



# Modifying hollow glass microspheres to obtain self-floating separation adsorbents for adsorbing pollutants in wastewater: A review

Ruisi Qiu<sup>a</sup>, Bing Wang<sup>a,b,\*</sup>, Jiajian Shang<sup>c</sup>, Guojun Hu<sup>d</sup>, Linwei Yu<sup>e</sup>, Xuan Gao<sup>a</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, PR China

<sup>b</sup> Sichuan Provincial Key Laboratory of Environmental Pollution Prevention On Oil and Gas Fields and Environmental Safety, Chengdu 610500, PR China

<sup>c</sup> Oil and Gas Field Production Capacity Construction Division, China National Petroleum Tarim Oilfield Branch, Korla 841000, PR China

<sup>d</sup> Tongwei Solar (Chengdu) Co., Ltd, Chengdu 610500, PR China

<sup>e</sup> Faculty of Education, University of Macau, Avenida Da Universidade, Taipa, Macau 999078, PR China

## ARTICLE INFO

### Keywords:

Self-floating adsorbents  
Hollow glass microspheres  
Modification  
Regeneration  
Adsorption

## ABSTRACT

The adsorption method is widely used in wastewater treatment because of its advantages of simple operation, high efficiency, no secondary pollution, and reusability. In the process of adsorption, the recovery of adsorbents determines their economic feasibility and suitability for large-scale practical applications, so it is of great significance to develop new functional adsorbents with self-floating separation characteristics to replace traditional adsorbents. Hollow glass microsphere (HGM) is a kind of hollow closed sphere, which has the advantages of low density, stable chemical properties, reusable, excellent compression resistance, etc. Due to the unique structure and chemical properties of HGM, it has extremely high potential value in the field of wastewater treatment, and is an ideal carrier for preparing adsorbents with self-floating adsorbents. In this paper, the modification of HGM, the regeneration of adsorbents, the factors affecting the adsorption performance and challenges are reviewed. It is found that most of the existing modification methods of HGM are surface chemical modification, and the adsorption effect and regeneration are significant, but the adsorption effect is greatly affected by the change of pH. This review aims to provide a theoretical basis for the application of HGM in wastewater treatment, and for relevant researchers to develop adsorbent with HGM as the main body, clarify ideas, and explore the potential of developing HGM into practice for large-scale wastewater treatment.

## 1. Introduction

In recent years, the wanton discharge of industrial chemical waste from the factories which are not treated results in the water being contaminated, and associated severe damage to the ecological environment has aroused widespread concern [1]. Industrial wastewater contains inorganic and organic pollutants that are difficult to biodegrade [2]. For example, heavy metals cannot be decomposed in water, and are harmful to human health because of teratogenic, carcinogenic, and mutagenesis [3]; antibiotics accumulate in the body and become resistant to disease-causing bacterial [4]; and dye wastewater, which will lead to changes in water transparency [5] also contain heavy metal ions, organic pollutants, and other harmful substances to the environment. Therefore, untreated sewage flowing directly into rivers and lakes can have harmful effects on aquatic plants, animals, and humans. Due to these factors, industrial sewage needs to be treated to meet the standards

before discharge. However, traditional water treatment methods have been unable to meet the needs of social development, and the high-efficiency water treatment method emerges at a historic moment. For current emerging water treatment methods, heterogeneous photocatalysis [6], membrane technology [7], enzymatic degradation [8], adsorption [9], etc. have been presented.

Adsorption is widely used in wastewater treatment because of its high efficiency, simple operation, reusable adsorbents, and no treatment by-products [10]. Adsorption types can be roughly divided into two categories: (a) physical adsorption, and (b) chemical adsorption. During the adsorption process, contaminants are adsorbed to the adsorbents, which can be removed from the wastewater after the reaction reaches equilibrium [11]. The environmentally friendly biopolymer adsorbents, cation exchange resins and anionic hydrogels prepared by Rachid et al. showed remarkable chemisorption effects on dyes [12–16]. And the porous MOF-derived carbon prepared by Wang et al. has a significant

\* Corresponding author at: School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, PR China.

E-mail address: [wangb@swpu.edu.cn](mailto:wangb@swpu.edu.cn) (B. Wang).

<https://doi.org/10.1016/j.molliq.2024.124965>

Received 18 February 2024; Received in revised form 22 April 2024; Accepted 6 May 2024

Available online 12 May 2024

0167-7322/© 2024 Elsevier B.V. All rights reserved.

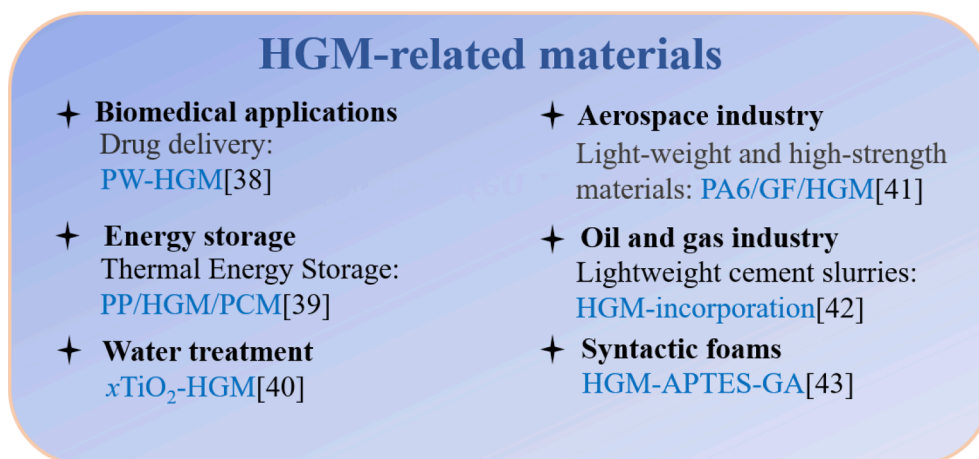
physical adsorption effect on bisphenol A [17]. Commonly used adsorbents are carbonaceous materials [18], transition metals oxide adsorbents [19], nano-adsorbents [20], metal-organic frameworks [21], magnetic adsorbents [22], and so on. In the adsorption process, the separation process of the adsorbent is an important influential part of the treatment efficiency of the whole process. And the above common adsorbents at this stage are difficult to achieve efficient and rapid solid-liquid separation, making it difficult to achieve the main treatment objectives of high efficiency and economy, and posing a great challenge for practical applications. The three traditional methods of separation include: (1) Precipitation. Requires regular scraping of the sediment tank; (2) Filtration. Requires backwashing and consumes filter material; (3) Magnetic separation. Requires external magnetic field. None of them are satisfactory for cost-effective separation. Therefore, the immediate goal is to develop a stable and lightweight self-floating adsorbent that can be quickly and effectively separated from water. This refers to the adsorbent that can be enriched on the water surface without external forces by the natural flow of water after the adsorption process, making it easy to collect and separate from water.

Hollow glass microspheres (HGM) are small, light white spherical particles with a diameter of 10–250  $\mu\text{m}$  [23]. As a kind of hollow and closed spherical material, HGM has many advantages, such as high-pressure resistance, low heat transfer coefficient, non-toxic, electrical insulation, good dispersity, and fluidity. It has been successfully used in aerospace [24], petroleum exploration [25], and other important industrial fields due to its stable physical and chemical properties. HGM is often combined with other compounds to provide superior performance. Epoxy resin is a good adhesive, but it is brittle, and the compressive strength of epoxy resin filled with HGM is improved [26]. The composite foam with low density, high compressive strength, low water absorption, and good thermal insulation can be obtained by mixing HGM into the foam matrix. By combining HGM with other materials, the compressive strength of composites can be improved effectively. In the study of Yoo et al., it was found that the collapse pressure increased with the decrease in the size of HGM [27], indicating that the compressive strength of the microspheres could be changed by controlling the radius of the microspheres. Photocatalysis is a common method for wastewater treatment, but its photocatalytic efficiency is often reduced due to its agglomeration or gravity deposition in an aqueous solution. Using HGM as a photocatalyst load can often improve this problem. According to Wang et al., a floating photocatalyst (ZIS@HGM) was prepared by loading the photocatalyst onto HGM, which significantly improved the light utilization rate and catalytic efficiency [28], and at the same time helped to recycle the catalyst and reduce the cost in practical application. The example of preparing synthetic foams with different densities

of low, medium, and high using HGM by Ozkutlu et al. shows that increasing the density of HGM can improve the mechanical properties of the composite foam while reducing the density [29]. In other words, this provides relevant insight into the use of HGM to maintain low weight while providing greater compressive strength to the polymer as the best candidate material for self-floating separation adsorption carrier. Fig. 1 shows the application and examples of HGM-related materials. Based on its modified and abundant applications in various industries and industries mentioned above, with multidimensional existing studies, examples of HGM being modified and successfully put into large-scale practice abound implying that it is quite possible and promising to modify HGM to prepare ideal self-floating adsorbent and to develop its large-scale applications for wastewater treatment. An et al. first proposed the concept of self-floating adsorbents and first prepared self-floating adsorbents for the treatment of dye wastewater in 2019 [30]. Subsequently, a series of functional self-floating adsorbents were prepared by grafting different functional groups onto the surface of HGM, thus providing specialized adsorption properties to specific pollutants and making its adsorption highly selective, which is different from traditional adsorption materials [30–37].

## 2. Scope of the review

Although there are few effective functional groups on the surface of HGM, the adsorption ability of HGM for specific pollutants, such as heavy metals, dyes, organic compounds, etc., can be obtained by modification after grafting with specific functional groups. The purpose of this review is to critically discuss the research results on self-floating adsorbents, with particular attention to modification methods, factors affecting adsorption effects, and regeneration methods for adsorbents. This is the first review that systematically summarizes the modification methods of HGM and its application as an adsorbent in wastewater treatment. In addition, the adsorption mechanisms, adsorption isotherms, and adsorption kinetics are also discussed to clarify the adsorption behavior of pollutants on the self-floating adsorbents based on HGM. However, the research on modified HGM as adsorbent is in its infancy, and most of the literature focuses on post-grafting method. By providing this paper, it offers more theoretical support for using modified HGM as an adsorbent, as well as providing new ideas for the development of novel functional adsorbents for researchers. This may guide the generation of new innovative modification methods, thereby obtaining self-floating adsorbents that can efficiently adsorb pollutants, rapidly separate and recover, and are environmentally friendly.



**Fig. 1.** Applications and examples of HGM-related materials: PW-HGM [38], PP/HGM/PCM [39], xTiO<sub>2</sub>-HGM [40], PA6/GF/HGM [41], HGM-incorporation [42], HGM-APTES-GA [43].

### 3. Synthetic of self-floating adsorbents

The surface functionalization methods of hollow glass microspheres include surface grafting, surface coating, surface metallization and surface zeolization. In existing studies, surface modification of HGMs for adsorption of pollutants in water are usually carried out by surface grafting. The modification methods of HGM are summarized and concluded as follows.

#### 3.1. Synthetic steps

According to existing studies, the preparation process of self-floating adsorbent can be roughly divided into three steps, and the overall process as shown in Fig. 2.

- (1) Alkali treatment (pretreatment) of HGM: The main component of HGM is silicon dioxide, when sodium hydroxide reacts with silica, the stable Si-O-Si bond can be broken to form Si-OH, and the hydrogen atom in Si-OH is easy to bond with the organic linkers. This chemical property is facilitative to the subsequent modification. According to the study of An et al., HGM reacts with an appropriate amount of sodium hydroxide solution at high temperature for several hours, and the surface roughness of HGM increases after alkali treatment [31]. There is a significant difference in adsorption performance between the unpretreated and pretreated adsorbents: by observing scanning electron microscope (SEM) images, the surface of the original HGM (Fig. 3a) without any treatment can be regarded as smooth; while the surface of PHGM (Fig. 3b) obtained after pretreatment has crumb-like material adhering under the effect of NaOH corrosion [32]. This significantly increased the specific surface area and surface roughness of PHGM, which means pretreatment facilitated more surface grafting, providing more possibilities for surface modification of HGM. An et al. prepared unpretreated adsorbent (UP-SFA) and pretreated adsorbent (SFA), and their SEM images are shown in Fig. 3c–d. The unpretreated microspheres have a smooth surface, which is not conducive to the subsequent grafting of silane coupling agents, resulting in a huge difference in the adsorption performance of SFA and UP-SFA, which is demonstrated by the maximum adsorption capacity of the adsorbent for AO7 and Amaranth, UP-SFA only showed

approximately 50 mg/g and 25 mg/g respectively, while SFA reached 428.99 mg/g and 145.62 mg/g, showing a great difference. Furthermore, Table 1 shows the EDS analysis of HGM, PHGM, UP-SFA, and SFA: UP-SFA and SFA contain nitrogen, indicating successful grafting of KH550; And the nitrogen content of SFA was higher than UP-SFA, indicating that pretreatment promoted the grafting of KH550 [32].

- (2) Coating of organic binding agent: HGM is difficult to bind directly to organic compounds because of the incompatibility of inorganic silica with organic matrices [44]. The coating of organic linker on rough PHGM surface is beneficial to the subsequent grafting reaction. Most of the existing studies have used silane coupling agents as organic linkers, and a few studies have used polydopamine and chitosan. The general structural formula of silica can be expressed as  $Y(CH_2)_nSiX_3$ , in the presence of water, the X group in silane coupling agent hydrolyzes to form Si-OH, and then condensates with Si-OH on the surface of PHGM to form Si-O-Si, the mechanism is shown in supplemental document Fig. S1 [45]. In the studies of Zheng et al., silane coupling agent A-1100 [30–34,46] and A-171 [47] were used as linkers to modify HGM, and a series of self-floating adsorbents were prepared for adsorbing dyes. Polydopamine modification is a simple and adaptable method for coating even on solid surfaces with low surface energy [48]. Messersmith found that when dopamine (DA) contacts with air under weakly alkaline conditions (pH = 8.5) [49], it polymerizes and forms a polydopamine (PDA) film on almost any solid surface, which contains large amounts of amino and hydroxyl groups and is easily functionalized. The formation mechanism of polydopamine is complex. As shown in supplemental document Fig. S2, the covalent oxidative polymerization and physical self-assembly mechanisms proposed by Kim et al are currently relatively comprehensive and widely accepted [50]. Zheng et al. [51] took advantage of the excellent self-assembly property of dopamine to form a polydopamine biomass coating on the surface of PHGM, and then introduced sulfonic acid groups to successfully prepare a self-floating adsorbent with significant adsorption effect on tetracycline. Chitosan is one of the most abundant polysaccharides in nature [52], which can form a stable film on the surface of inorganic substances. As shown in supplemental document Fig. S3, chitosan contains a large number of amino and hydroxyl functional groups

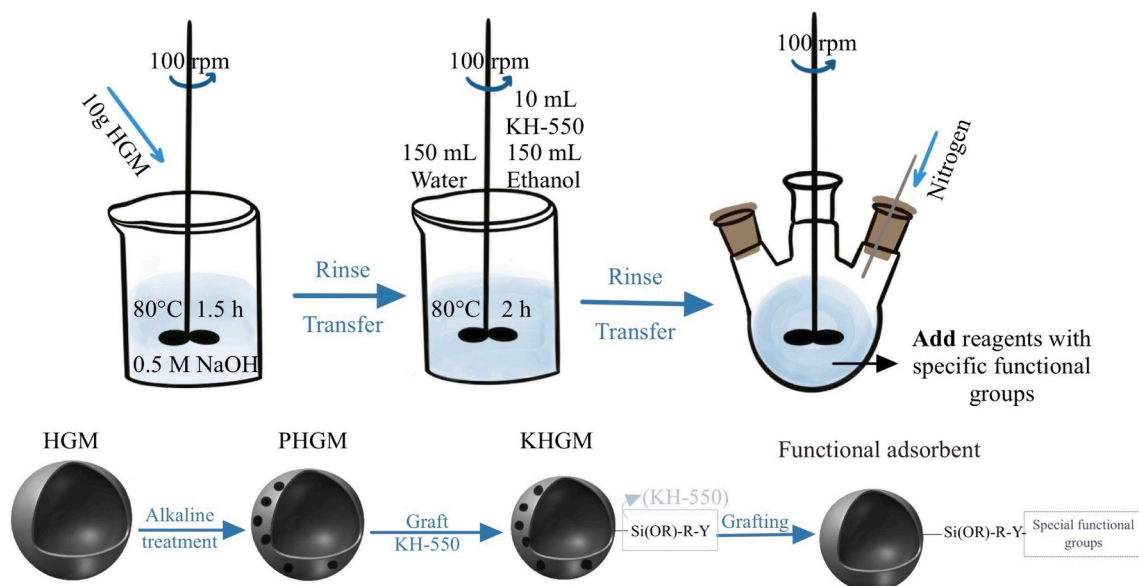


Fig. 2. Overall preparation process of the self-floating adsorbent.

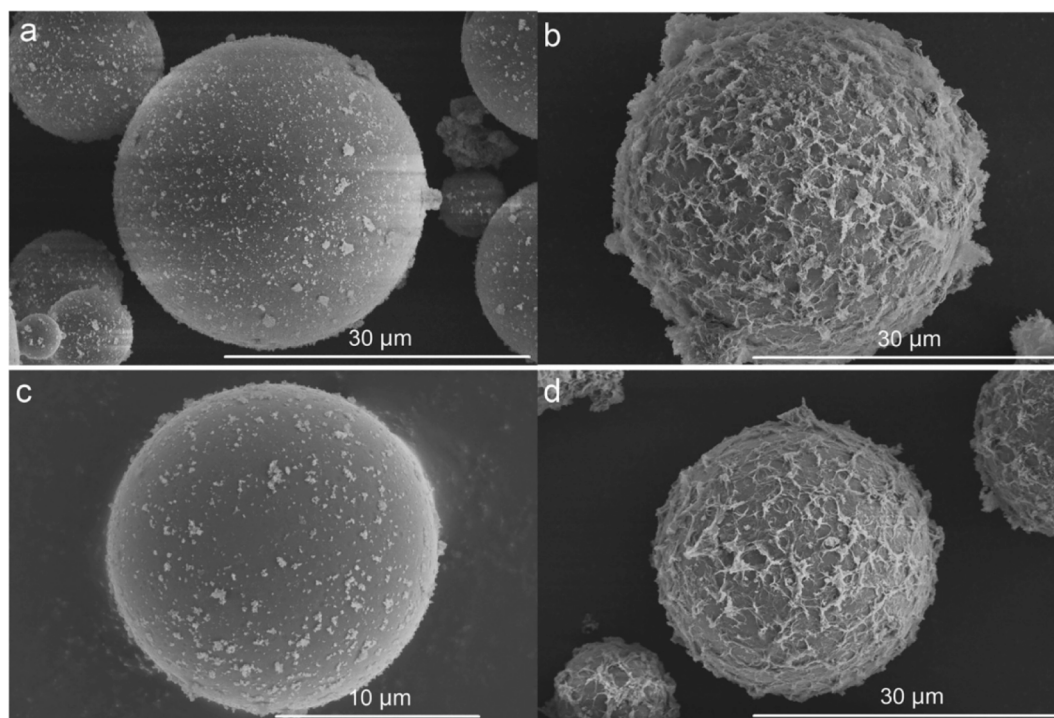


Fig. 3. SEM images of HGM (a), PHGM (b), UP-SFA (c), and SFA (d) [32].

Table 1

Comparison of main elements content of HGM, PHGM, UP-SFA, and SFA [32].

Microparticles	HGM	PHGM	UP-SFA	SFA
Content of C (Wt. %)	11.42	10.37	12.08	14.83
Content of N (Wt. %)	—	—	0.83	4.71
Content of O (Wt. %)	31.72	33.52	31.47	29.50
Content of Si (Wt. %)	41.91	41.19	40.81	38.78
Others (Wt. %)	14.95	14.92	14.81	12.18

[53], it has strong bonding effect on various pollutants, so chitosan is often impregnated on the surface of the carrier as adsorption sites. In the study of Zhao et al. [54], chitosan was coated on the surface of HGM as an intermediate layer, which improved the modifiability of HGM and prepared pH-independent adsorbent for anionic dyes. Compared with silane coupling agents, polydopamine and chitosan have the advantages of non-toxicity and are environment-friendly. In follow-up studies, non-toxic and harmless reagents with significant adhesion effect should be considered as organic coatings for PHGM.

- (3) The grafting of different functional groups: The surface of PHGM coated with organic linkers contains a large number of functional groups, such as hydroxyl and amino groups, which not only increase the adsorption active sites, but also provide reaction sites for subsequent functional groups grafting. In most existing studies, modification of HGM is usually achieved by ammonification or acidification. The effects of different group-functionalized HGM on the adsorption of pollutants in wastewater are summarized below.

### 3.2. Modification with different functional groups

The low content of functional groups on the surface of raw HGM limits its application as floating adsorbents. Some researchers have done a series of studies on the modification of HGM, and the modified adsorbents have high adsorption capacity for anionic dyes, cationic dyes, heavy metals and antibiotics, and also can achieve self-floating

separation. The following is a summary of different functional groups modified HGM.

An et al. aminated HGM and prepared several self-floating adsorbents for the treatment of dye wastewater. According to their studies [32,34], the aminosilane coupling agent  $\gamma$ -Aminopropyl triethoxysilane (KH550) was grafted on the surface of alkali-treated HGM to obtain amination HGM. The adsorption effect of KH550 functionalized HGM on anionic dyes was greatly affected by pH, when the pH ranged from 2.1 to 2.4, the adsorption capacity suddenly decreased (Fig. 4a) [33]. This is due to  $-\text{NH}_2$  being more likely to protonate under a strongly acidic environment, lone paired electrons of nitrogen atoms combined with protons to form a positive charge  $-\text{NH}_3^+$ , which adsorbed anionic dyes through electrostatic interaction. And then they co-grafted KH550 and methacryloxyethyl trimethyl ammonium chloride (DMC) to the surface of HGM to prepare polymer-grafted DFA. The surface area of DFA was  $40.146 \text{ m}^2/\text{g}$ , and the specific surface area of AFA was  $10.904 \text{ m}^2/\text{g}$ , which was mainly caused by multilayer grafting of DMC. The results showed that AFA had better adsorption capacity, while DFA had stronger pH and temperature adaptability (Fig. 4a). In the follow-up study of An et al. [35], KH550 and ethylenediaminetetraacetic acid (EDTA) were co-grafted to the surface of HGM (A-E@HGM) to selectively and efficiently adsorb  $\text{Co}^{2+}/\text{Ni}^{2+}$  in the cathodic leachate of lithium batteries, reducing the loss of lithium to 1 %, providing a new strategy for lithium recovery of waste lithium batteries. The carboxyl groups in EDTA and the amino groups in APTES are dehydrated and condensed to form amide groups, which can chelate with  $\text{Co}^{2+}/\text{Ni}^{2+}$ ; In addition, the carboxyl groups in EDTA are deprotonated with the increase of pH to form an electrostatic attraction between  $-\text{COO}^-$  and  $\text{Co}^{2+}/\text{Ni}^{2+}$ . The above studies indicate that amino functionalized self-floating adsorbents can be successfully prepared by single grafting amino-silane coupling agent or co-grafting amino-silane coupling agent and other nitrogen-containing reagents on HGM surface, but this modification method is greatly affected by pH, and its application in practical wastewater treatment is hindered. Zhao et al. grafted the cationic monomer methacryloxy ethyl dimethylammonium chloride with aromatic groups on the surface of chitosan-coated HGM to prepare the adsorbent BDSA, and the removal rate of AG25 was more than 90 %



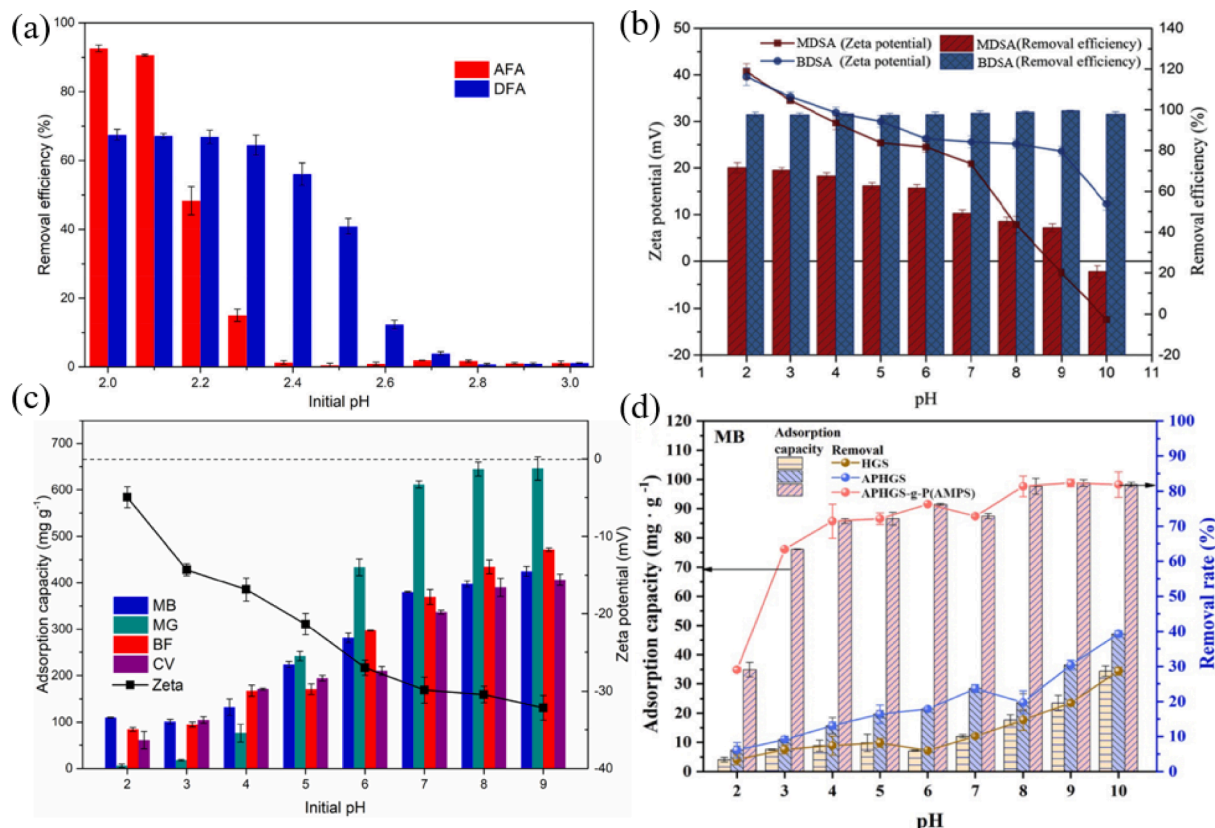


Fig. 4. Effect of pH on adsorption performance (a: [33]; b: [54]; c: [30]; d: [47]).

in the pH range of 2–10 [54]. The AG25 removal rate and pH adaptability of MDSA grafted with traditional cationic monomer ethyl acrylate trimethylammonium chloride without aromatic groups were much lower than that of BDSA (Fig. 4b). The introduction of aromatic groups makes the  $\pi$ - $\pi$  stacking effect between the adsorbent and the aromatic ring in the AG25, enhances the adsorption effect, solves the problem that anionic dyes can only be adsorbed under strong acidic conditions, and provides theoretical support for the application of HGM in a wider range of pH.

In addition to introducing nitrogen-containing functional groups to aminate HGM, sulphonated HGM can also be obtained by introducing sulfur-containing functional groups on the surface of HGM. An et al. [36] introduced trimethoxysilyl propanethiol to the surface of pretreated HGM, and then oxidized it to obtain sulphonated HGM( $\text{SO}_3\text{H}$ -HGM), which has good adsorption properties to ciprofloxacin (CIP) and nickel ions, and has a broad pH adaptability. Zheng et al. [30] grafted silane coupling agent A-1100 on the surface of PHGM, and then introduced AMPS to prepare adsorbent AFA. As shown in Fig. 4c, AFA is negative charged in the pH range of 2–9, and has a good adsorption capacity for cationic dyes in a wide pH. Tang et al. [47] co-grafted silane coupling agents KH550 and A-171 on the surface of HGM (APHGS), and then introduced 2-acrylamide-2-methylpropane sulfonic acid (AMPS) to prepare the self-floating adsorbent APGS-G-P. It can be seen from Fig. 4d that APGS-G-P has adsorption effect on methylene blue and Pb (II) in a wide pH range. Compared with APHGS, the adsorption effect of APHGS-G-P is significantly improved, because the introduction of sulfonic acid groups attracts cationic methylene blue through electrostatic attraction and chelating with metal ions. The above studies show that the introduction of sulfonic acid groups can improve the adsorption capacity of the self-floating adsorbents on cationic dyes to a certain extent, because the sulfonic acid groups can be completely ionized in the pH range of 2–10, resulting in a decrease in the zeta potential of the adsorbents and enhanced the electrostatic attraction between the self-floating

adsorbents and the cationic dyes. In the subsequent study of Zheng et al. [46], a floating-magnetically responsive adsorbent (FMSA) was prepared by embedding  $\text{Fe}_3\text{O}_4$  and grafting organic monomer sodium propylene sulfonate, which achieved high adsorption capacity of cationic dyes (Basic Blue 7:  $1632.55 \text{ mg g}^{-1}$ ; Crystal Violet:  $1587.23 \text{ mg g}^{-1}$ ) and a more efficient and rapid separation. In the same way, the introduction of negatively charged functional groups on the HGM surface can have a good adsorption effect on cationic dyes. Wang et al. [55] combined HGM with a new composite material of tetrafluoroterephthalic acid-crosslinked cyclodextrin polymer, and the obtained self-floating adsorbent FTFCD had a removal rate of malachite green (MG) above 95 % in the pH range of 1–10. Because the surface of the adsorbent contains phenolic acid groups, cationic dyes can be adsorbed by electrostatic action. In addition, the hydrophobic cavity structure of cyclodextrin is also the main reason for the removal of MG.

The above studies show that the amination modification of HGM can remove anionic pollutants at the appropriate pH, while the acidified HGM can adsorb cationic pollutants significantly. These adsorption processes are mainly dependent on electrostatic interactions.

Based on these, amination and acidification modification can be applied to HGM at the same time to achieve multi-functional adsorption performance. An et al. [31] grafted KH550 on the surface of HGM and subsequently co-grafted m-phenylenediamine (MPD) and sodium allyl sulfonate (ALS) on the surface (Fig. 5a) to obtain the self-floating adsorbent HGM@MPD-ALS. The surface of HGM@MPD-ALS contains aromatic rings, amino and sulfonic acid groups, which can attract both anion green 25 and cationic basic fuchsin. The adsorption mechanisms involved mainly include electrostatic attraction, hydrogen bonding and  $\pi$ - $\pi$  stacking (Fig. 5b). It is possible to introduce different functional groups with opposite charges on the HGM surface to obtain the self-floating adsorbents which can adsorb both anionic and cationic pollutants.

In addition to using silane coupling agents as the intermediate layer,

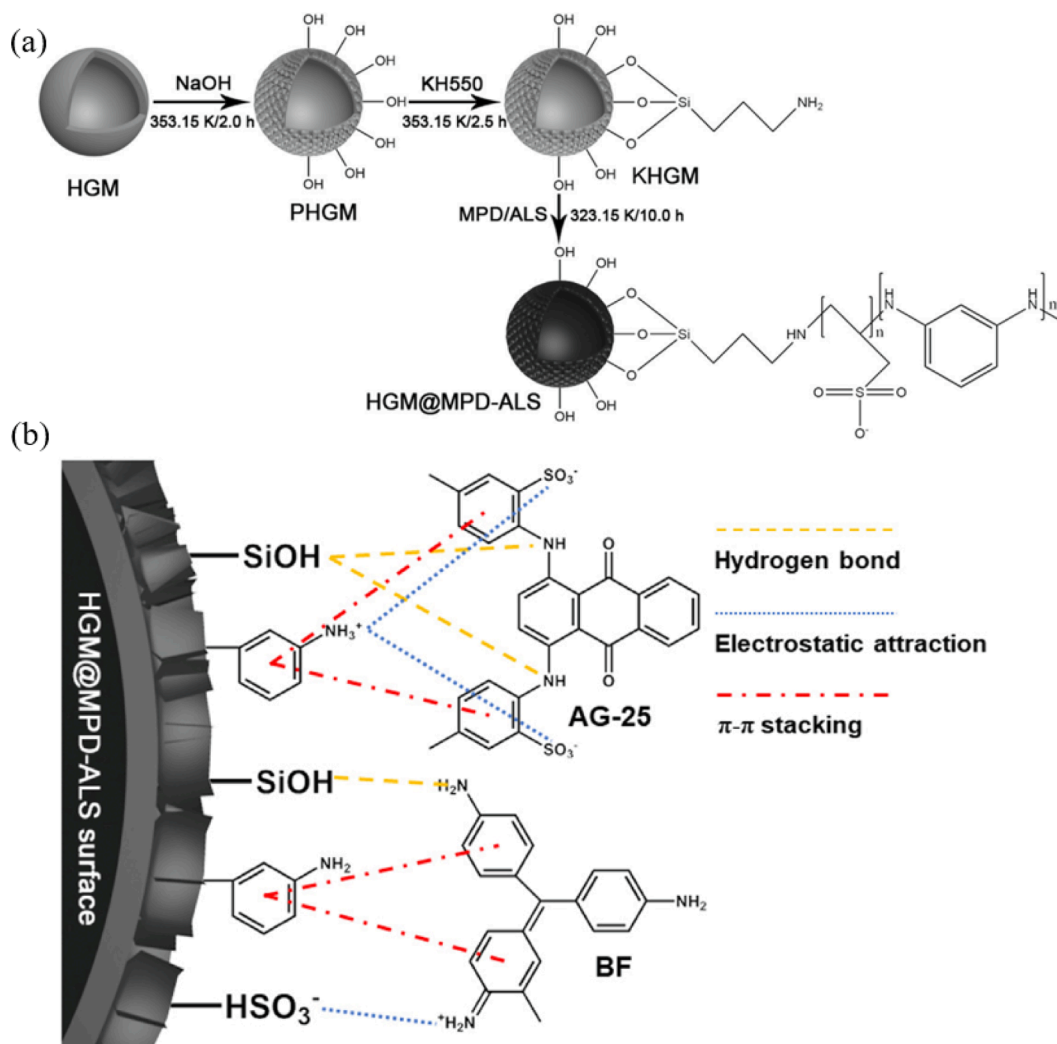


Fig. 5. (a)The synthesis procedure of HGM@MPD-ALS, (b)Adsorption mechanisms of HGM@MPD-ALS for AG-25 and BF removals [31].

the surface of HGM can also be coated with polydopamine to achieve subsequent modification. An et al. [37] grafted polydopamine and methacryloyloxyethyl trimethyl ammonium chloride (DMC) onto HGM to prepare an enhanced functional adsorbent (EPDA-SA). The graft of DMC not only increased the molecular weight of the polymer but also made its surface carry a positive charge, which caused an excellent adsorption effect on alizarin anthocyanin green F. In consideration of environmental friendliness, HGM can be modified with natural substances. Taurine is an amino acid that is converted from sulfur-containing amino acids. Taurine is widely distributed in various tissues and organs in the body, and is mainly present in the interstitial fluid and intracellular fluid in a free state [56], and was first found in the bile of bulls. Hu et al. [51] coated the surface of HGM with polydopamine and grafted taurine to prepare an eco-friendly self-floating adsorbent (HGM@PDA-SO<sub>3</sub>H) with a theoretical saturated adsorption capacity of 333.70 mg g<sup>-1</sup> for tetracycline. The existence of polydopamine can improve the hydrophilicity and biocompatibility of the substance, and at the same time, polydopamine can have π-π interaction and hydrogen bonding between PDA and tetracycline molecules. However, these forces are weak, and it is necessary to introduce sulfonic acid groups to improve the adsorption effect.

In summary, the above are the latest studies on modification of HGM as an adsorbent, and the adsorption properties of self-floating adsorbents modified with different functional groups are summarized in Table 2. As can be seen from Table 2, the current self-floating adsorbents

modified by HGM are mainly used for the adsorption of dyes, mainly relying on the electrostatic attraction between adsorbents and dye molecules. Hagio [57] deposited silicalite-1 and TiO<sub>2</sub> layer by layer on the surface of HGM to prepare a tri-layer floating photocatalyst/adsorbent with both adsorption and catalytic functions, which carried out thorough mineralization of pollutants while adsorbing them, and fundamentally eliminated the impact of pollutants on the environment. Using HGM as the substrate to load photocatalytic nanoparticles can not only achieve rapid separation, but also improve the efficiency of light utilization. According to the latest retrieval data on Web of Science, the adsorption of emerging pollutants (such as perfluorinated compounds and endocrine disruptors, etc.) has become a hotspot. Basheer [58] reviewed the new nano adsorbents for the removal of emerging pollutants. In the later research, HGM can be used as a carrier to prepare self-floating adsorbent through post-grafting modification, and can also be loaded with photocatalytic materials to enable them to have both photocatalytic and adsorption functions, which can effectively treat emerging pollutants.

### 3.3. Self-floating separation ability

The rapid separation of adsorbents from wastewater is important in the entire adsorption process. In past studies, magnetizing the adsorbent is the main method for rapid separation, but this method involves the design of the magnetic separation device [59]. In recent years, hollow

**Table 2**  
The adsorption performances of the adsorbents are modified by different functional groups.

Adsorbent	Target pollutant	S <sub>BET</sub> (m <sup>2</sup> /g)	Adsorption mechanism	q <sub>e</sub> (mg/g)	Kinetics/isotherms model	Ref.
Am-SA	AO7-CV	32.73	electrostatic	—	PSO/Langmuir	[34]
SFA	AO7	9.56	electrostatic	428.99	PSO/Langmuir	[32]
	amaranth			145.62		
DFA	AO7	40.15	electrostatic	77.52	PSO/Langmuir	[33]
A-E@HGM	Co <sup>2+</sup> /Ni <sup>2+</sup>	9.12	electrostatic, chelation, ion exchange	94.23/ 62.41	The kinetic model changes with the adsorption stage; Langmuir	[35]
MDSA	AG25	5.36	electrostatic	260.98	PSO/Both Langmuir and Freundlich can fit well.	[54]
BDSA	AG25	3.16	electrostatic, $\pi$ - $\pi$ stacking	326.92	PSO/Both Langmuir and Freundlich can fit well.	[54]
SO <sub>3</sub> H-HGM	CIP	14.95	electrostatic, hydrogen bonding, hydrophobic, surface complexation	464.78	PSO/Langmuir	[36]
	Ni <sup>2+</sup>			19.65		
AFA	MB	8.89	electrostatic	436.8	PSO/Langmuir	[30]
	MG			637.6		
	BF			457.8		
	CV			399.4		
APGS-G-P	MB	33.36	electrostatic, chelation, hydrogen bonding, cation exchange	249.33	PSO/Langmuir	[47]
	Pb (II)			345.93		
FMSA	BB-7	58.85	electrostatic, cation exchange	1632.55	PSO/Langmuir	[46]
	CV			1587.23		
FTFCD	MG	105.36	electrostatic, hydrophobic	1390.26	PSO/Langmuir	[55]
HGM@MPD-ALS	AG25	9.30	electrostatic, $\pi$ - $\pi$ stacking, hydrogen bonding	454.55	PSO/Langmuir	[31]
	BF			588.24		
EPDA-SA	alizarin cyanine green F	21.87	electrostatic, $\pi$ - $\pi$ stacking	63.40	PSO/Langmuir	[37]
HGM@PDA-SO <sub>3</sub> H	TC	74.99	electrostatic, hydrogen bonding, $\pi$ - $\pi$ stacking	333.70	PSO/Langmuir	[51]

glass microspheres have attracted more and more attention because of their green and stable characteristics, and the floating adsorbent using HGM as the carrier came into being. To evaluate the floating performance of a series self-floating adsorbents, a certain amount of adsorbent powder was mixed with an appropriate amount of ultrapure water and placed in a measuring cylinder, and the turbidity of the suspension was measured at a certain time interval. In the series studies of the functionalized HGM, the adsorbents all had the desired uplift rate, and the experimental data are shown in Table 3. The density of the prepared microspheres is lower than that of water, thus they can float in most liquids. It indicates that the self-floating ability of HGM modified by various functional groups is not damaged, and the upward floating speed of microspheres is fast at first and then becomes slow. According to Stokes equation (Eq. (1)), the floating speed is proportionate to the square of the radius of the microsphere. The microspheres with a larger radius float to the surface of the water first, while the remaining microspheres with a smaller radius need more time to float. In addition, the self-floating speed of these adsorbents is moderate, which not only avoids insufficient contact between the adsorbent and the adsorbate but

also does not make the self-floating separation time too long.

$$v = \frac{2(\rho - \sigma)ga^2}{9\mu} \tag{1}$$

where  $v$  is the self-floating equilibrium velocity;  $\rho$  and  $\sigma$  are the densities of the adsorbent and the medium, respectively;  $\mu$  is the viscosity of the medium.

3.4. Regeneration

Considering the economic feasibility of the practical application, the reusability of adsorbents plays an important role. The regeneration of adsorbents not only reduces the cost of the adsorption process but also can recycle some pollutants (such as dye concentration and recovery of precious metals). Adsorbents regeneration technologies include chemical regeneration, thermal regeneration, microwave regeneration, biological regeneration [60], and so on. Many factors of the regeneration process of adsorbents need to be considered, such as pH, temperature, and contact time [61].

In chemical regeneration, the selection of a desorption agent is contrary to the principle of the adsorption process. For example, the desorption agent should be acidic if the best adsorption is achieved under strongly alkaline conditions [62]. In the study of Hu et al., SO<sub>3</sub>H-HGM adsorbed with cationic contaminants (ciprofloxacin and nickel ions) was desorbed using 0.1 M HCl as an eluent [36]. Hydrogen ions in HCl have a stronger affinity to the active adsorption sites on SO<sub>3</sub>H-HGM and can replace ciprofloxacin and nickel ions for desorption. Additionally, HCl can protonate the functional groups on the surface of the adsorbents and weaken the interaction with the adsorbed molecules. The charge on the surface of the adsorbent can be changed by varying the pH value of the solution. In the study of An et al. [37], NaOH was used as the

**Table 3**  
The self-floating ability of modified HGM.

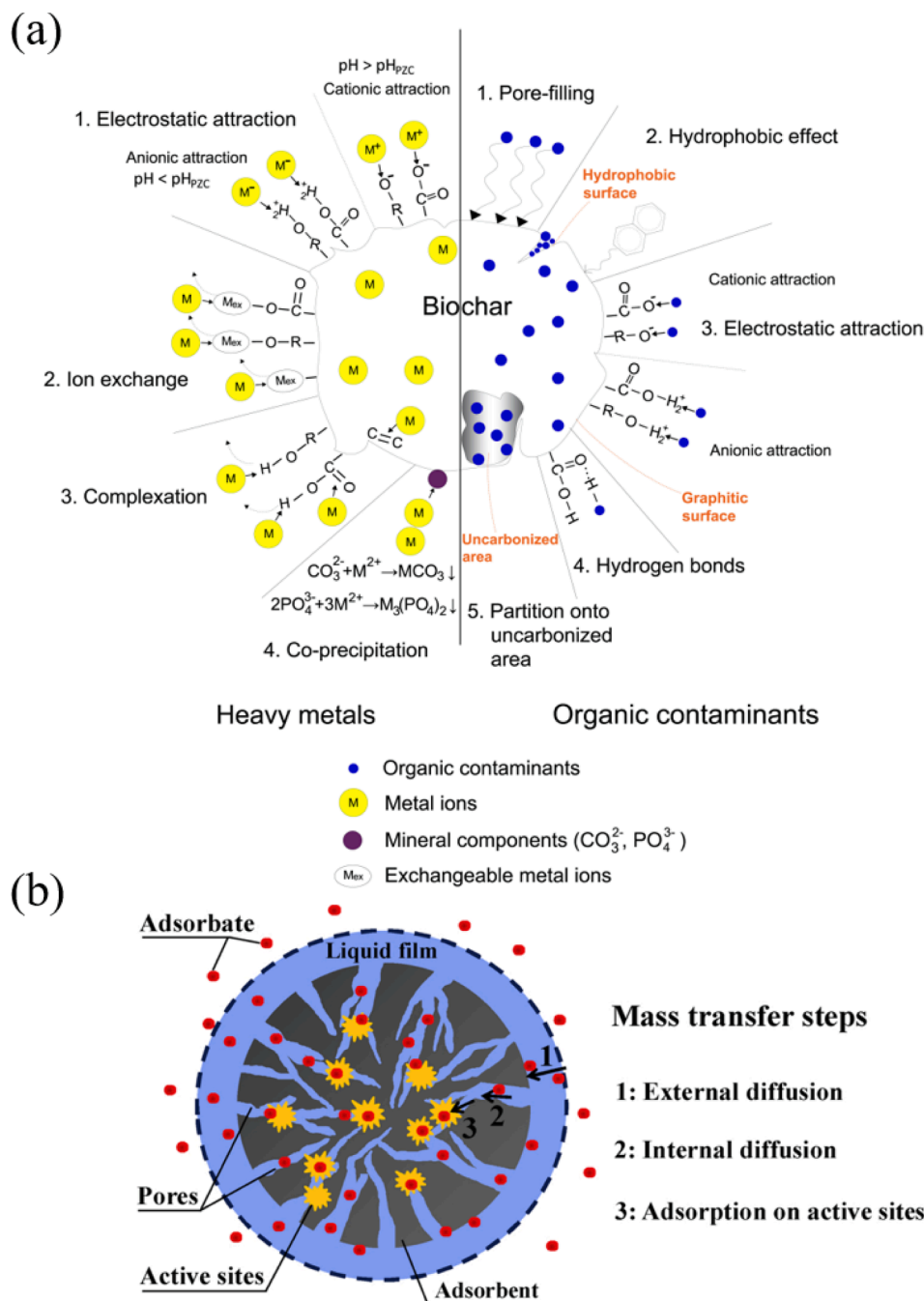
Adsorbent	Density (g·cm <sup>-3</sup> )	Average diameter (μm)	Self-floating rate	Ref.
EPDA-SA	0.4762	13.55	98.5 % 3 h	[37]
HGM@MPD-ALS	0.52	15.82	95.7 % 12 min	[31]
FMSA	0.20	28.04	95 % 40 min	[46]
SFA	0.42	13.46	97.5 % 3 h	[32]
AFA	0.302	13.26	97.5 % 3 h	[30]
HGM@PDA-SO <sub>3</sub> H	—	—	90 % 60 min	[51]

eluent for the desorption of EPDA-SA. With the increase of pH, the surface of EPDA-SA turned from a positive charge to a negative charge, which generated repulsion with the anionic dye Alizarin Cyanine green F adsorbed on its surface, and thus the desorption was achieved. In the desorption process, the adsorption capacity of the adsorbent will be reduced, and other chemical agents can be used to restore it to its original state. The EPDA-SA desorbed by sodium hydroxide had a large amount of negative charge, which was not conducive to the reuse of anionic dye adsorption, so it was soaked in hydrochloric acid to restore the positive charge on its surface for the next cycle.

Moreover, temperature also plays an important role in the regeneration of adsorbents. Most adsorbents can be regenerated by desorbing the adsorbate by heating. Different adsorption processes require different temperatures, the stronger the adsorption is, the higher the

desorption temperature is required. Per- and polyfluoroalkyl substances can be desorbed and volatilized at about 175 °C, but mineralization occurs when the temperature is too high [63]. The temperature during desorption can be selected according to the characteristics of the pollutants. The adsorption/desorption of P-GO for norfloxacin and bisphenol A was as follows [64]: norfloxacin was adsorbed at 15 °C and desorbed at 35 °C; bisphenol A was adsorbed at 35 °C and desorbed at 15 °C. This is because the hydrophilicity of norfloxacin and bisphenol A is different: when the temperature was 35 °C, PNNPAM grafted on P-GO was hydrophobic, which inhibited the adsorption of norfloxacin; while when the temperature was 15 °C, PNNPAM grafted on P-GO was hydrophilic and inhibited the adsorption of hydrophobic bisphenol A molecules.

The economics of the recovery methods used in the above-mentioned



**Fig. 6.** (a) Schematic diagram showing some mechanisms involved in the application of biochar for the removal of pollutants [68]; (b) Adsorption mass transfer steps [69].



literature could be improved, as the regeneration step uses many acids and bases and partly high-temperature conditions, which are not considered to be very economical. Future research could incorporate the emerging approaches of environmentally friendly with economical desorption and auxiliary adsorbent regeneration that have been proposed: biological and microbial assisted desorption, magnetic separation, thermal desorption, etc., to develop more cost-effective and environmentally friendly regeneration methods for HGM-related adsorbents. The recycling of adsorbents not only enables the reuse of adsorbents but also enriches and concentrates the desorbed pollutants in order to realize resource reuse of precious metals, dyes, etc., and subsequent harmless treatment of toxic and harmful substances.

#### 4. Adsorption mechanism and factors affecting adsorption effect

The main adsorption mechanisms include electrostatic interaction, hydrogen bond,  $\pi$ - $\pi$  bond interaction, chelation, ion exchange, pore-filling and others. Electrostatic interaction refers to the interaction between charged groups on the surface of the adsorbents and groups with opposite charges in the pollutant [65]. The adsorption effect based on electrostatic interaction usually depends on the pH value of the solution and the Zeta potential of the adsorbent. Hydrogen bonds are formed between two atoms of H of "X-H" and "Y" (X-H...Y), where X and Y are both electronegative atoms. Some functional groups can act as both hydrogen-bond acceptors and hydrogen-bond donors, which is depending on their protonated state [66].  $\pi$ - $\pi$  stacking is a kind of weak interaction between aromatic rings and usually occurs between relatively electron-rich and electron-deficient molecules, which is a non-covalent bond interaction [67]. As shown in Fig. 6a, Wang et al. summarized the adsorption mechanism of pollutants on biochar [68] to help readers understand the adsorption process more clearly.

##### 4.1. Effect of dosage and temperature

It is essential to explore the influence of adsorbent dosage and temperature on the removal effect and determining the optimal dosage and reaction temperature is the basis of exploring the subsequent influencing factors.

In the case of a certain concentration of pollutants, the removal efficiency will increase with the increase of adsorbent dosage, but when it achieves a certain extent, the removal rate will not improve. The determination of the optimal dosage should consider the relationship between removal rate and cost, which facilitates the application of practical wastewater treatment. The effect of temperature on the adsorption performance is also very significant. In general, adsorption is exothermic, and when adsorption reaches equilibrium, increasing the temperature causes the adsorption capacity to decrease. While some adsorption is an endothermic process, with the rise of temperature, the amount of adsorption capacity will increase. The adsorption capacity of AFA for MB, MG, BF, and CV dyes increased in the same direction of temperature [30], which indicated that the adsorption process was endothermic and that the increase in temperature would accelerate the thermal movement rate of molecules.

##### 4.2. Effect of initial pH

In the adsorption process, pH value has a significant influence on the adsorbate state and the surface properties of the adsorbent, so it is necessary to explore the influence of pH value on the adsorption efficiency. The influence of pH value on the adsorption effect is usually realized by electrostatic interaction.

If the functional groups on the surface of the adsorbent contain lone pair electrons, it is easy to protonate to obtain  $H^+$  under acidic conditions. The protonated adsorbent surface is positively charged, which will produce electrostatic repulsion to cations and electrostatic attraction to anions that is conducive to the removal of anionic pollutants. In the

study of An et al., it was found that the removal rate of ACGF by PDA-SA decreased with the increase of pH value in the low range because the amino groups on the surface of PDA-SA were more prone to protonation under strongly acidic conditions and had an electrostatic attraction to anionic dye ACGF [37]. The results show that the charge on the adsorbent surface is related to the pH value. Within a certain pH range, the adsorbent surface has a positive/negative charge, which is conducive to the adsorption of anions/cations. The change in pH will not only affect the charge of functional groups but also the form of the presence of pollutants. For example, phosphoric acid in an aqueous solution can exist in the form of  $H_3PO_4$ ,  $H_2PO_4^-$  and  $HPO_4^{2-}$  depending on the pH [70]; when the solution pH is less than 2, phosphoric acid exists mainly in the form of  $H_3PO_4$ , which is electrically neutral and does not interact electrostatically with the adsorbent surface; but when the pH is higher than 2, phosphoric acid exists in the form of  $H_2PO_4^-$  and  $HPO_4^{2-}$ , both of which are electronegative ions and are conducive to removal by adsorption through electrostatic interaction. Under acidic conditions, many hydrogen ions in the solution will occupy the effective adsorption sites on the adsorbent surface and produce competitive adsorption of cationic pollutants such as heavy metal ions and cationic dyes. But as the pH increases, the hydrogen ions adsorbed on the adsorbent surface gradually decrease, and the competitive adsorption is weakened, making the adsorption of cationic pollutants more likely to occur. After modification of HGM, the optimal pH for the removal of various pollutants is shown in Table 4 (All the experiments were repeated three times and the standard deviations were within 5 %). From the data in Table 4, the adsorption effect of the adsorbent on the pollutants is more desirable only within a certain pH range. This is since the surface charge of the adsorbent and the dissociation state of the pollutant change with the pH value of the solution. However, the pH value of wastewater is unpredictable, and it is not economical to maintain the wastewater in the optimal pH range at all times by consuming a large amount of acid-based solution in practical application. To further improve the economic utility of self-floating adsorbents, adsorbents with broader pH range adaptability need to be developed in future research.

##### 4.3. Effect of ion concentration

Ion concentration has a non-negligible influence on the adsorption effect, so it is necessary to explore the ion concentration. The interference ions in the solution will produce competitive adsorption with the pollutants, resulting in the reduction of the adsorption capacity. When the NaCl concentration was  $600.0 \text{ mmol}\cdot\text{L}^{-1}$ , the adsorption capacity of APGS-G-P for MB decreased by 78.27 %, which was because the high concentration of  $Na^+$  occupied the negative charge on the surface of the adsorbent [47], reflecting from the side that electrostatic attraction was the key factor of adsorption. Interference ions affect the adsorption performance to some extent, but the anti-interference ability of modified HGM is good, and the adsorption effect does not decrease significantly.

##### 4.4. Adsorption kinetics and isotherms

To better explore the adsorption process, it is usually necessary to study adsorption isotherms and adsorption kinetic models.

###### 4.4.1. Adsorption kinetics

The adsorption kinetic model is conducive to measuring the adsorption equilibrium time, adsorption rate and studying the mass transfer mechanism. The adsorption process consists of three steps [69], (external diffusion; internal diffusion; adsorption on active sites.) as shown in Fig. 6b.

Pseudo-first-order kinetic model (PFO) and pseudo-second-order kinetic model (PSO) are commonly used to describe adsorption kinetics. The differential equations of PFO and PSO are shown in Equations (2) and (3) respectively.

**Table 4**  
Optimal pH of different modified HGM for the removal of various pollutants.

Adsorbent	Pollutant	Charge conditions at different pH	Optimum pH	Ref.
SO <sub>3</sub> H-HGM	Ciprofloxacin (zwitter-ion)	pH < 2.8, silanol groups on the microsphere surface are positively charged; many H <sup>+</sup> in the solution will compete for negative charge adsorption sites. pH > 7, CIP exists mainly as an anion.	3 < pH < 7	[36]
EPDA-SA	Alizarin Cyanine Green F (Anionic dye)	Under strongly acidic conditions, quaternary amino groups on DMC have stronger cationic properties. Under alkaline conditions, the anions in the solution consume part of the cationic quaternary amino groups.	2 < pH < 3	[37]
HGM@MPD-ALS	Acid Green 25 (Anionic dye)	pH < 3, protonation of -NH <sub>2</sub> and -NH- in MPD.	2	[31]
HGM@MPD-ALS	Basic Fuchsin (Cationic dye)	The sulfonic acid groups in ALS become more electronegative as the pH increases.	7	[31]
FMSA	Basic Blue 7 and Crystal Violet (Cationic dye)	pH < 3, the silanol groups on the surface of FMSA are positively charged, and the large amount of H <sup>+</sup> in the solution competes with pollutants; pH > 3, negatively charged sulfonic acid groups can adsorb cationic dye; With the increase of pH, the Zeta potential of FMSA decreased gradually	10	[46]
SFA	Acid Orange 7 (Anionic dye)	Under strongly acidic conditions, the -NH <sub>2</sub> groups are easy to protonate, so the SFA has a positive charge.	2	[32]
AFA	Methylene Blue (Cationic dye)	The grafted sulfonate groups provide a large negative charge. With the increase in pH, the deprotonation of sulfonic acid groups is enhanced. pH > 7, the negative charges on the AFASurface no longer increases significantly	7 < pH < 8	[30]
BDSA	Acid Green 25 (Anionic dye)	The zeta potential of BDSA decreased slightly with the increase in pH, but it was still positive.	2 < pH < 10	[54]

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

Due to the simplicity of the method, the linear regression equation is most used to fit the kinetics data. The linear expressions of PFO and PSO are shown in Equations (4) and (5) respectively. However, the linear transformation of nonlinear models may lead to errors in the results. To

eliminate this error, the experimental data is usually fitted into a linearized model, which becomes nonlinear regression, and the best-fitting data is selected by comparing the regression coefficients [71].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where  $q_e$  and  $q_t$  are the equilibrium adsorption capacity and the adsorption capacity at time  $t$  respectively;  $k_1$  and  $k_2$  are rate constants of the pseudo-first-order model and pseudo-second-order model respectively.

The PFO model is suitable to describe adsorbents with few active sites; while the PSO model is suitable to describe adsorbents with many active sites. The adsorption process conforming to the PFO model may be dominated by physical adsorption, while the adsorption process conforming to the PSO model may be dominated by chemical adsorption.

#### 4.4.2. Adsorption isotherms

Adsorption isotherms are used to reflect the concentration of adsorbates in the two phases at a certain temperature when adsorption reaches equilibrium. The study of adsorption isotherms is helpful to understand the adsorption mechanisms and calculate the maximum adsorption capacity of adsorbents. Adsorption is the phenomenon that one or more components of the fluid accumulate on the solid surface when the fluid meets the porous solid [72]. Adsorption is mainly divided into two categories: one is chemical adsorption by forming chemical bonds and a single molecule adsorption layer; the other is physical adsorption by van der Waals forces which can adsorb a variety of adsorbates and form a multi-molecular adsorption layer. Langmuir and Freundlich have commonly used adsorption isotherms, and their nonlinear equations are shown in Equations (6) and (7) respectively. Langmuir isotherm indicates that the adsorbent forms a monomolecular adsorption layer on the surface of the homogeneous adsorbent, usually belonging to chemisorption [73]. Freundlich isotherm shows that the adsorption of adsorbents on heterogeneous surfaces is multilayered and usually belongs to physical adsorption [74].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

where  $q_m$  is the maximum adsorption capacity;  $C_e$  is the concentration of adsorbates in solution at equilibrium time;  $K_L$  is the constant of Langmuir isotherm;  $K_F$  and  $n$  are constants of the Freundlich isotherm.

As shown in Table 2, most of the self-floating adsorbents conform to the PSO model and Langmuir model, indicating that the adsorption process of modified HGM is usually a chemisorption on the surface of the adsorbent. Although the existing chemical modification methods can adsorb pollutants efficiently, the effect of chemical adsorption is greatly affected by the pH of the solution, which is not conducive to the treatment of actual wastewater. Furthermore, it can be seen from Table 2 that the specific surface area of the self-floating adsorbents obtained by the existing modification methods are small, so physical adsorption relying on pores is not the main adsorption mechanism. In the later study, it can be considered to load microporous and mesoporous materials on the surface of HGM, increase the specific surface area and pore volume, and expect pollutants to be adsorbed inside the pores through intra-particle diffusion, so as to obtain a self-floating adsorbent with high pH adaptability.

## 5. Conclusions, current status, and prospects

In this paper, the chemical modification methods of HGM such as

amination and acidification are sorted out, and the reasons for the improvement of adsorption properties after modification are discussed. The modified HGM has remarkable adsorption effect on dyes, heavy metal ions and antibiotics, and the adsorption mechanisms involve electrostatic interaction,  $\pi$ - $\pi$  interaction, hydrogen bonding, ion exchange and surface complexation. At the same time, the removal efficiency of pollutants depends on the dosage of adsorbents, reaction temperature, contact time, initial pH of the solution, concentration of interfering ions and other factors. However, the removal efficiency of existing modification methods on pollutants depends on the change of pH, which is not conducive to the actual wastewater treatment. Future research should focus on the pH adaptability of adsorbents. For example, it is possible to try to load porous materials (metal-organic framework, mesoporous silica materials, etc.) onto the surface of HGM to prepare self-floating adsorbents with high specific surface area. It is expected that various modification methods can be applied to HGM to obtain self-floating adsorbents with good adsorption capacity for different pollutants under various conditions. Additionally, the design of the adsorbents should also be considered, and the adsorbents should be as stable as possible to avoid the collapse of the structure in the actual process of treatment.

In the battle against environmental pollution, wastewater treatment plays a pivotal role. China has the largest wastewater industry and water market in the world, and the corresponding water pollution treatment is one of the most urgent challenges faced by China. Although the development history of wastewater treatment in China is short over the past 40 years, the development speed is rapid, with the world's leading innovation and treatment capacity. However, the existence of low sustainability of the treatment process, high energy consumption, high cost, and lack of consideration of nature still need to be given high priority. For China and the world, the more common wastewater treatment plants mainly use AAO and oxidation ditch technologies currently, and wastewater treatment has been regarded as a high energy consuming and high-cost industry for municipal wastewater treatment. The extremely high operating costs, personnel costs, equipment depreciation, and chemical consumption of wastewater treatment plants have been pending. The development of self-floating adsorbent by modified hollow glass microspheres for wastewater treatment can theoretically solve the above problems, and the low density and low weight of HGM can reduce transportation and personnel costs. Based on its stable chemical properties, HGM can be recycled and reused under a wide range of chemical conditions, which ensures sustainability and solves the cost problem, and ensures the harmonious relationship between human beings and nature. In other words, HGM can theoretically solve the biggest challenges faced by the wastewater treatment industry in China and even the world and has great development prospects and potential.

Modifying to obtain low-cost, high selectivity, high capacity and high pH adaptability, and exploring the possibility of putting them into the large-scale wastewater treatment industry will be the key goal of researchers' future work. Making the regeneration process more economical and environmentally friendly and to further improving the economic efficiency of the recycling method is the direction of future research.

#### CRedit authorship contribution statement

**Ruisi Qiu:** Writing – review & editing, Writing – original draft, Investigation, Conceptualization. **Bing Wang:** Project administration. **Jiajian Shang:** Resources. **Guojun Hu:** Resources. **Linwei Yu:** Data curation. **Xuan Gao:** Supervision.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Acknowledgments

We gratefully acknowledge the support from Science and Technology Plan Project of Sichuan Province (2021YFG0116 and 2022ZYD0044), Opening Project of Oil & Gas Field Applied Chemistry Key Laboratory of Sichuan Province (YQKF202107) and Production-Education Integration Demonstration Project of Sichuan Province “Photovoltaic Industry Production-Education Integration Comprehensive Demonstration Base of Sichuan Province (Sichuan Financial Education [2022] No.106)”.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2024.124965>.

#### References

- [1] Q. Xie, et al., Water pollutant discharge permit allocation based on DEA and non-cooperative game theory, *J. Environ. Manage.* 302 (2022) 113962.
- [2] P. Sharma, J. Prakash, R. Kaushal, An insight into the green synthesis of SiO<sub>2</sub> nanostructures as a novel adsorbent for removal of toxic water pollutants, *Environ. Res.* 212 (2022) 113328.
- [3] C. Wu, et al., High-gravity intensified electrodeposition for efficient removal of Cd<sup>2+</sup> from heavy metal wastewater, *Sep. Purif. Technol.* 289 (2022) 120809.
- [4] K. Soni, et al., Bacterial antibiotic resistance in municipal wastewater treatment plant; mechanism and its impacts on human health and economy, *Bioresour. Technology Reports* 19 (2022) 101080.
- [5] W. Li, B. Mu, Y. Yang, Feasibility of industrial-scale treatment of dye wastewater via bio-adsorption technology, *Bioresour. Technol.* 277 (2019) 157–170.
- [6] X.L.X.Z. Huijie Wang, A review on heterogeneous photocatalysis for environmental remediation: from semiconductors to modification strategies, *Chin. J. Catal.* (2022).
- [7] S.P. Bera, M. Godhaniya, C. Kothari, Emerging and advanced membrane technology for wastewater treatment: a review, *J. Basic Microbiol.* 62 (3–4) (2022) 245–259.
- [8] W. Zhou, W. Zhang, Y. Cai, Laccase immobilization for water purification: a comprehensive review, *Chem. Eng. J.* 403 (2021) 126272.
- [9] B.S. Rath, P.S. Kumar, P.L. Show, A review on effective removal of emerging contaminants from aquatic systems: current trends and scope for further research, *J. Hazard Mater.* 409 (2021) 124413.
- [10] N.A. Khan, Z. Hasan, S.H. Jung, Adsorptive removal of hazardous materials using metal-organic frameworks (MOFs): a review, *J. Hazard Mater.* 244–245 (2013) 444–456.
- [11] Y. Dehmani, et al., Review of phenol adsorption on transition metal oxides and other adsorbents, *J. Water Process Eng.* 49 (2022) 102965.
- [12] A. El Amri, et al., Investigation of Typha Latifolia (TL) as potential biosorbent for removal of the methyl orange anionic dye in the aqueous solution. kinetic and DFT approaches, *J. Mol. Struct.* 1272 (2023) 134098.
- [13] J. Bensalah, et al., Investigation of the cationic resin as a potential adsorbent to remove MR and CV dyes: kinetic, equilibrium isotherms studies and DFT calculations, *J. Mol. Struct.* (2023).
- [14] L. Kadiri, et al., Adsorption properties of coriander seeds: Spectroscopic kinetic thermodynamic and computational approaches, *J. Mol. Liq.* 343 (2021) 116971.
- [15] I. Lebkiri, et al., Investigation of the anionic polyacrylamide as a potential adsorbent of crystal violet dye from aqueous solution: equilibrium, kinetic, thermodynamic, DFT, MC and MD approaches, *J. Mol. Liq.* 372 (2023) 121220.
- [16] A. Jebli, et al., Synthesis of a chitosan@hydroxyapatite composite hybrid using a new approach for high-performance removal of crystal violet dye in aqueous solution, equilibrium isotherms and process optimization, *J. Taiwan Inst. Chem. Eng.* 149 (2023) 105006.
- [17] B. Wang, et al., Effective adsorbent for the removal of bisphenol A from water: MOF-derived carbon, *Microporous Mesoporous Mater.* 346 (2022) 112285.
- [18] J. Scaria, et al., Carbonaceous materials as effective adsorbents and catalysts for the removal of emerging contaminants from water, *J. Clean. Prod.* 350 (2022) 131319.
- [19] T. Nkomzwayo, et al., Adsorptive desulfurization using period 4 transition metals oxide: a study of Lewis acid strength derived from the adsorbent ionic-covalent parameter, *Chem. Eng. J.* 444 (2022) 136484.
- [20] E.C. Emenike, et al., Recent advances in nano-adsorbents for the sequestration of copper from water, *J. Water Process Eng.* 47 (2022) 102715.

- [21] F.F. Sukatis, S.Y. Wee, A.Z. Aris, Potential of biocompatible calcium-based metal-organic frameworks for the removal of endocrine-disrupting compounds in aqueous environments, *Water Res.* 218 (2022) 118406.
- [22] K. Chan, A. Zinchenko, Conversion of waste bottle PET to magnetic microparticles adsorbent for dye-simulated wastewater treatment, *J. Environ. Chem. Eng.* 10 (3) (2022) 108055.
- [23] P. Liu, et al., Study on a new method of controlling casing shear deformation based on hollow glass microspheres cement sheath, *Energy Rep.* 8 (2022) 5192–5203.
- [24] S. Anirudh, et al., Epoxy/hollow glass microsphere syntactic foams for structural and functional application-a review, *Eur. Polym. J.* 171 (2022) 111163.
- [25] A. Konbul, E.M. Ozbayoglu, C. Mata, Survival of hollow glass microspheres in drilling fluids applications – effect of drill bit/formation contact, *J. Pet. Sci. Eng.* 189 (2020) 106966.
- [26] T.D. Singewald, et al., Water-uptake in hollow glass microspheres and their influence on cathodic and anodic delamination along the polymer/metal-interface, *Corros. Sci.* 196 (2022) 110045.
- [27] J. Yoo, et al., Collapse pressure measurement of single hollow glass microsphere using single-beam acoustic tweezer, *Ultrason. Sonochem.* 82 (2022) 105844.
- [28] L. Wang, et al., Floating microparticles of ZnIn<sub>2</sub>S<sub>4</sub> @hollow glass microsphere for enhanced photocatalytic activity, *Int. J. Hydrogen Energy* 46 (15) (2021) 9678–9689.
- [29] M. Ozkutlu, C. Dilek, G. Bayram, Effects of hollow glass microsphere density and surface modification on the mechanical and thermal properties of poly(methyl methacrylate) syntactic foams, *Compos. Struct.* 202 (2018) 545–550.
- [30] Y. An, et al., Use of a floating adsorbent to remove dyes from water: a novel efficient surface separation method, *J. Hazard. Mater.* 375 (2019) 138–148.
- [31] Y. An, et al., Multi-functionalized self-floating microspheres for dyes capture: amphoteric adsorption and rapid surface solid-liquid separation, *J. Clean. Prod.* 296 (2021) 126535.
- [32] Y. An, et al., Two-step synthesis of a single-layer grafting self-floating adsorbent for anionic dyes adsorption, surface separation and concentration, *J. Hazard. Mater.* 384 (2020) 121262.
- [33] Y. An, et al., A novel floating adsorbents system of acid orange 7 removal: polymer grafting effect, *Sep. Purif. Technol.* 227 (2019) 115677.
- [34] Y. Li, et al., Synergetic removal of oppositely charged dyes by co-precipitation and amphoteric self-floating capturer: mechanism investigation by molecular simulation, *Chemosphere* 296 (2022) 134033.
- [35] T. Wang, et al., Hollow self-floating microspheres capture cobalt (Co<sup>2+</sup>)/nickel (Ni<sup>2+</sup>) ions from the acidic leachate of spent lithium-ion battery cathodes, *Chem. Eng. J.* 465 (2023) 142950.
- [36] C. Hu, et al., A novel self-floating silica adsorbent for antibiotic ciprofloxacin and nickel (II) ion, *Chem. Eng. J.* 429 (2022) 132227.
- [37] Y. An, et al., Functioned hollow glass microsphere as a self-floating adsorbent: rapid and high-efficient removal of anionic dye, *J. Hazard. Mater.* 381 (2020) 120971.
- [38] S. Li, et al., Porous-wall hollow glass microspheres as novel potential nanocarriers for biomedical applications, *Nanomed. Nanotechnol. Biol. Med.* 6 (1) (2010) 127–136.
- [39] F. Galvagnini, et al., Thermophysical properties of multifunctional syntactic foams containing phase change microcapsules for thermal energy storage, *Polymers* 13 (11) (2021) 1790.
- [40] X. Zhang, Cr/S/TiO<sub>2</sub>-loaded hollow glass microspheres as an efficient and recyclable catalyst for the photocatalytic degradation of indigo carmine under visible light, *Química Nova*, 2016.
- [41] T.R.M. Ferreira, et al., Effect of hollow glass microspheres addition on density reduction and mechanical properties of PA6/glass fibers composites, *Polimeros* 32 (1) (2022).
- [42] N. Kabay, A.B. KIZILKANAT, B. Akturk, Y. Kahraman, Lightweight cement-based composites incorporating hollow glass microspheres: fresh and hardened state properties, *Teknik Dergi* (2022).
- [43] C. Huang, et al., Surface modification of hollow glass microsphere with different coupling agents for potential applications in phenolic syntactic foams, *J. Appl. Polym. Sci.* 134 (4) (2017).
- [44] Z. Zhang, et al., The effect of nano-silica modified with silane coupling agents on the diffusion behavior of water molecules in palm oil based on molecular simulation, *IEEE Access* 9 (2021) 82213–82220.
- [45] Chen Kailing, et al., Chemical modification of silica: method, mechanism, and application, *PROGRESS IN CHEMISTRY* (in Chinese) (2013).
- [46] C. Hu, et al., Structural design of a floating-magnetically responsive silica adsorbent and efficient removal of dyes, *J. Clean. Prod.* 302 (2021) 126985.
- [47] Q. Tang, et al., Floating-separation adsorbent for methylene blue and Pb(II) removal: structure construction and adsorption mechanism, *Sep. Purif. Technol.* 295 (2022) 121332.
- [48] J.H. Ryu, P.B. Messersmith, H. Lee, Polydopamine surface chemistry: a decade of discovery, *ACS Appl. Mater. Interfaces* 10 (9) (2018) 7523–7540.
- [49] V. Ball, et al., Kinetics of polydopamine film deposition as a function of pH and dopamine concentration: insights in the polydopamine deposition mechanism, *J. Colloid Interface Sci.* 386 (1) (2012) 366–372.
- [50] S. Hong, et al., Non-covalent self-assembly and covalent polymerization Co-contribute to polydopamine formation, *Adv. Funct. Mater.* 22 (22) (2012) 4711–4717.
- [51] C. Hu, et al., Eco-friendly poly(dopamine)-modified glass microspheres as a novel self-floating adsorbent for enhanced adsorption of tetracycline, *Sep. Purif. Technol.* 292 (2022) 121046.
- [52] C. Choi, J. Nam, J. Nah, Application of chitosan and chitosan derivatives as biomaterials, *J. Ind. Eng. Chem.* 33 (2016) 1–10.
- [53] Y. Zhou, et al., Sorption of heavy metals on chitosan-modified biochars and its biological effects, *Chem. Eng. J.* 231 (2013) 512–518.
- [54] C. Zhao, et al., A novel surface-active monomer decorating a self-floating adsorbent with high pH adaptability for anionic dyes:  $\pi$ - $\pi$  stacking, *J. Mol. Liq.* 321 (2021) 114864.
- [55] Z. Wang, et al., A novel self-floating cyclodextrin-modified polymer for cationic dye removal: preparation, adsorption behavior and mechanism, *Sep. Purif. Technol.* 290 (2022) 120838.
- [56] J. Marcinkiewicz, E. Kontny, Taurine and inflammatory diseases, *Amino Acids* 46 (1) (2014) 7–20.
- [57] S. Nijpanich, et al., A tri-layer floating photocatalyst/adsorbent for the removal of organic compounds from wastewater: layer-by-layer deposition of silicalite-1 and titania on hollow glass microspheres, *Environ. Technol. Innov.* 26 (2022) 102242.
- [58] A.A. Basheer, New generation nano-adsorbents for the removal of emerging contaminants in water, *J. Mol. Liq.* 261 (2018) 583–593.
- [59] J. Gómez-Pastora, E. Bringas, I. Ortiz, Recent progress and future challenges on the use of high performance magnetic nano-adsorbents in environmental applications, *Chem. Eng. J.* 256 (2014) 187–204.
- [60] A.V. Baskar, et al., Recovery, regeneration and sustainable management of spent adsorbents from wastewater treatment streams: a review, *Sci. Total Environ.* 822 (2022) 153555.
- [61] A. Jain, et al., Water purification via novel nano-adsorbents and their regeneration strategies, *Process Saf. Environ. Prot.* 152 (2021) 441–454.
- [62] A.A. Aryee, et al., A review on functionalized adsorbents based on peanut husk for the sequestration of pollutants in wastewater: modification methods and adsorption study, *J. Clean. Prod.* 310 (2021) 127502.
- [63] F. Xiao, et al., Thermal decomposition of PFAS: response to comment on “thermal stability and decomposition of perfluoroalkyl substances on spent granular activated carbon”, *Environ. Sci. Technol. Lett.* 8 (4) (2021) 364–365.
- [64] N. Yao, et al., Norfloxacin and bisphenol-A removal using temperature-switchable graphene oxide, *ACS Appl. Mater. Interfaces* 10 (34) (2018) 29083–29091.
- [65] Y. Hu, et al., Dye adsorption by resins: effect of ionic strength on hydrophobic and electrostatic interactions, *Chem. Eng. J.* 228 (2013) 392–397.
- [66] L.J. Karas, et al., Hydrogen bond design principles, *WIREs Computational Molecular Science* 10 (6) (2020).
- [67] R. Thakuria, N.K. Nath, B.K. Saha, The nature and applications of  $\pi$ - $\pi$  interactions: a perspective, *Cryst. Growth Des.* 19 (2) (2019) 523–528.
- [68] X. Wang, et al., Recent advances in biochar application for water and wastewater treatment: a review, *PeerJ* (2020).
- [69] J. Wang, X. Guo, Adsorption kinetic models: physical meanings, applications, and solving methods, *J. Hazard Mater.* 390 (2020) 122156.
- [70] H. Diallo, et al., On the electrostatic interactions in the transfer mechanisms of iron during nanofiltration in high concentrated phosphoric acid, *J. Membr. Sci.* 427 (2013) 37–47.
- [71] M.Z.I.A. Hridam Deb, Kinetics & dynamic studies of dye adsorption by porous graphene nano-adsorbent for facile toxic wastewater remediation, *Journal of Water Process Engineering* (2022).
- [72] X.G. Jianlong Wang, Adsorption isotherm models: classification, physical meaning, application and solving method, *Chemosphere* (2020).
- [73] X. Guo, J. Wang, Comparison of linearization methods for modeling the Langmuir adsorption isotherm, *J. Mol. Liq.* 296 (2019) 111850.
- [74] H. Chung, et al., Application of Langmuir and Freundlich isotherms to predict adsorbate removal efficiency or required amount of adsorbent, *Journal of Industrial and Engineering Chemistry* (seoul, Korea) 28 (2015) 241–246.