Regeneration and Recycling of Spent Bleaching Earth

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Abstract

Spent bleaching earth, a solid waste from the edible oil refining industry with unpleasant odor, usually consists of clay minerals and residual oil. The residual oil can be rapidly oxidized to the point of spontaneous autoignition due to the autocatalysis action of clay minerals, so that the direct discard and landfill of spent bleaching earth result in the fire danger and environmental pollution. In order to minimize the risk of pollution, much effort has been devoted to explore the feasible approach for recycling the spent bleaching earth. Therefore, this chapter reviewed the recent research progress in regeneration and recycle of

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spent bleaching earth by summarizing the comprehensive literatures and our group's latest research achievements.

Introduction

The color of edible oil is usually the most important aspect affecting the choice of the consumer, which is mainly derived from the chlorophyll-α and β-carotene presented in the crude oil. These natural pigments are sensitive to light, heating, and oxygen, which go against the oil storage and people's health, so it is necessary to remove these pigments via a refining process to meet the standard consumption before eating. The refining process of the crude oil usually consists of four operations of degumming, neutralization, bleaching, and deodorization. Among them, the bleaching step is a crucial for removal of the natural pigments, non-glyceride components, trace metals, free fatty acids, and hydroperoxides using activated clay (bleaching earth) as adsorbents. However, the bleaching operation produces great quantities of solid wastes, namely, spent bleaching earth (SBE). SBE often contains 20–40% (w/w) of the residual oil and other organic matters, and they can rapidly oxidize to the point of spontaneous autoignition due to the autocatalysis of the clay minerals. Therefore, it is classified as a hazardous waste in many countries, and it is inadvisable and unscientific to directly discard and bury the spent bleaching earth. With the continuous increase in the consumption of the edible oil, the worldwide generation SBE is estimated to be up to about 2 million tonnes per year, based on world consumption of vegetable oils of 128 million tonnes (USDA 2009) with a 1 wt.% addition [1]. It is an urgent need to develop the feasible approaches for the regeneration and the recycling of SBE in the fields of adsorption of pollutants, bleaching of the edible oil, and others via pyrolysis, hydrothermal treatment, surface modification, etc.

Regeneration and Recycling of SBE

Thermal Treatment

Pyrolysis

Pyrolysis is a process of thermochemical decomposition of organic compounds in the absence of oxygen or air to produce various carbon-rich solid as well as a volatile matter [2]. Hence, pyrolysis causes severe thermal cracking on the compounds and subsequent rearrangements of the cracked fragments. SBE containing 26.6 wt.% of residual palm oil was pyrolyzed using a tubular furnace, and it was found that carboxylic acids ranging from C9 to C18 and alkanes ranging from C16 to C44 were the major compounds in the pyrolytic products analyzed using GC-MS (Fig. 1a). Meanwhile, significant amounts of monoaromatic compounds, alkenes, alcohols, ketones, aldehydes, esters, nitrogenated compounds, and polycyclic aromatic hydrocarbons were found in the bio-oil produced in this study [3]. In addition, the

regenerated bleaching earth as adsorbent was prepared in the activation conditions of constant ramp rate of 10 °C/min under N_2 flow of 0.3 L/min and CO_2 flow of 0.3 L/min at activation temperature of 800 °C for 2 h. The results demonstrated that the clay resource regenerated from bleaching earth waste could be used as a low-cost adsorbent for the removal of cationic pesticides (e.g., paraquat) from an aqueous environment [4]. Especially, our groups employed one-step calcination to regenerate SBE for adsorption of heavy metal ions of Cu(II), Pb(II), and Cd(II) (Fig. 1b) [5]. Typical rodlike morphology of the as-prepared APT/C nanocomposites could be clearly revealed by SEM (Fig. 1c). It also was observed that the nanorod-like morphologies gradually increased with the increase in the calcination temperature, which might be attributed to the fact that the high calcination temperature was favorable to improve the aggregate phenomenon of crystal bundles due to the carbonization of organic matters and the decomposition of the associated carbonates. Solvent extraction followed by a heat treatment was also one of most effective processes to utilize SBE. The SBE was reactivated by heat treatment at 370 °C after extraction of residual oil with the excess methyl ethyl ketone, and the regenerated material showed a commendable adsorption ability to Cu(II) in aqueous solution [6].

It is well known that the operation of a pyrolysis process depends on several parameters such as the feedstock and operating conditions including pyrolysis temperature, holding time, heating rate, and flowing gas, and different operation conditions lead to the different products with different properties. For instance, SBE was thermally regenerated by a rotary furnace under inert atmosphere (i.e., N_2). Under the experimental conditions, pyrolysis temperature (500–660 °C) was an important operating parameter, and the effect of processing parameters such as pyrolysis temperature (> 660 °C), holding time, and flowing gas (N_2 vs. CO_2) on the characterizations of the resulting solids was negligible compared with the fresh bleaching earth [7]. Hence, it is clear that the pyrolysis process offers more opportunities for the rational recycling SBE by reconverting into useful materials.

Hydrothermal Carbonization

Sustainable chemistry aspires to raise the value of less dangerous chemicals as well as tries to produce high-quality products in an environmentally friendly manner from preferably renewable resources. The thermal treatment of water mixed with organic substances such as saccharides (glucose, sucrose, or starch) or simpler compounds such as furfural at 150–350 °C (autogenous pressure) gives rise to water-soluble organic substances and a carbon-rich solid product. This process, termed hydrothermal carbonization (HTC), can be applied to realize the transformation of the low-value and widely available SBE into various carbonaceous materials and hybrids at mild temperatures and in pure water inside closed recipients and under self-generated pressure [8]. These as-prepared carbon materials can be designed for applications in crucial fields such as adsorption, energy conversion, and catalysis. Besides controlling the chemistry of carbonization, two other important prerequisites for the achievement of useful properties are the control over morphology both at nano- and macroscale and the control over functionality by chemical means in hydrothermal

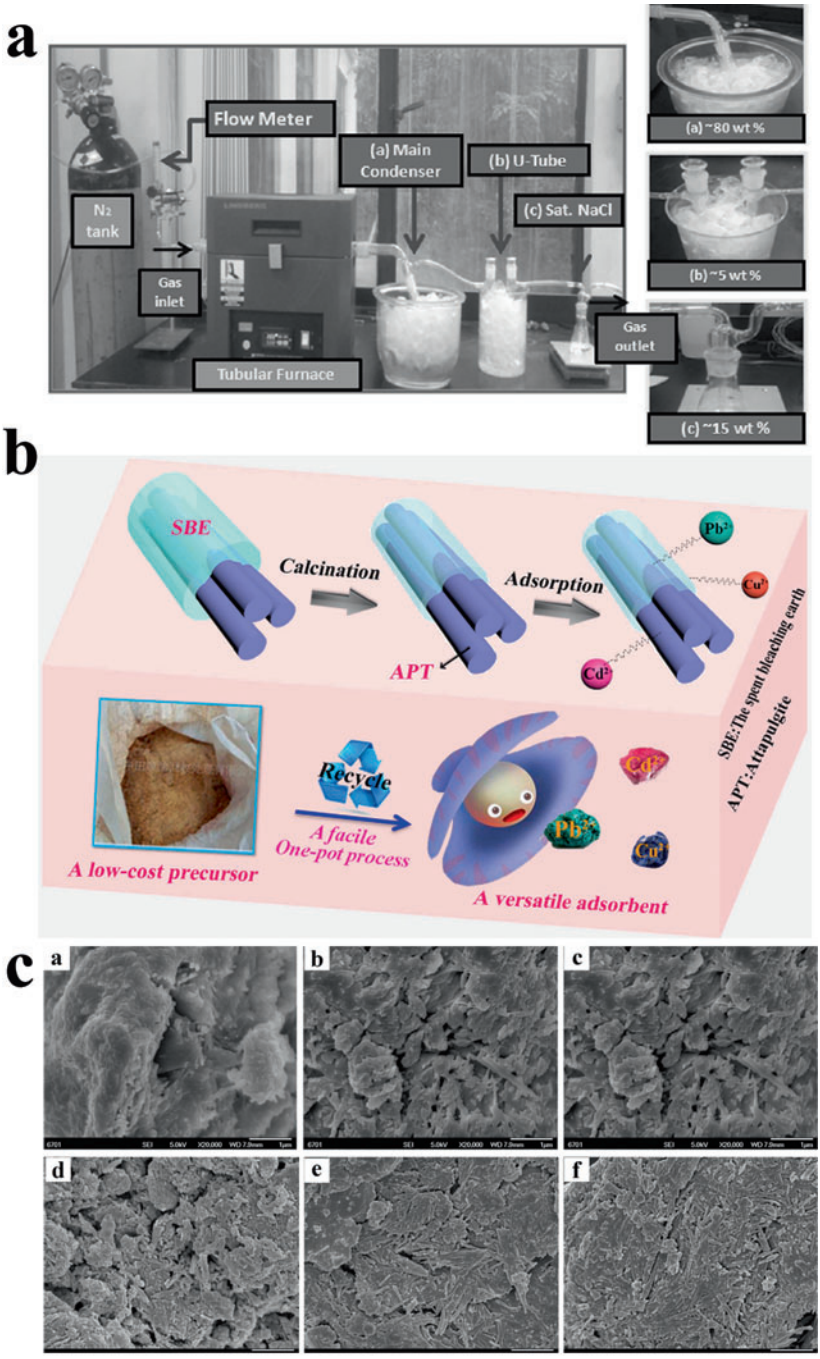

Fig. 1 (continued)

carbonization [9]. Natural bentonite spent in the bleaching of plant oil was used as an initial material for preparation of carbon-mineral adsorbents. The results showed that hydrothermal treatment, applied before raw material pyrolysis, made it possible to prepare adsorbents of higher carbon deposit contents than in the case of using direct pyrolysis of wastes [10].

A facile HTC process might have the opportunity to turn into a powerful technique for the synthesis of valuable carbon materials from SBE, especially clay/carbon composites. Compared with conventional carbonaceous materials, the combination of clay minerals and carbon species could fulfill an affordable composite to remove various contaminants from wastewater [11]. However, the adsorption capacity of clay/carbon composites toward pollutants was also restricted due to the scarcity of functional groups and the defect inherited from the feedstock. Hence, our groups reported a hydrothermal strategy to prepare manganese dioxide/carbon/attapulgite (MnO_2/C/APT) ternary composites based on SBE in the presence of KMnO4 (Fig. 2a). It was worth noting that the residual organic matter of SBE was served as both of a low-cost available carbon precursor and a reductant for the formation of manganese dioxide based on the redox with $KMnO_4$, which was confirmed from the color of the composites. With the increase in the concentration of $KMnO_4$, the color of the composites changed from light yellow to crimson (Fig. 2b). Furthermore, the adsorption properties of the as-prepared composites were well dependent on the concentration of $KMnO_4$, and the maximum adsorption capacity toward brilliant green and Pb(II) reached 199.99 mg g^{-1} and 166.64 mg g^{-1}, while the concentration of $KMnO_4$ was 12% and 16%, respectively (Fig. 2c) [12].

In addition, the traditional separation technique (centrifugation or filtration) is time-consuming and uneconomic to separate the adsorbents from the treated water for recycling owing to the small size [13]. Therefore, magnetic clay/carbon composites have received an increasing attention due to the easy separation from solution for recycling by an external magnetic field. Based on our previous study, a facile and green hydrothermal approach was employed to fabricate the magnetic carboxyl-functionalized attapulgite/carbon (CFAC) nanocomposites based on the spent bleaching earth [14]. This process simultaneously involved the growth of magnetic nanoparticles and the coating of carbon species with carboxyl groups on the surface of attapulgite via hydrothermal redox reactions between Fe(III) and sodium citrate in the aqueous solution. As shown in Fig. 3, the composition, magnetic response, as well as adsorption properties of as-prepared nanocomposites could be facilely controlled by adjusting the concentration of sodium citrate. While the concentration of sodium citrate was 0.6 M, the resultant adsorbents exhibited fast adsorption kinetics. The maximum adsorption capacity toward MB and Pb(II) could reach

Fig. 1 (**a**) Self-designed tubular furnace set up for pyrolysis (Copyright 2011, reproduced with permission from Elsevier). (**b**) Schematic illustrating the synthetic route of the APT/C nanocomposites and (**c**) SEM images of (a) APT/C-250, (b) APT/C-300, (c) APT/C-350, (d) APT/C-400, (e) APT/C-450, and (f) APT/C-500 (Copyright 2015, reproduced with permission from American Chemical Society)

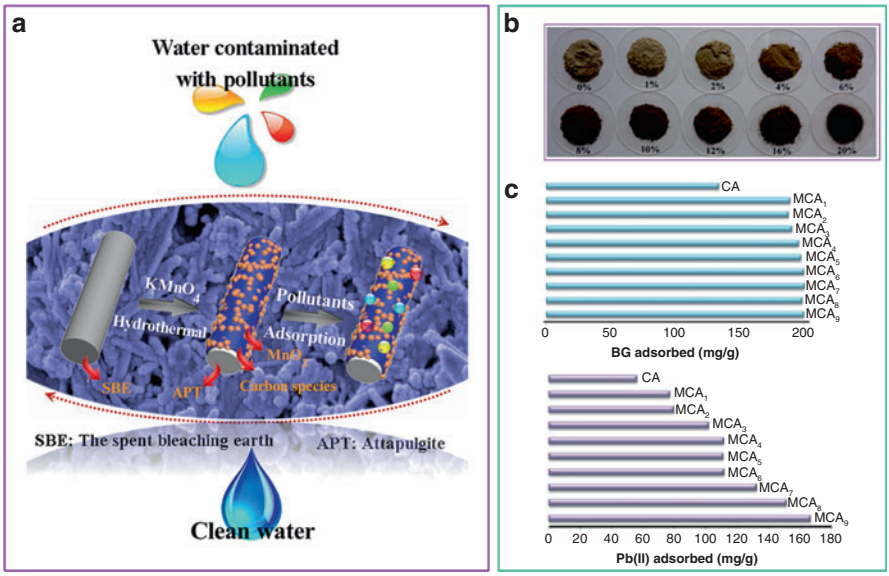

Fig. 2 (**a**) Schematic illustration of the synthetic route of the MnO_2/C/APT ternary composites for the adsorption of BG and Pb(II). (**b**) Digital photographs of the MnO_2/C/APT ternary composites obtained after hydrothermal treatment at 140 °C for 1 h at different initial $KMnO_4$ concentration and (**c**) effect of initial $KMnO_4$ concentration on adsorption for BG and Pb(II) (Copyright 2016, reproduced with permission from Royal Society of Chemistry)

254.83 mg g^{-1} and 312.73 mg g^{-1}, respectively. In addition, the adsorbent could be easily recycled using a magnet, and the adsorption capacity had no obvious decrease after six adsorption-desorption cycles.

Using this approach, the properties of the obtained materials can be facilely adjusted by controlling the hydrothermal time, hydrothermal temperature, precursor concentration inside the autoclave, as well as additives and stabilizers potentially to be added to the primary reaction recipe. In summary, HTC is a green and sustainable alternative for most of biomass or waste, and the reaction takes place in pure water at mild temperatures without employing any hazardous surfactants or catalysts. Furthermore, the resulting materials are solid particles or high-surface-area scaffolds, and their surfaces also can be well decorated with polar functional groups to enhance their corresponding properties.

Solvent Extraction

Solvent extraction is a common strategy to regenerate SBE by removing the residual oil and other organics using the organic solvents. Depending on the extracted oil, several nonpolar or polar solvents can be considered as extracting medium. Polar solvents such as acetone, methyl ethyl ketone, perchloroethylene, methylene chloride, isopropyl alcohol, and chloroform were used to extract the polar components

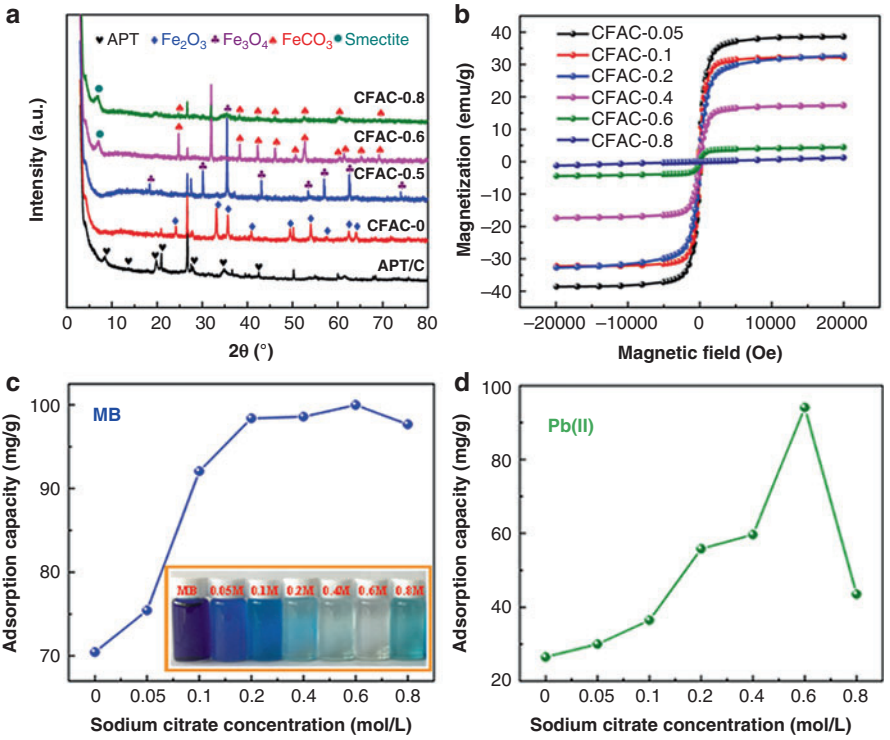

Fig. 3 (**a**) XRD patterns of APT/C, CFAC-0, CFAC-0.05, CFAC-0.6, and CFAC-0.8, (**b**) magnetic hysteresis loops of the CFAC nanocomposites, and effect of initial sodium citrate concentration on adsorption for (**c**) MB and (**d**) Pb(II) (inset is the photograph of the MB solution of different dosage of sodium citrate) (Copyright 2017, reproduced with permission from Elsevier)

and the coloring matters from SBE. By contrast, nonpolar solvents such as petroleum ether, petroleum benzene, xylene, toluene, and hexane were employed to extract the nonpolar fractions such as triglycerides as well as other useful nonpolar components. The solvent type and the method of oil extraction usually determine the quality of the extracted oil from SBE. For instance, different types of organic solvents (methanol, toluene, benzene, xylene, carbon tetrachloride, and acetone) were used to de-oil SBE. It was found that methanol was much recommended than other organic solvents in the extraction process of oil from SBE. This was attributed to the fact that it was low cost and less hazardous than other solvents with a higher yield and a better quality of oil than other organic solvents. The treated SBE could be used as a new low-cost adsorbent to remove Ni(II) from aqueous solutions, and it was in favor of reducing the cost of waste disposal and providing an alternative sorbent [15]. In addition, SBE could be served as a useful sorbent for removal of organic basic dyes after being extracted with hexane. It was noted that the use of hexane-extracted SBE to remove dyestuff from wastewater was a program aiming at cleaning up the environment by the use of SBE as it was inexpensive and easily available [16].

Chemical Treatment

Acid Treatment

From an environmental and economic standpoint, it is a good solution to treat the wastewater using a low-cost adsorbent derived from SBE after acid regeneration process. The adsorbent was produced from SBE by H_2SO_4 impregnation method to remove arsenic(III), suggesting the possibility of utilizing this material in water treatment systems [17]. In addition, the acid-treated SBE was applied to remove beta-picoline under various laboratory conditions [18].

Base Activation

Another method for the SBE regeneration is directly activated using the common bases. A spent diatomaceous earth has been tentatively activated by sodium hydroxide at about 100 °C. The resulting product was used as a novel adsorbent for adsorption of herbicide paraquat from aqueous solution in a continuously stirred adsorber and batch flasks, respectively. Taken into account of the negatively charged surface of diatomaceous earth and cationic property of paraquat, it was reasonable to explain the interaction between adsorbents and paraquat molecules using physical adsorption in the ion-exchange process [19]. In addition, spent diatomaceous earth (SDE) was successfully converted into mesoporous silica adsorbents using alkaline activation method. Under the experimental conditions investigated, it was found that sodium hydroxide significantly etched to proceed inwardly to the interior of the existing pore structure in the clay minerals, leaving a framework possessing a large Brunauer-Emmett-Teller surface area (over 100 $m^2\ g^{-1}$) and total pore volume (over 0.3 $cm^3\ g^{-1}$), as shown in Fig. 4. This observation was also in close agreement with the examinations on the SEM, XRD, and FTIR [20]. Furthermore, it was also reported that the regeneration with 1 M NaOH had the most obvious influence on SBE for fluoride adsorption than other regeneration methods. Compared with the adsorption capacity of various materials, it was found that the regenerated SBE was a promising, low-cost, and relatively efficient adsorbent for fluoride removal [21].

Salt Treatment

The SBE regeneration also can be achieved by chemical activation with salt solution. SBE was regenerated by chemical activation with low-cost and low-pollution chlorides as activating agents. Under the conditions of 600 °C for 1 h, the fresh bleaching earth and regenerated SBE were type IV with H3 hysteresis loops from nitrogen adsorption-desorption isotherms. Furthermore, the pore properties of these chemically activated samples were higher than those of the heat regeneration, but only an approximate 45% of surface area was reclaimed. It implied that the carbon residues were retained within pores and/or clogged the entrance of pores, resulting in a decrease in pore properties [22].

Surfactant Modification

Surfactant treatment can be employed to regenerate SBE from an edible oil refinery. It was reported that SBE was treated with cetyltrimethylammonium bromide

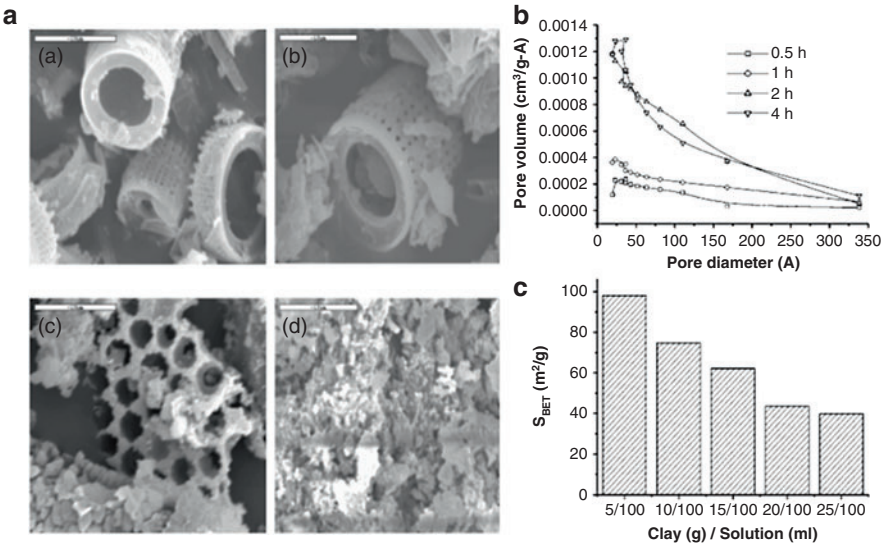

Fig. 4 (**a**) SEM photographs of the starting solids (DE and SDE) and the resulting activated solids (ASDE-T80 and ASDE-t3), (**b**) pore-size distributions of the resulting solids, and (**c**) effect of the solid/liquid ratio on BET surface areas of the resulting solid prepared at a NaOH concentration of 2.24 M, an activation temperature of 100 °C (boiling), and a holding time of 2 h (Copyright 2004, reproduced with permission from American Chemical Society)

solution not only to remove the oily residue impregnating the clay but also to insert the organic cation into the interlayer space leading to an organophilic clay. The prepared organophilic bentonite was used to remove the dye acid black 10B from the aqueous solution, and the maximum removal capacity was better than those of some nonconventional sorbents [23].

Combining of Various Methods

At present, it is generally believed that no single regeneration technique holds the key to an efficient regeneration of various SBE. A combination of regeneration techniques at minimal cost and better efficiency will certainly provide the optimum SBE regeneration alternative, which also is in line with the current trend of increasing the effective utilization of SBE for various purposes.

Solvent Extraction Followed by Thermal Process

SBE was subjected to ultrasound-aided in situ transesterification with a cosolvent to convert the oil into methyl esters (biodiesel). The remaining bleaching clay was then calcined at 500 °C for 30 min and reutilized for bleaching. The absence of -CH absorption peaks in the FTIR and TGA-FTIR analysis of regenerated clays showed the regeneration efficiency of this method. In situ transesterification and heat

regeneration helped to restore pores without adversely affecting the clay structure. The use of ethyl methyl ketone (EMK) as the cosolvent in the transesterification process produced clay with better bleaching qualities [24]. In addition, it was reported that solvent extraction of residual oil using excess EMK followed by heat treatment at 370 °C was the most effective SBE-regenerating protocol for copper adsorption. The obtained materials exhibited large cation exchange capacities of 6000 mg kg^{-1} of Na^+ ion equivalents favorable for cation uptake. This value was higher than the net negative surface charge of regenerated SBE, indicating that additional copper adsorption mechanisms play a role in addition to electrostatic interaction [25].

Acid Activation Followed by Thermal Process

The regeneration of SBE is conducted generally by preliminary acid impregnation followed by thermal process. The research has regenerated SBE by the impregnation of SBE in different amounts of sulfuric acid and under different activation temperatures. The optimum treatment process involved 10% sulfuric acid at 350 °C, and then the SBE was investigated for its potential in removing Cr(VI) from aqueous solution [26]. Similar regeneration method was applied for acid-treated SBE, which was prepared by treating spent bleaching earth, a waste material from the palm oil industry, with 20% sulfuric acid and heated at 350 °C for 3 h. The obtained material could be employed to adsorb a variety of organic dyes especially reactive and acid dyes, with maximum sorption capacity in the order of 2–300 mg g^{-1} [27]. In order to investigate the heat regeneration of SBE and to evaluate the performance of the heat-treated SBE in bleaching crude oil, two types of SBE were used, i.e., (a) acid-activated clay and (b) natural clay. Two types of regeneration processes were performed including (a) solvent extraction followed by heat treatment and (b) direct heat treatment. The results showed that SBE produced by the direct heated-regenerated spent bleaching clay yielded higher regeneration efficiency than the de-oiled-heated-regenerated spent bleaching clay produced by solvent extraction and heat treatment. It might be ascribed to the more complete removal of the moisture, impurities, and dirt by direct heating than by solvent extraction. Moreover, the direct heated-regenerated spent bleaching clay at 500 °C exhibited a higher specific surface area and total pore volume, as well as a better bleaching efficiency than that of at 400 °C and 800 °C [28].

Salt Activation Followed by Thermal and Acid Treatment

The SBE was first impregnated with a 3 M ammonium chloride solution, and then it was treated directly in furnace at 400 °C during an hour followed by washing with the cold HCl. The characterization results revealed that the heat treatment in furnace and the chemical treatment (decomposition of NH_4Cl) didn't affect the structure of montmorillonite of regenerated material. The study of porous texture by the nitrogen adsorption technique at −196 °C suggested that the decomposition of NH_4Cl under the heat effect caused an increase in microporosity in the regenerated material [29].

Base Impregnation Followed by Thermal Process

SBE has been treated by impregnation with a normal sodium hydroxide solution followed by mild thermal treatment (100 °C). The results indicated that the clay structure in the obtained was not apparently affected by the treatment, and the impregnated organic matter was quantitatively removed. Compared with the reported relevant references, the regenerated SBE exhibited good adsorption capacity of 258.4 mg g^{-1} and 555.6 mg g^{-1} for MB and safranine, respectively [30].

Application of the Regenerated SBE

Decontamination of Wastewater

Water pollution now becomes a worldwide problem that threatens human health, and the pollutants usually include heavy metal ions, dyes, pesticides, and antibiotics. Recently, researchers gradually focus on the adsorption materials derived from SBE for removal of those pollutants due to the abundant potential adsorption sites.

Removal of Heavy Metal Ions

The removal of heavy metal ions has been one of the main research interests in application of SBE-based materials for decontamination of wastewater. Heavy metal ions removed using the regenerated SBE-based materials have been published at least once including Cu(II), Pb(II), Cd(II), Cr(III), Ni(II), and Cr(VI). The adsorption of Ni(II) on treated SBE has been studied as a function of pH, adsorbent dosage, contact time, temperature, and initial Ni(II) concentration. The adsorption amount of Ni(II) increased with the increasing shaking time and temperature. Adsorption equilibrium was achieved in approximately 180 min. The removal ratio was up to about 99% at pH 11. This study will be contributed to solve this problem by recovering residual vegetable oil contained in spent bleaching clay and reuse the bleaching clay as a low-cost adsorbent [15]. The treated SBE was also investigated for removal of Cr(VI) from aqueous solution. The effects of contact time, pH, initial concentration, adsorbent dosage, temperature, adsorption isotherms, and the presence of other anions on the adsorption capacity were studied in detail. Isotherm data was fitted into a modified Langmuir isotherm model implying monolayer coverage of Cr(VI) on acid-activated SBE. The maximum adsorption capacity derived from the Langmuir isotherm was 21.2 mg g^{-1}, and this value was compared to those of some other low-cost adsorbents [26]. Among the heavy metal ions, Cd(II), Pb(II), and Cu(II) are the most commonly studied. Our studies indicated that the obtained APT/C nanocomposites derived from the low-cost available SBE exhibited high adsorption capacity within a wide pH range, and the faster equilibrium was achieved at lower concentration. As shown in Fig. 5, the maximum adsorption capacity for Cu (II), Cd(II), and Pb(II) was 32.32 mg g^{-1}, 46.72 mg g^{-1}, and 105.61 mg g^{-1}, respectively. The as-prepared nanocomposites displayed an excellent desorption performance and reusable ability for heavy metal ions. Using the adsorption of Cd

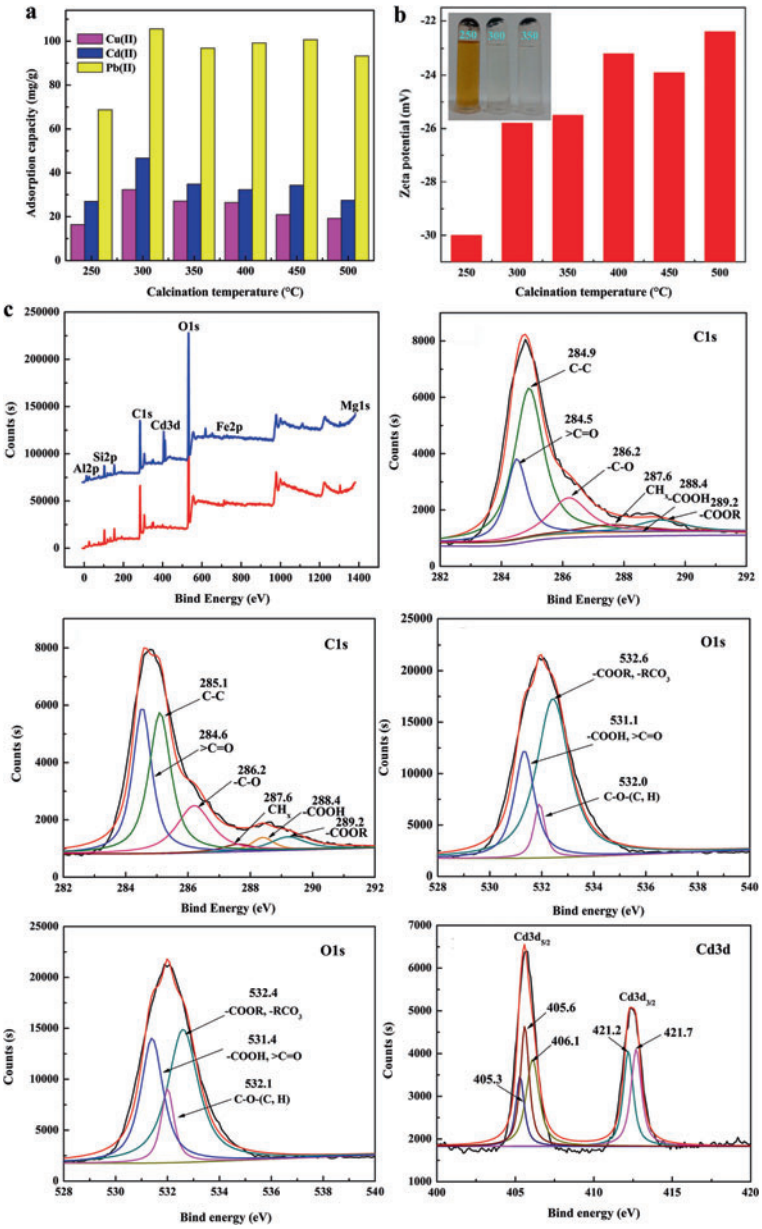

Fig. 5 (**a**) Effect of calcination temperature on adsorption capacity of Cu(II), Pb(II), and Cd(II), (**b**) ζ-potential of APT/C nanocomposites at different calcination temperatures (inset of the digital photograph of APT/C-250, APT/C-300, and APT/C-350 in ethanol), and (**c**) XPS spectra of APT/C-300 before and after Cd(II) adsorption. (Copyright 2015, reproduced with permission from American Chemical Society).

(II) as an example, it has been confirmed that the electrostatic interaction, cation exchange, and surface complexation between Cd(II) and functional groups on the attapulgite/carbon nanocomposites were the dominant mechanisms according to the results of the adsorption studies and XPS analysis [5].

To gain insight into the interaction between SBE-based adsorption materials and pollutants during the adsorption process, the effects and mechanisms of different treated SBEs on the adsorption of heavy metals were studied. Their effects are mainly manifested in the following aspects: (1) improvement or deterioration on the pore structure of the treated SBE, (2) effect on the surface functional groups of treated SBE, and (3) serving as active sites themselves. Compared with SBE, the amount of oxygen-containing functional groups (such as -COOH, -OH and -C=O, etc.) increased on the surface of the treated SBE after the mild treatment. The improvement of functional groups may provide more available bonding sites for heavy metal ions. And these functional groups might strengthen the interactions between the treated SBE and heavy metal ions by forming surface complexes, electrostatic attraction, and ion exchange, which might be applied to repair the polluted soil due to the high adsorption ability and strong bonding interaction to heavy metal ions. In addition, incorporating of nanometal oxide (e.g., MnO_2, ZnO, and Fe_3O_4) based on the treated SBE could obviously enhance the adsorption capacity to heavy metals [31].

Removal of Organic Pollutants

Dyes

SBE-based adsorbents also showed high adsorption capacity for organic pollutants. The concerned organic dyes include basic blue 3, MB, basic violet 4, basic violet 3, basic red 9, ethyl violet, methyl violet, acid black 10B, etc. The adsorption ability of these organic contaminants depended on the various treatment methods and the structure of the target organic contaminants. The potential application of carbonized SBE (CSBE) for removal of acid and basic dyes in aqueous solution was investigated. It was confirmed that CSBE was more effective for removal of basic dyes. According to Langmuir isotherms, the maximum adsorption capacities of CSBE for basic blue 3 and MB were 102.6 and 94.5 mg g^{-1}, respectively. Hence, CSBE could be a useful adsorbent for removal of basic dyes in wastewater [32]. Regenerated SBE was also used for the removal of three basic dyes (violet 4, violet 3, and red 9) from aqueous solution. The adsorption of the basic dyes by regenerated SBE at lower initial concentrations followed the order of basic violet 4 > basic violet 3 > basic red 9, which paralleled to the molecular weights and molecular sizes of the basic dyes [33]. In addition, the adsorption of ethyl violet and basic violet 4 from aqueous solution onto the regenerated SBE was carried out by varying the process parameters such as initial concentration, pH, and temperature. The experimental results showed that the adsorption of basic dye was pH and temperature dependent, and the maximum adsorption capacity of ethyl violet from aqueous solution took place at basic condition (pH 11) or acidic condition (pH 3) [34]. In addition, a study aimed at providing one option for utilizing SBE in the water treatment applications. SBE was

firstly burned to eliminate the oil traces, and then it was valorized according to two ways: (i) chemically using phosphoric acid to obtain SBEC and (ii) thermally at 750 °C to have SBEH. Three materials exhibited very interesting adsorption properties with specific surfaces of 194.2, 784.6, and 888.5 $m^2\ g^{-1}$ while the adsorption capacities to MB were 123.3, 185.2, and 188.7 mg g^{-1} for SBE, SBEH, and SBEC, respectively [35]. In our work, the attapulgite/carbon composites fabricated via one-step calcination of the SBE served as adsorbents for the removal of MB, with a maximum adsorption capacity of 132.72 mg g^{-1}, and the electrostatic attractions and hydrogen bonding between the attapulgite/carbon composites and MB molecules played a primary role in the whole adsorption process [36]. In addition, the organophilic bentonite derived from SBE was also used to remove the dye acid black 10B from the aqueous solution, and the maximum removal capacity obtained (100 mg g^{-1}) was superior to some nonconventional sorbents [23].

Herbicides and Pharmaceuticals

Herbicides and pharmaceuticals are emerging fetal pollutants with severe harm to organism, ecosystem, and human health, because they can kill the microorganism and induce the generation of "super-bacteria" [37]. An active carbonaceous char supported on a aluminosilicate matrix has previously been prepared by the chemical activation of SBE, and the adsorption experiments of phenol, 3-chlorophenol, and 2,3-dichlorophenol suggested that the surface char of the treated spent clay was sufficiently active to warrant a pilot investigation of this low-cost adsorbent for applications relating to wastewater treatment [38]. Furthermore, SBE was regenerated by the physical activation with CO_2 and steam, and the resulting solids with mesoporous structure possessed *BET* high surface area and had a high affinity to paraquat. Thus, the regeneration of this agro-industrial waste is one option for utilizing the clay resource, and it may be used for water treatment applications to remove organic contaminants [39].

Pesticides

2,4-Dichlorophenoxyacetic acid (2,4-D), an aryloxyalkanoic acid known as "phenoxy herbicide," is one of the most widely used pesticides around the world. 2,4-D is toxic to broad-leaved plants due to its polar nature; once absorbed it is translocated within the plant and accumulates at the growing points of roots and shoots where it inhibits growth [40]. The activated SBE can be proposed to be used to effectively treat wastewater containing 2,4-D. The removal of 2,4-D was found to depend on adsorbent dose, time, initial concentration of 2,4-D, and particle size [41]. In addition, the removal of MCPA (4-chloro-2-methylphenoxyacetic acid) from aqueous solutions using activated SBE was also studied as a function of time, initial concentration, adsorbent concentration, and temperature, and it was found that the acid-treated SBE could be used as an efficient adsorbent for the removal of MCPA-bearing wastewater effluents [42]. Activated carbon produced from SBE can be considered as an effective adsorbent for removal of carbamazepine. The adsorption equilibrium was achieved within 1 h, and pH effect on the adsorption of carbamazepine was not very significant [43].

Pyridines

Pyridine and its derivatives (alpha-picoline, gamma-picoline, etc.) are volatile, toxic, and flammable, with a pungent and unpleasant odor [44]. Acid-treated SBE was an excellent adsorbent for the removal of pyridine from wastewaters. The dependence of the adsorption of pyridine on the pH of the solution was studied to find the optimum pH value. The maximum adsorption was found to occur at pH 6.5 [45]. In addition, adsorbents were produced from SBE, and the individual adsorption of alpha-picoline and gamma-picoline by them was studied as a function of time, pH, and initial concentration. Maximum adsorption capacity was observed at pH between 8.13 and 8.77 [46].

From the views of environmental protection and resource recycling, the clay adsorbent prepared from spent bleaching earth is an option for the removal of environmental organic pollutants from the aqueous medium. As for the regenerated SBE, several mechanisms might be involved in the adsorption processes by the interactions between organic contaminants and functional groups of regenerated SBE, including π-π interactions, hydrogen bond, electrostatic attraction, and hydrophobic interaction. Our groups also prepared magnetic carboxyl-functionalized attapulgite/carbon nanocomposites derived from SBE for the high efficient adsorption of organic contaminants, which was mainly attributed to the strong interactions between the organic contaminant molecules and the adsorbent including π-π interaction, hydrogen bond, and electrostatic attraction [14].

Removal of Inorganic Pollutants

Apart from heavy metals and organic contaminants, removal ability of the regenerated SBE for other inorganic pollutants such as fluoride and ammonium ions was also investigated. Of which, fluoride is the most commonly studied inorganic pollutants. A study on the adsorption of fluoride using the regenerated SBE confirmed that the fluoride removal efficiency increased with the increase in the adsorbent dose, contact time, and pH. The maximum adsorption capacity of the regenerated SBE was 0.6 mg/g toward fluoride. When 10 g RSBE/L was added to Kuhbonan water, fluoride residual could reach levels allowable by WHO guidelines [21]. In addition, acid-treated SBE was studied to assess its capacity for adsorption of fluoride from aqueous solutions. It was found that the maximum adsorption of fluoride from aqueous solution took place at pH 3.5, and the influence of coexisted anions on the adsorption of fluoride was also studied to simulate industrial wastewater, and it was found that the addition of anions decreased the adsorption capacity of acid-treated SBE to fluoride [47]. In addition, the release of nitrogen compounds into the environment is also a major concern worldwide. It was reported that the regeneration of SBE acquired from the vegetable oil industry was surveyed via different methods, and the regenerated SBE (RSBE) was used for ammonium ion removal from aqueous solution in batch experiment. The survey showed the adsorbent possessed high selectivity toward ammonium ion, and the maximum removal efficiency of ammonium ion was up to 81% [48].

The adsorption of inorganic contaminants on the treated SBE could be governed by multiple mechanisms. Two main strategies were employed to adsorption

properties of the treated SBE to inorganic contaminants: (1) enhancing the surface area of the treated SBE and (2) designing nanocomposites on the treated SBE surface, which may dramatically increase the adsorption of inorganic contaminants from water. Several interactions between the treated SBE and the inorganic contaminants were proposed to explain the underlying adsorption mechanisms, including electrostatic attraction, surface complexation, hydrogen bond, and ion exchange.

Bleaching for the Edible Oil

Among the criteria of quality of edible oil, the color is certainly the most important factor for the commercial value of this oil. The color is due to the presence of pigments in the crude oil, such as chlorophyll-α and β-carotene. A paper reported on the efficiency of a spent bleaching earth regeneration process achieved by a thermal process, followed by acid leaching under a variety of experimental conditions. Optimal regeneration conditions have been controlled by decolorization tests of degummed and neutralized crude edible oil. Optimal values (temperature, 500 °C; carbonization time, 1 h; and HCl concentration, 1 M) gave a material as an efficient virgin bleaching earth. The percentage uptake of chlorophyll derivatives and β-carotenoids calculated at 410 and 460 nm is, respectively, 92.8 and 95% for oil processed by the regenerated spent bleaching earth, against 77.4 and 92.7% for the same oil processed by a commercial virgin bleaching earth. It was worth noting that the resultant oil did not undergo any changes in the iodine value, the free fatty acid content, and the saponification value after decolorization using the regenerated spent bleaching earth [49].

In addition, SBE can be converted to a clay-carbon adsorbent for potential reuse in the adsorptive cleansing of vegetable oils. Commercial and laboratory-prepared adsorbents were screened for their ability to remove colored pigments, impurities, and trace contaminants from rapeseed and crude coconut oils. Activated SBE demonstrated efficient removal to benzo[α]pyrene from crude coconut oil reducing the concentration from 12.8 μg kg^{-1} in the crude oil to 1.3 μg kg^{-1} (89.8% w/w removal) in the treated product at a 2.0% w/w adsorbent dose. Soybean and rapeseed process wastes activated under identical conditions exhibited similar removal efficiencies of 89 and 86% w/w, respectively. This removal ratio was compared to a reduction in benzo[α]pyrene concentration to 10.8 μg kg^{-1} for virgin bleaching earth (15.6% w/w) and to less than 0.1 μg kg^{-1} for commercial powdered activated carbon (> 99.2% w/w). However, activated SBE exhibited a limited removal of chlorophyll derivatives (27% w/w) and negligible uptake of the β-carotenoids and phosphorus from degummed rapeseed oil compared with the virgin bleaching earth, which showed effective bleaching of chlorophyll derivatives (98% w/w) and the β-carotenoids and removal of phosphorus (71% w/w). These adsorptive differences between these materials were interpreted with reference to interactions at the surfaces of acidulated montmorillonite and activated carbon [50].

Dehumidification

To circumvent the current pollution-prone disposal of SBE, an experimental program was conducted to recover the waste SBE and to use it for air dehumidification application. Waste SBE was obtained from the damping site of the oil industry, and the entrained oil was recovered via hexane extraction while the remaining hydrocarbons were oxidized with 30% H_2O_2 and heated at 550 °C. This reactivation procedure afforded oil useful in other ole-chemical applications and activated SBE for air dehumidification. For the purpose of adsorbent development, SBE regeneration was found to follow two routes, solvent extraction followed by oxidation using 30% H_2O_2 which retained the elasticity of the clay crucial in molding the adsorbents and thermal processing at 550 °C after molding. The adsorption characteristic of the adsorbent established two peaks when activated at 550 °C and 650 °C with a capacity of 27.07 and 26.63%, respectively. The regenerated SBE proved to be a promising adsorbent for moisture since its adsorption capacity was higher than that of clay (15%) which was commonly used as commercial desiccant [51].

Conclusions and Further Outlook

The latest progress on the regeneration and recycling of SBE has been concluded and discussed based on reviewing a comprehensive literature combined with our group's relevant research achievements. It can be safely concluded that the optimum regeneration method of SBE is thermal treatment followed by chemical activation, and the application of the as-prepared regenerated SBE-based materials is mainly focused on the adsorption materials, especially for removal of pollutants from wastewater, such as dyes, heavy metal ions, pesticides, etc. Beyond all question, it is also the main approach to realize the reasonable application of SBE in the future. Although SBE has been proved to be extremely successful in preparation of many materials with different distinctive structures and functional groups, there are still many aspects that need study, especially the practical application.

Progress has already been made in understanding some of the factors affecting the properties of SBE-based materials. Many factors have significant influences on the properties of the resulted materials. Among them, feedstock plays an important role in the fabrication process. This is mainly attributed to the different composition of various types of feedstock, such as the content of organic matters and the types of clay minerals. Therefore, the suitable feedstock with appropriate composition is needed to be chosen for preparation of SBE-based materials in the future studies, which is crucial to improve the adsorption properties for specific contaminants. In addition, pyrolysis conditions (thermochemical treatment, pyrolysis temperature, holding time, flowing gas, etc.) also have great effect on the adsorption performance of the regenerated SBE-based materials. However, little information is available about the effects of these factors, which are needed to be systematically studied in the future.

Apart from the synthesis methods existed and proposed during the review process, there are other potential methods which are suitable for the regeneration and recycling of SBE. It is essential to develop novel and environment-friendly technologies for producing SBE-based materials with suitable properties in a cost-effective way in the future. For instance, the immobilization of different kinds of organic functional groups onto SBE may achieve the selective removal of various pollutants from wastewater, especially non-regulated trace organic emerging contaminants (ECs). It includes halogenated flame retardants, surfactants, pharmaceuticals, illicit drugs, and personal care products which have caused increasing public concerns. These ECs have been widely detected and ubiquitous in the aquatic environment, which are mainly derived from the discharge of municipal wastewater effluents. The presence of ECs is of concern on account of their potential toxicological impacts on the environment ecosystem and human health (e.g., endocrine disruption). Therefore, it is imperative to tackle the ECs entering wastewater before discharging into the aquatic environment. Further studies about producing SBE-based functional materials with appropriate properties for EC removal should be conducted.

Although many potential applications of SBE-based materials have been widely studied combine the advantages of SBE matrix and various materials, more systematic and sustainable work should be conducted. For instance, the regenerated SBE materials exhibit excellent adsorption ability toward water pollutants, and it may be used as new potential in situ amendment sorbent for contaminated soil or sediment management. In addition, catalytic materials or microorganism can be incorporated into the regenerated SBE to be applied for simultaneous adsorption and in situ degradation of contaminants in soil or sediment.

For the future practical engineering application of the regenerated SBE-based materials in industrial scale as cost-effective materials, it should get insight into these important aspects regarding their reuses, the large-scale production, pollutant resource recycling, and the management of spent SBE-based materials. However, very little information is available about these aspects, which need the further investigations. The laboratory studies are commonly concentrated on the application of the regenerated SBE-based materials for simulated wastewater treatment, while their application in actual wastewater treatment is still lacked. The actual wastewater usually consists of divers pollutants; thus the selective removal and resource recycling of these pollutants are of great significance. During the engineering application process, it should be focused on the design and preparation of the regenerated SBE-based materials with selective adsorption ability for various pollutants in order to remove these pollutants separately, followed by desorption of pollutants and regeneration of adsorbent. Recycling studies of the regenerated SBE-based materials after adsorption are largely missing in the literature, with only several available researches. Therefore, desorption/regeneration properties are needed to be investigated, which is in favor of determining the reusability of SBE-based materials and evaluating the economic feasibility.

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