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The use of perlite to remove dark colour from repeatedly used palm oil

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ABSTRACT: Expanded perlite was used as a bleaching agent to remove dark colour from repeatedly used palm oil. It was found that non-activated expanded perlite was able to bleach the dark colour. The expanded perlite samples were also activated by acid and base before use. The base-activated perlite was able to bleach the dark colour of the repeatedly used palm oil but acid-activated perlite was not. The efficiency of base activated perlite was slightly better than that of non-activated expanded perlite. The bleaching mechanism could be explained mainly by physical adsorption. It was found that not only the colour of used oil was reduced but also the peroxide and acid values. Perlite could also adsorb the toxic compound benzo(a)pyrene from palm oil. Apart from measurement of the colour of oil, the peroxide and acid values as well as compositions of oil before and after bleaching were studied. Perlite samples before and after use were studied by scanning electron microscopy and Fourier transform infrared spectroscopy. The non-activated and activated perlite samples were also studied with X-ray diffraction.

KEYWORDS: expanded perlite, bleaching agent, adsorption, benzo(a)pyrene

INTRODUCTION

Perlite is a volcanic acidic glassy rock which consists mainly of silica (72–75%) and Al_2O_3 (12–15%) and usually contains 2–6% water. When heated rapidly at 700–1200 °C, it can expand to as much as 20 times its original volume. Natural perlite is commonly grey, but can also be green, brown, blue, or red. After heating, perlite becomes a light weight material and is typically light grey to white in colour[1]. The silicon atoms at the surface of perlite glass maintain their tetrahedral coordination with oxygen. They complete their coordination at room temperature by attachment to monovalent hydroxyl groups, forming silanol and silanediol groups[2].

During frying, food is submerged in oil which is heated in the presence of air. Therefore, the oil is exposed to the moisture from the foodstuff, oxygen from the atmosphere, and high temperature. The moisture from the foodstuff causes hydrolytic reactions which yield free fatty acids, monoglycerides, diglycerides, and glycerol. The atmospheric oxygen causes oxidation giving rise to oxidized monomers, dimers, and polymers. Some carbonyl compounds are also formed. These compounds are responsible for the dark colour of used oils, especially when the oils are repeatedly used[3]. The quality of oil drops due to decreases in heat capacity and surface and interfacial tensions, and increases in specific gravity, viscosity, acid values, and polymer content[4].

Several groups of researchers have studied physical and chemical properties of perlite as well as its uses, but to the best of our knowledge, so far there have been no reports on using perlite to remove dark colour from used cooking oil. Unexpanded perlite has been used as a filter aid in industrial processes[1]. Studies of perlite samples from different places found that all perlite samples were amorphous with similar ratio of silica to alumina (SiO_2:Al_2O_3) but differed in the amount of accessory minerals[5,6]. There is also a study of Si-OH stretching frequency in perlite by infra-red spectroscopy[7]. Furthermore, there are a number of studies on the use of perlite as an adsorbent for organic and inorganic compounds[8–12].

Previously, we reported the use of bentonite to remove dark colour in repeatedly used palm oil[13]. The objective of this research was to use expanded perlite which is also a good adsorbent to remove dark colour from repeatedly used palm oil.

MATERIALS AND METHODS

Perlite and palm oil samples

The 80 mesh expanded perlite was obtained from Klong Yang Co. Ltd., Lopburi, central Thailand. Perlite samples were washed with distilled water and dried in an oven at 110 °C before use. The repeatedly used palm oil samples had been used to fry ‘patonggo’ (yóutiáo, starch fingers) several times and they were obtained from a market in Nontaburi province, west of Bangkok.

Acid and base activation of perlite

To compare the efficiency of expanded natural unmodified and modified perlite, the perlite was activated by reacting with acid and base before it was used to bleach the oil. Acid activation of perlite was performed by refluxing perlite with 10% v/v H_2SO_4 for 3 and 5 h, using a perlite:acid ratio of 1:10 w/v. After reflux, the mixture was washed with distilled water to remove excess acid, and then drained. Various pH values (1, 2, 3, and 5) of the perlite suspension were tried in order to find the optimum one. These acid-activated perlite samples were kept in a dessicator until use.

Base activation of perlite was performed according to a modified method of zeolitization of perlite[14, 15]. The procedure was to reflux perlite with 20% w/v NaOH for 3 and 5 h (perlite:NaOH = 1:10 w/v). After reflux, excess NaOH was washed off by distilled water until pH 10, then the perlite was filtered off. These base-activated perlite samples were also kept in a dessicator until use.

Bleaching of used palm oil

The bleaching method was similar to that used for bentonite[13]. Briefly, 300 ml of used palm oil were placed in a 600 ml beaker and heated while being stirred with a magnetic stirrer. When the temperature reached 60 °C, a few drops of 50% citric acid were added to prevent oxidation of oil during heating. Non-activated and acid or base-activated perlite was gradually added with stirring. The amount of added perlites varied from 1 to 15% by weight of oil, in 1% increments. The mixture was then heated and stirred at various temperatures (60–70 °C, 70–80 °C, 80–90 °C, and 90–100 °C) with various bleaching times (15, 30, 45, and 60 min). After cooling the mixture to room temperature, perlite was filtered through paper (Whatman no. 42) under vacuum. The colour of the oil before and after bleaching was measured by Lovibond tintometer (Pardero Model E), using a 5.25 inch cell.

Analyses of perlite

The chemical composition of perlite was determined by X-ray fluorescence spectrometry, (Philips PW 1480 XRF spectrometer). The texture and morphology of the expanded perlite were studied by scanning electron microscopy (JEOL JSM-6301F). Functional groups and interaction at the surface of the perlite were confirmed by Fourier transform infrared (FT-IR) spectroscopy in the mid-IR region (Bruker Equinox 55 FTIR spectrometer). The mineralogy of perlite before and after activation were studied by X-ray diffraction (XRD), (X′pert Model PW 3719).

Characterization of the repeatedly used palm oil

The repeatedly used palm oils were characterized before and after removing dark colour by determining fatty acid compositions, peroxide value and acid value. To determine fatty acids, the American Oil Chemist’s Society standard method was used. The oil was esterified by methanol in bromine trifluoride and the resulting methyl ester of fatty acids was analysed by gas-liquid chromatograph (Perkin Elmer model Auto system XL) with polyethylene glycol succinate and helium used as stationary phase and carrier gas, respectively. The peroxide value of oil was determined by the iodometric method. The oil samples were dissolved in acetic acid and chloroform and then reacted with potassium iodide to produce iodine. Iodine was then titrated with standard sodium thiosulphate solution, using starch solution as an indicator. The peroxide value is the number of milligrams of peroxide oxygen in 1 kg oil, and it was calculated in milli-equivalent per kg. The peroxide value indicates the degree of oxidation reaction in oil. The oil that had been used repeatedly is expected to have higher peroxide value than unused oil. The acid value of oil is the number of milligrams of KOH which is equivalent to free fatty acid in 1 g of oil. The acid value of the palm oil samples was measured by using the AOAC standard method, i.e., titration of oil in ethanol and diethyl ether with KOH in ethanol, using phenolphthalein as an indicator.

Adsorption of contaminants and a toxic compound in oil

Adsorption of contaminants was studied by UV-visible spectrometry (Jasco7800). To study contaminants in oil, absorption spectra of unused palm oil and repeatedly used palm oil before and after treatment with perlite were analysed in the spectral range 280–300 nm. Benzo(a)pyrene was used as a representative of toxic compounds in oil.

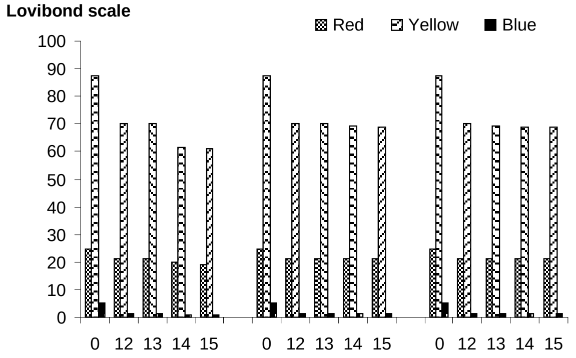

Fig. 1 Oil colour (in Lovibond scale) dependence on the % w/v of added (*left*) non-activated expanded perlite, (*middle*) 3 h base-reflux perlite, and (*right*) 5 h base-reflux perlite.

To study its adsorption, 25 ppm of benzo(a)pyrene were added to the unused oil. The maximum absorption was found at 363 nm. Perlite sample was then added (3 g in 50 ml of oil) and the mixture was left at room temperature for up to 6 days. The absorption intensities at 363 nm of unused oil, unused oil with benzo(a)pyrene, and unused oil with benzo(a)pyrene and perlite were measured and compared. The amounts of benzo(a)pyrene adsorbed by perlite were determined from a calibration graph.

RESULTS AND DISCUSSION

By varying the bleaching conditions, non-activated and base-activated perlite were able to bleach the repeatedly used palm oil since the oil became clearer after bleaching. Acid-activated perlite did not bleach used oil, even in large amounts. With non-activated and base-activated perlite, colour changes were only observed after adding 14 and 12% w/v, respectively.

The optimum temperature and time to bleach the repeatedly used palm oil by non-activated perlite were 80–90 °C and 30 min, respectively. The oil colours were constant when at least 14% perlite was used (Fig. 1).

The base-activated expanded perlite samples were also able to bleach the dark colour of the repeatedly used palm oil. Bleaching efficiencies were slightly higher than the non-activated expanded perlite. Both for 3 and 5 h refluxing, 12% of perlite was used before the oil colours became constant (Fig. 1).

The results from the characterization of contaminants in oil are shown in Fig. 2. The number and intensity of the peaks are smaller in the treated-used oil (Fig. 2c) than with the untreated-used oil (Fig. 2b). Hence, as with bentonite, perlite can also remove some contaminants in used oil. However, the contaminants were not identified.

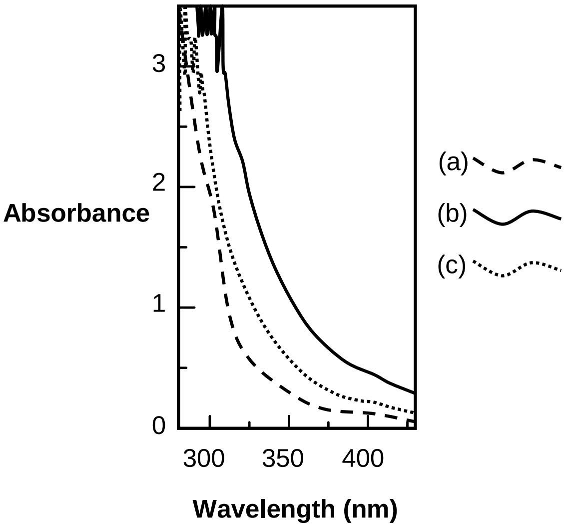

Fig. 2 Absorption spectra of (a) unused palm oil (b) repeatedly used palm oil (c) repeatedly used palm oil after treatment with non-activated perlite.

Table 1 The peroxide and acid values of palm oils.

Type of oil	Peroxide value	Acid value
Un-used	2.73	0.42
Used	6.72	1.14
Used and bleached	3.25	0.74

After 3 days, it was found that the maximum absorption of benzo(a)pyrene at 363 nm (the highest peak in Fig. 3b) decreased. Further decrease was observed after the mixture was left for 5 days, (Fig. 3c). By using a calibration graph, it was found that the absorbance of 2.05 corresponds to 20.18 ppm of benzo(a)pyrene. Hence, some benzo(a)pyrene was adsorbed by perlite. The absorption intensity did not show a significant change after the mixture was left for more than 5 days.

The peroxide and acid values of the repeatedly used palm oil decreased after bleaching with expanded perlite (Table 1). Although these values were still higher than that of the unused oil, the main purpose of this work was not to regenerate the oil to be reused for frying but to remove some colourants which contain toxic compounds. The treated oil may be used for biodiesel production. The viscosity of the oil also decreased, probably because some polymer compounds which imparted viscosity to the oil were also adsorbed by perlite.

The fatty acid content of the original and the

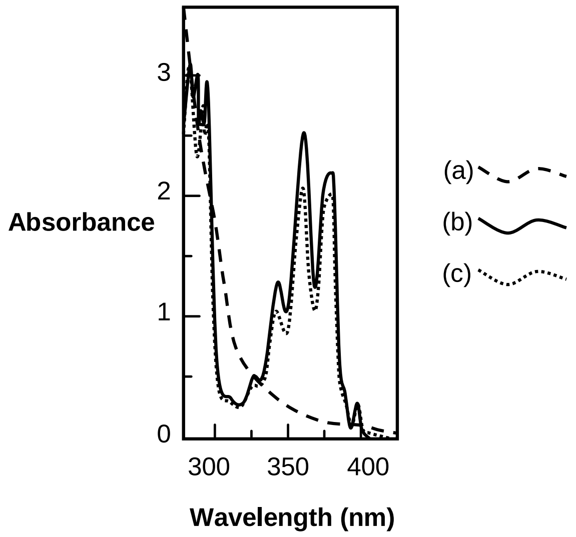

Fig. 3 Absorption spectra of (a) unused palm oil, (b) benzo(a)pyrene in unused palm oil, and (c) benzo(a)pyrene in unused palm oil after treatment with non-activated expanded perlite.

Table 2 Fatty acid composition of palm oils.

Fatty acid	% Fatty acid in oil		
	Unused	Used	Treated used
Carprilic acid	0.21	-	-
Carpric acid	0.20	-	-
Lauric acid	1.60	0.60	1.10
Myristic acid	1.40	1.00	1.00
Palmitic acid	35.00	41.00	42.00
Heptadecanoic acid	0.20	-	-
Stearic acid	3.20	2.50	2.80
Oleic acid	46.00	45.00	45.00
Linoleic acid	11.02	9.60	9.80
Linolenic acid	0.25	-	-
Arachitic acid	0.20	-	-
cis-11-icosenoic acid	0.10	-	-

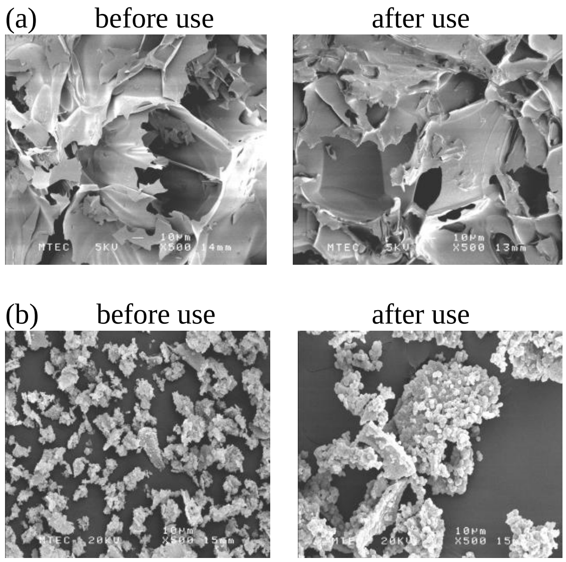

Fig. 4 Scanning electron micrographs of (a) expanded non-activated perlite and (b) base-activated perlite.

treated oil are shown in Table 2. The relative abundance of some fatty acids such as lauric, palmitic, stearic, and linoleic acid increased after the oil was treated by perlite, probably because some contaminants in oil were adsorbed by perlite.

Expanded perlite consists mainly of silica (75.2%) and alumina (12.8%). The composition of perlite remained essentially unchanged after use (Table 3). The small variations in composition were within the range of experimental errors.

The scanning electron micrograph of non-activated expanded perlite before use (Fig. 4a) shows that the non-activated, expanded perlite surface is mainly smooth and thin as a result of the expansion process. In contrast, the surface of base-activated perlite in Fig. 4b is covered by aggregates. After perlite was used, the adsorption of colourants and organic matter in used oil caused the perlite surfaces to be smoother and thicker (Fig. 4a).

Stretching vibrations of free SiO-H were not found in the IR spectra of the perlite samples as they were hidden by noise (Fig. 5). H-bonding between OH of the silanol or silanediol groups at the surface of expanded perlite is also possible (Fig. 6). Alternatively, there could be H-bonding between OH of the silanol or silanediol groups of perlite and free water molecules[7] because this band appeared at a rather lower frequency, i.e., 3448 cm^{-1} instead of around 3690 cm^{-1} for free SiO-H stretching.

The FT-IR spectrum of perlite after use shows some additional bands due to $\nu_{\mathrm{C-H}}$, $\delta_{\mathrm{C-H}}$, $\nu_{\mathrm{C-C}}$, and $\nu_{\mathrm{C=O}}$ (Fig. 5b). These additional bands may originate from vibrations of bonds in polymeric products of alkane as well as carbonyl compounds which were formed in oil during frying. This confirms the adsorption of the mentioned compounds on the perlite surface. Similar observations have been made during bleaching with acid activated bentonite[16]. It should be noted that before the IR experiments were performed, used perlite samples were washed well with NaOH solution to remove non-adsorbed oil. The interpretation of the IR bands is shown in Table 4.

In Table 4, it can be seen that the vibrational frequencies of perlite skeleton at the surface of perlite

Table 3 Chemical composition of perlite samples before and after use.

Chemical composition (%)	Perlite samples							
	Non-activated		Acid-activated		Base-activated			
	before use	after use	before use	after use	before use[a]	after use[a]	before use[b]	after use [b]
SiO_2	75.20	75.21	74.55	74.60	35.67	35.60	35.39	35.40
TiO_2	0.14	0.16	0.14	0.15	0.12	0.13	0.14	0.14
Al_2O_3	12.75	12.60	13.58	13.50	26.07	26.10	26.52	26.35
Fe_2O_3	0.99	0.96	0.94	0.92	1.87	1.87	1.84	1.83
MnO	0.05	0.03	0.05	0.03	0.08	0.06	0.08	0.08
MgO	<0.10	<0.10	<0.10	<0.10	0.13	0.14	<0.10	<0.10
CaO	0.38	0.38	0.34	0.34	0.79	0.79	0.75	0.73
Na_2O	2.85	2.87	2.71	2.73	18.04	18.00	18.32	18.30
K_2O	5.12	5.13	5.16	5.12	0.58	0.58	0.61	0.61
P_2O_5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
LOI[c]	1.50	1.53	2.09	2.07	11.54	11.50	11.16	11.25
H_2O	0.43	0.42	0.24	0.24	4.58	4.56	4.57	4.57

[a] = 3 h reflux
[b] = 5 h reflux
[c] LOI = loss on ignition

Table 4 Assignment of FT-IR bands of perlite before and after use.

Functional group	Wave number (cm^{-1}) of perlite	
	Before use	After use
ν_{OH} (H-bonding between SiO-H at surface)	3448	3449
ν_{C-H} alkane	-	2854, 2925
$\nu_{C=O}$ aldehyde, ketone	-	1747
δ_{OH} bending vibration of H_2O	1642	1642
δ_{CH} bending of alkane	-	1459, 1152
ν_{Si-O} asymmetric stretching vibration of SiO_4 tetrahedra (out of plane)	1192	1192
ν_{C-C} stretching	-	1152
ν_{Si-O} asymmetric stretching vibration (in plane)	1048	1048
T-O-T bending vibration (T = Si or Al)	451	451

did not shift after perlite was used. Therefore, the adsorption of compounds which are responsible for the dark colour in repeatedly used palm oil on the surface of perlite should be mainly physical adsorption. The role of chemical adsorption seems of lesser importance in this study. Sari et al[17,18] studied the adsorption of Pb(II) and Cr(III) on Celtek clay and adsorption of Pb(II) on Turkish clay. They found that the thermodynamical parameters indicated that the adsorption of the ions should be spontaneous and exothermic.

The XRD trace of the non-activated perlite shows a glass hump which indicates that perlite is an amorphous material (volcanic glass), which contains mostly SiO_2 and Al_2O_3 (Table 3). Other minerals such as quartz, feldspar, biotite, and hornblende, which are often present in perlite, are absent. The X-ray diffractogram of acid-activated perlite is not different from that of non-activated perlite which means that acid treatment did not change the structure and mineralogy of perlite. On the other hand, the X-ray diffractogram of base-activated perlite showed that the original material has been converted to new crystalline phases, namely zeolite Linde Type A and hydroxysodalite (Fig. 7).

CONCLUSIONS

Expanded perlite from Thailand can be used to remove the dark colour from used palm oils. The appropriate condition is to add at least 14% w/v of perlite directly to the oils and followed by heating to 80–90 °C and then stirring for 30 min. Modifications of perlite by base or acid are not necessary. Base-activated perlite has a slightly higher efficiency than the non-

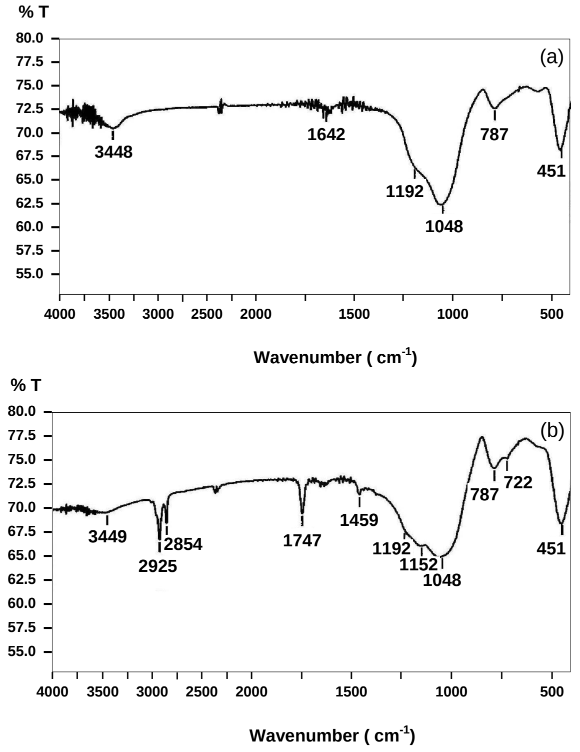

Fig. 5 FT-IR spectra of expanded perlite (a) before use and (b) after use.

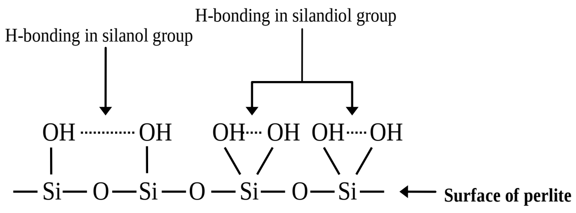

Fig. 6 Possible hydrogen bondings at the surface of perlite.

activated one (12 versus 14%) but this raises cost. Acid-activated perlite cannot bleach used oil, even in large amounts. The bleaching mechanism appears to be mainly physical adsorption, as shown by the IR spectra. As bentonite needs acid-activation, perlite appears to be a better choice for used oil bleaching.

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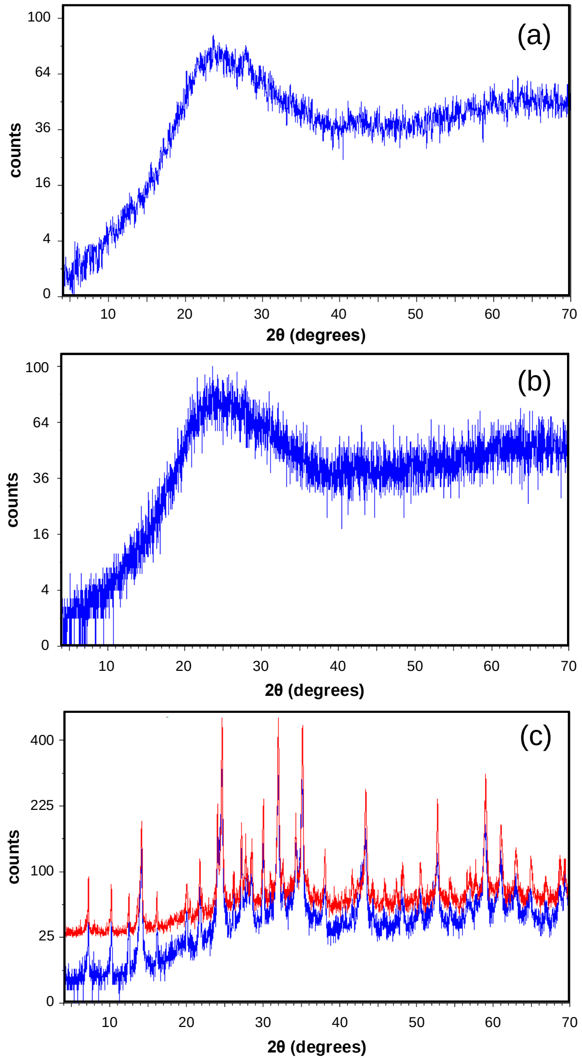

Fig. 7 X-ray diffractogram of (a) non-activated expanded perlite, (b) acid-activated perlite, and (c) base-activated perlite. Upper spectrum: 3 h reflux; lower spectrum: 5 h reflux.

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