physical interaction on the OH groups. The shifting of 1216.36 cm^{-1} peak to 1223.16 cm^{-1}, displays the C-O bond attached with –OH group. The C-H, C=O and C = C peaks was seen at 2880.90 cm^{-1}, 1714.43 cm^{-1} and shrinkage 1536.03 cm^{-1} peaks respectively. This is explained that no interactions were observed with these peaks. The PC based AC with interaction of $Fe_2Fe_3O_4$ exhibited the shifting of OH peak from 3019.96 cm^{-1} to 3421.76 cm^{-1}. This is suggested that the hydrogen bonds between -COO group and –OH molecules caused during the synthesized of PBS/MagAC. Also, the C=O bond seen at 1648.86 cm^{-1} confirmed this reality. With the connecting of hydrogen bond decreased the peak intensity at 1648.86 cm^{-1}. The 603.39 cm^{-1} peak in polycarbonate-bonded MagAC composite material was not showed the Fe-C bond in MagAC sample. In addition, the peak of C-O bond at 1223.16 cm^{-1} in Mag/AC sample showed the less interactions between polycarbonate and MagAC with confirming the 1171.22 cm^{-1} peak. Also, the IR spectra of the polymeric samples obtained with $Fe_2Fe_3O_4$ coated activated carbon was seen [17,18].

Table 1a. In phenol adsorption of AC and Mag AC and I. II. degree kinetic model and particle diffusion data

Parameters	AC									MagAC								
	First-order	Pseudo-second-order				Intra-particle diffusion				First-order	Pseudo-second-order				Intra-particle diffusion			
	R^2	$q_{e(calcul)}$ (mgg^{-1})	$q_{e(exp)}$ (mgg^{-1})	k_2x10^{-3} (g/mgmin)	R^2	k_1 (g/mgmin)	C	R^2	$t_{1/2}$ (min)	R^2	$q_{e(calcul)}$ (mgg^{-1})	$q_{e(exp)}$ (mgg^{-1})	k_2x10^{-3} (g/mgmin)	R^2	k_1 (g/mgmin)	C	R^2	$t_{1/2.}$ (min)
Ads. dos. (gL^{-1})																		
0.5	0.90	196.07	186.98	0. 5	0.99	8.58	86.15	0.89	10.70	0.88	169.49	163.35	1.00	0.99	6.74	89.74	0.77	6.12
1.0	0.84	153.84	147.21	0.8	0.99	7.09	68.36	0.72	8.49	0.84	185.18	162.33	0. 20	0.99	12.26	12.12	0.93	30.80
2.0	0.85	78.74	72.91	0.8	0.99	4.40	20.79	0.93	17.14	0.86	101.01	87.21	0.05	0.99	6.53	13.97	0.89	22.93
Temp. (K)																		
291	0.79	51.28	44.50	0.9	0.98	2.88	4.37	0.94	24.97	0.88	76.33	38.50	0.3	0.87	3.82	6.46	0.93	6.58
298	0.88	36.10	36.45	0.8	0.99	0.43	29.01	0.91	34.29	0.74	34.36	34.07	11.1	0.99	0.44	28.54	0.85	2.67
308	0.82	34.36	34.41	11	0.99	3.21	6.16	0.96	2.64	0.81	33.33	34.01	6.01	0.99	0.39	27.09	0.72	4.90
Initial Con.(mgL^{-1})																		
125	0.85	46.94	46.16	3.0	0.99	3.21	6.16	0.96	7.22	0.84	40.81	40.70	0.41	0.99	1.01	27.18	0.95	61.43
250	0.70	70.42	70.91	5.1	0.99	0.66	27.71	0.75	2.82	0.85	68.49	68.14	7.01	0.99	0.90	57.61	0.85	2.10
500	0.77	135.13	134.01	3.1	0.99	0.40	29.12	0.91	2.49	0.85	129.87	128.20	3.03	0.99	1.31	111.48	0.88	2.60
Initial pH																		
3.0	0.86	38.46	35.66	1.35	0.98	1.94	11.09	0.97	28.04	0.87	24.75	24.48	4.04	0.99	0.89	13.20	0.96	10.21
5.0	0.77	39.21	36.99	1.10	0.98	1.91	13.17	0.98	27.03	0.87	27.70	25.06	2.02	0.98	1.57	6.23	0.95	19.95
7.0	0.86	40.16	36.41	1.21	0.98	2.25	8.76	0.97	27.46	0.86	19.76	18.90	4.01	0.99	0.99	7.17	0.89	13.23
9.0	0.58	38.16	34.94	1.12	0.98	2.03	10.69	0.94	28.62	0.86	11.45	10.29	5.02	0.99	0.83	0.77	0.83	19.44

Table 1b. Phenol adsorption. SBS / MagAC and PC / MagAC I.II.degree kinetic model and particle diffusion data

Parameters	SBS/MagAC									PC/MagAC								
	First-order	Pseudo-second-order				Intra-particle diffusion				First-order	Pseudo-second-order				Intra-particle diffusion			
	R^2	$q_{e(calcul)}$ (mgg^{-1})	$q_{e(exp)}$ (mgg^{-1})	k_2x10^{-3} (g/mgmin)	R^2	k_1 (g/mgmin)	C	R^2	$t_{1/2}$ (min)	R^2	$q_{e(calcul)}$ (mgg^{-1})	$q_{e(exp)}$ (mgg^{-1})	k_2x10^{-3} (g/mgmin)	R^2	k_1 (g/mgmin)	C	R^2	$t_{1/2}$ (min)
Ads. dos. (gL^{-1})																		
0.5	0.85	200.00	183.77	0.03	099	11.78	44.58	0.92	181.39	0.85	188.67	168.37	0.2	0.97	10.81	35.78	0.96	27.21
1.0	0.85	185.18	156.28	0.01	0.96	12.74	2.79	0.93	639.88	0.88	144.92	122.14	0.2	0.99	9.37	9.36	0.94	31.99
2.0	0.82	84.74	63.93	0.03	0.98	5.61	4.39	0.95	521.40	0.85	120.48	50.58	0.2	0.97	4.86	11.84	0.94	78.21
Temp. (K)																		
291	0.77	31.05	24.08	10.1	0.98	2.15	1.68	0.94	4.11	0.86	45.45	30.52	0.06	0.97	2.88	4.37	0.94	6.14
298	0.75	27.39	27.03	11.0	0.99	0.44	21.59	0.87	3.36	0.86	29.15	28.66	13	0.99	0.45	23.59	0.86	2.85
308	0.56	24.57	24.92	100	0.99	0.03	24.76	0.87	0.40	0.82	26.88	27.55	17	0.99	0.57	25.44	0.89	2.36
Initial Conc.(mgL^{-1})																		
125	0.82	29.23	29.19	16	0.99	0.52	23.19	0.66	2.14	0.86	34.12	33.90	0.8	0.99	0.69	25.40	0.92	42.82
250	0.86	56.49	55.94	4.2	0.99	1.07	42.40	0.95	4.26	0.82	58.13	57.33	7.0	0.99	0.76	48.58	0.72	2.55
500	0.81	140.84	139.94	3.1	0.99	1.54	121.37	0.94	2.31	0.86	126.58	126.22	2.0	0.99	2.19	97.61	0.95	3.57
Initial pH																		
3.0	0.75	24.27	14.50	1.0	0.86	1.46	3.14	0.94	68.97	0.82	28.01	27.57	6.0	0.99	0.76	18.23	0.94	11.49
5.0	0.86	36.49	18.73	0.6	0.95	1.85	3.70	0.95	88.98	0.80	31.25	30.64	4.0	0.99	1.02	18.04	0.96	13.35
7.0	0.85	20.53	14.83	1.6	0.94	1.50	2.39	0.91	42.14	0.85	27.54	26.57	4.0	0.99	0.98	14.49	0.94	16.86
9.0	0.86	4.79	3.65	6.1	0.98	0.29	0.23	0.97	44.91	0.80	19.96	18.78	5.0	0.99	1.03	7.26	0.84	54.79

3.6. Adsorption Kinetics

The modified adsorbents are potential adsorbents due to their non-toxicity and efficiency. They contain chemically active functional groups that serve as efficient sites to bind adsorbents. The functional groups present in modified AC have affinity for removal phenol such as chemisorption, complexation, adsorption on surface. To obtain the kinetics of the phenol adsorption process on all adsorbents. Three kinetic models were studied (i.e. pseudo-first-order. pseudo-second-order and intra-particle diffusion kinetic models). The obtained results are shown in Table 1a and Table 1b.

When the data obtained from this study were evaluated, it was seen that the pseudo-first order model for all adsorbents was not suitable for seeing the interaction between phenol and all adsorbents due to lower R^2 values (0.56-0.90) and smaller theoretical q_e values. When the R^2 value obtained from the intraparticle diffusion model is examined, it is in the range of 0.72-0.96 and is false-second (0.99). The R^2 value obtained from the intraparticle diffusion model is in the range of 0.72-0.96 and is pseudo-second order (0.99). These results showed that adsorption of phenol on AC and magnetic materials followed pseudo second order in all parameters examined. The higher R^2 value of the intraparticle diffusion kinetics indicates that the ongoing adsorption process can also conform to the intraparticle diffusion kinetics. The theoretical q_e values (from the so-called second order model) are close to the values obtained from the experimental results which further confirms their suitability. In this case the adsorption process of phenol can be described as chemisorption and the rate determination step is suggested to be surface adsorption. Given the intraparticle diffusion model it can be said that there is a close agreement between the experimental and theoretical q_e value confirming the applicability of this model to explain phenol adsorption by all adsorbents. This shown that surface adsorption and intraparticle diffusion occur simultaneously. This can be mainly attributed in two stages firstly the outer surface of the adsorbents and later one the diffusion into the pores [19].

4. CONCLUSION

From The presented study, it was seen that AC, MagAC, SBS / MagAC and PC / MagAC can be used as good adsorbents to remove high phenol matter from wastewater. Different characterization study was investigated for the structural characterization of adsorbents such as; Scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis and Brunauer Emmett Teller (BET) measurements. Adsorption kinetics were conducted to investigate the adsorption potential of all adsorbents for phenol removal. The kinetic models appeared that the adsorption process onto adsorbents at all temperatures obeyed pseudo-second-order and intra-particle diffusion models rather than the pseudo-first-order kinetic model (R^2: 0.98-1.00). It has been seen that the efficiency realized in the whole adsorption can be realized as AC ≥ MgAC ≥ PC/MagAC ≥ SBS/MagAC samples, respectively. As a result, although higher efficiency is obtained with AC, it is observed that phenol can be removed from the aqueous environment more easily, especially when magnetic and polymeric materials are studied.

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Compliance with Ethical Standards

There is no conflict of interest to disclose.

Conflict of Interest

The author(s) declares no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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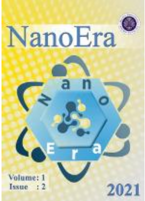

REVIEW ARTICLE

Development of Clay Nanoparticles in Pharmaceutical Industry

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HIGHLIGHTS

> The properties of mineral-based drugs were examined.
> The use of nanotechnology in the preparation of therapeutic nano-clays was discussed.
> Purification and modification of clay minerals to prepare nano-clay was investigated.

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ABSTRACT

Nanotechnology has grown significantly in the medical field in recent years. This new technology, with the synthesis and introduction of a new drug system, has made a huge difference in the discussion of treatment and health. The preparation and production of drugs based on natural and mineral compounds and the drug delivery system to specific organs of the body is an example of this technology in the field of pharmacy. Mineral drugs, unlike chemical drugs, have no negative effects on various organs of the body. Nano-clays - with their unique properties - are an example of mineral drugs that play a very important role in the pharmaceutical industry today. Bentonite is a clay mineral that is mainly composed of smectite minerals. Ionic substitution, ductility, high cation exchange are important properties of smectite minerals. Due to the weak bond between the layers in this group, it is easy to add different molecules and polymers between their layers, and for this reason, the clay minerals of the smectite group are very important in the pharmaceutical industry. Scientists are conducting research to purify, modify and optimize bentonite minerals and obtain mineral drugs compatible with the body's biological system.

1. Introduction

In general, clay minerals are hydrated alumino-silicates containing alkaline and alkaline earth metals. Much attention has been paid to them, since the early days of humankind, for various purposes because they are abundant in nature and inexpensive, and because they have unique structural properties [1–3]. Among the layered clay minerals, only some of them, including kaolin, talc, smectites, and fibrous clays can be used as excipients in the formulation of different dosage forms such as solid, liquid, or semisolid. The application of each clay mineral is determined by the individual intrinsic properties derived from the structure type (1:1 or 2:1 layer type) and chemical composition [3].

Clay minerals are a well-known class of compounds that have been used for pharmacological applications since ancient times. They were used for the treatment of minor ailments including infections, pains, aches, and food poisoning in prehistory [1,4]. The medicinal use of clay minerals became more and more prominent when, during the Renaissance, Pharmacopoeia classified clay minerals as

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drug. Up to now, clay minerals are widely employed in the pharmaceutical industry as common additives. They are for example used as an oral treatment of diarrhea or as gastrointestinal protector; or for topical dermatological applications Also, they have found application as diluents, lubricants, flavor correctors, carriers of active ingredients in pharmaceutical products, and so on [1,5–9].

Clay nanoparticles attracted much attention in recent years due to their widespread applications are natural materials in nanoscale that originate from clay. The interest in exploiting clay nanoparticles for various purposes is due to their high surface and unique physical and chemical properties [10]. Clay nanoparticles are minerals in clay that have attracted much attention due to the biological application of their abundance in nature, simplicity of construction, and biocompatibility [11–13]. Also, they have a great potential for nutrition because they have been used to treat and protect as a traditional medicine since the beginning of human civilization [14,15]. Clay minerals have been used as laxatives, antidiarrhea, anti-inflammatory agents, blood purification, reducing infections, and healing of stomach ulcers [10,16].

Nanotechnology has grown significantly in recent years, especially in the medical field. This new and valuable technology, with the synthesis and introduction of a new drug system, has taken a huge change and a fundamental step in the discussion of treatment and health. The preparation and production of drugs based on natural and mineral compounds and the drug delivery system to specific organs of the body is an example of the fruit of this technology in the field of pharmacy that has transformed the world of the pharmaceutical industry [17–19] (Fig. 1).

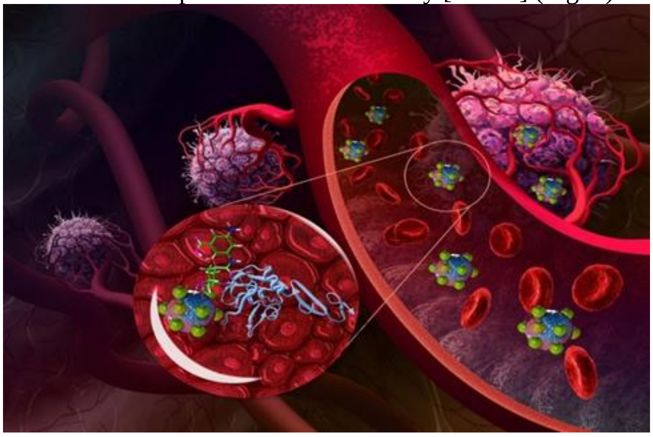

Fig. 1. Nanotechnology for drug delivery applications

The new drug system has no adverse effects on other organs of the body and is compatible with the body's biological environment. Clay minerals are among the most important natural materials used in the preparation and synthesis of drugs of modern pharmaceutical technology. Clay minerals are a group of phyllosilicates or sheet silicates minerals that are very important in the pharmaceutical and nanotechnology industries for various reasons such as abundance, low cost, excellent adsorption properties, etc (Fig. 2). Pharmacists hope to mass-produce this drug to achieve promising results in the treatment of specific and incurable diseases such as cancer [17,20,21].

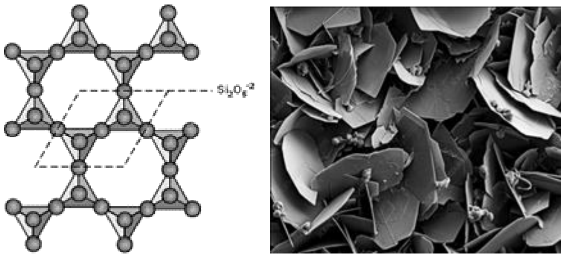

Fig. 2. The Mineral structure of phyllosilicate.

Nano-clays are a group of minerals that are at least one nanometer in size. This group of minerals has attracted the attention of nanotechnology scientists due to its unique properties (Fig.3). By purifying, modifying and optimizing nano-clays, valuable medicinal composites can be obtained that play an important role in health.

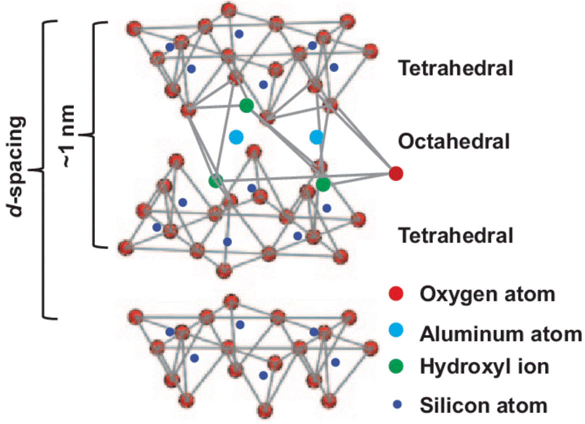

Fig.3. Structure of nano-clay (montmorillonite)

Extensive production of mineral therapists using nanotechnology, which not only has no side effects but also provides minerals needed by various organs of the body, will be an essential step in ensuring human health [20,22].

2. Nano-clays

Clay minerals are inorganic products obtained from the chemical weathering of sedimentary rocks They have a nanometer-scale layering and are often named just nano-clays [23–28]. The term “nano-clays” is used here to denote clay sand clay minerals whose particles have at least one dimension in the nanoscale range (1-100 nm). The best-known example of a nano-clay is montmorillonite [29–31], a species of the smectite group of hydrous phyllosilicates [23,32].

Nano-clay is composed of thin layers each layer has a thickness of one to a few nanometers’ lengths from a few hundred to several thousand nanometers [33]. It consists of silicon-oxygen tetrahedral sheet and aluminum-oxygen octahedral sheet, which are joined to form 1:1 or 2:1 type minerals by sharing the apical oxygens or hydroxyls [34]. Due to the significant presence of clay minerals on earth, people have been collecting this material for thousands of years using them in pottery and medical formulations [25,28,35–37].

3. Results and Discussion

Nano-clays are a group of minerals that are at least one nanometer in size. This group of natural materials has been considered by many nanotechnology scientists due to its special structural properties, cheapness and expansion and abundance. The advent of nanotechnology, despite its infancy, has been accompanied by major changes in medicine and health. Modification of various properties of materials by changing ions, impregnation with metal elements and treatment with acids in this technology, has provided natural drugs without side effects to the pharmaceutical industry. Bentonite is a clay mineral that is mainly composed of smectite minerals. Ionic substitution, ductility, and high cation exchange are important properties of smectite minerals. Due to the weak bond between the layers, in this group of clay minerals, it is easy to add different molecules and polymers between their layers, and for this reason, the smectite group clay minerals are very important in the pharmaceutical industry [38] (Fig. 4).

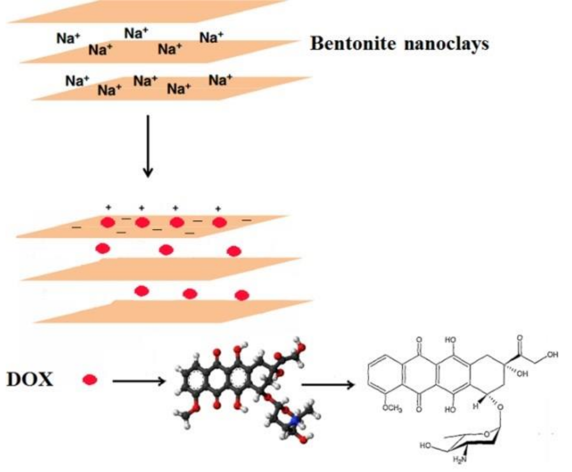

Fig. 4. Addition of effective drugs between cavities and structural spaces of clay mineral layers (bentonite)

The word bentonite was first used in 1898 by a scientist named Knight. The term is derived from the Benton shale area of Wyoming in USA. Bentonite is a clay mineral that is mainly composed of smectite minerals. Smectite consists of dioctahedral series (including montmorillonite, bidlitite, nantronite) and tetrahedral series (including hectorite and saponite clay minerals). The clay structure of the smectite group consists of a layer one nanometer thick. The horizontal dimensions of the layers of these clays vary from 30 nm to several micrometers and depend on the type of silicate [39].

The placement of the layers on top of each other creates a certain space between them, which is known as the interlayer space or the Gallery. Conformal substitution in mineral layers usually results in a negative charge, which is neutralized by alkali or alkaline earth cations (Ca^{+2}, K^{+}, Na^{+}, ...). The preparation and production of drugs based on natural and mineral compounds and drug delivery system to specific organs of the body is an example of the fruit of this technology in the field of pharmacy that has changed the world of the pharmaceutical industry and has eliminated the damage caused.

Unlike chemical drugs, these mineral drugs do not have any adverse effects on other organs of the body. The addition of effective drugs between cavities and structural spaces of clay mineral layers after refining and modification processes as well as strengthening structural cavities by various physical and chemical methods and finally the preparation of mineral therapeutic nano-fibers is the main method of synthesis of these drugs (Fig. 5).

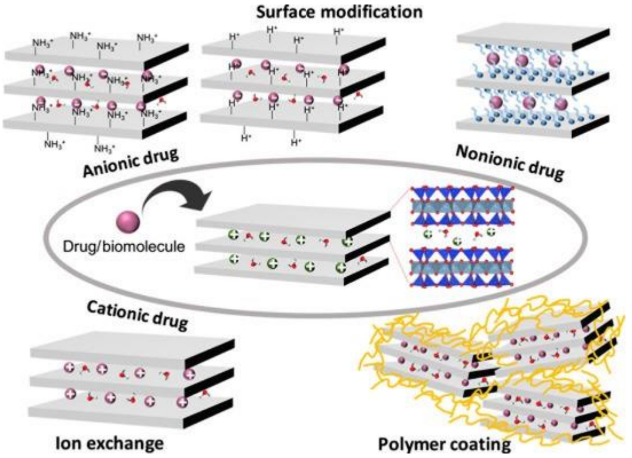

Fig. 5. Layered silicates as a drug carrier

The basic properties of drug carriers (such as nano-clays) are that they protect the drug against degradation, increase its absorption efficiency by facilitating its distribution through the intestinal membrane, and modulate tissue distribution by modulating body function. Also, these mineral drugs do not have any negative or destructive effects on various organs of the body [40].

4. Conclusion

Nano-clays - with their unique properties - are an example of mineral drugs that play a very important role in the pharmaceutical industry today and are one of the most basic nanotechnology tools in the modern pharmaceutical industry. Preparation and production of drugs based on natural and mineral compounds and drug delivery system to specific organs of the body is the product of this technology in the field of pharmacy which has transformed the world of the pharmaceutical industry and eliminated the disadvantages of chemical drugs.

Compliance with Ethical Standards

There is no conflict of interest to disclose.

Conflict of Interest

The author(s) declares no known competing financial interests or personal relationships.

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