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Intensive adsorption and degradation of environmental hormone micro-contaminated water by a new g-C_3N_4 based composite photocatalyst coupled modified mesoscopic carbon

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ABSTRACT

Despite low exposure level in the water, environmental hormone pollutants can still inflict significant biological effects that endanger ecological safety and human reproduction. However, they are unable to be effectively removed using ordinary water treatment methods, which makes the deposition of environmental residues highly likely. In light of this demand, this study synthesized metal-doped g-C_3N_4 composite photocatalysts and coupled them with nitrogen doped ordered mesoporous (NMC) carbon to treat water contaminated by environmental hormone micropollutants. The experimental results show that $AgIn_5S_8$/g-C_3N_4 (25%) makes the prime candidate for degrading bisphenol A (BPA), displaying the highest degradation rates of 82%. Moreover, h^+ and·O^{2-} were found to be the main active substances in the photocatalytic process, while the degradation rate of BPA by $AgIn_5S_8$/g-C_3N_4 (25%) was still over 80% after 5 repeated photocatalyses. When the nitrogen doped ordered mesoporous carbon was coupled with $AgIn_5S_8$/g-C_3N_4 (25%), the degradation and removal rates of BPA were greatly improved, demonstrating up to 94.8% removal rate in batch treatment. Furthermore, NMC/$AgIn_5S_8$/g-C_3N_4 also exhibited good adsorption–photocatalytic synergy under continuous flow conditions of the fluidized bed, and the highest removal rate of BPA in the dark-free adsorption experiment was about 98.1%.

Keywords: Graphitic carbon nitride; Modified mesoporous carbon; Environmental hormone; Adsorption; Photocatalysis

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1. Introduction

With the rapid development of industry and the rapid growth of population, water environmental pollution is increasingly serious, the issue of water environmental governance has become an important subject of common concern and strive to solve. What needs special attention is that environmental hormone pollutants, although with their low exposure levels in water bodies, can produce strong biological effects, endangering ecological safety and human reproduction [1–3]. It has been shown that some wild animals exposed to such pollutants for a long time can cause their reproductive organs always to not develop and mature, the number has decreased sharply and is in

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an endangered state [4,5]. At the same time, environmental hormone pollutants have also caused great harm to human health, especially to human reproductive system, which is manifested as a sharp decrease in the number of sperm, endometriosis, and increased incidence of testicular cancer, breast cancer and other diseases. In addition, the potential toxicity of environmental hormones may also cause serious impact on future generations [6,7]. Due to the low level of exposure to such pollutants (nanograms to micrograms per liter), most people still have a weak awareness of harm. Environmental estrogens are refractory lipid-soluble compounds, low environmental concentrations that gradually accumulate and enrich through the water cycle and through the food chain. And the common water treatment methods cannot effectively remove it, very easy to cause environmental residues [8]. Therefore, it is of great significance to explore the effective removal of environmental oestrogen in water.

At present, the removal methods of environmental hormone pollutants in water bodies mainly include biological treatment technology, advanced oxidation technology and adsorption treatment technology [8]. Biological treatment is one of the most commonly used methods in traditional sewage treatment technology, but screening and cultivating a high efficiency of specific strains requires a lot of time and cost, and many highly toxic pollutants in polluted water have a certain resistance and toxicity to microorganisms, resulting in a long treatment cycle, and the effect is not stable enough. Radical oxidation-based advanced oxidation processes, because of its outstanding high activity and low selectivity, is now widely used in the treatment of organic pollutants in the environment [9–13]. Among them, photocatalytic technology is an advanced high-grade oxidation water treatment technology emerged in recent years, which can effectively destroy the structure of organic pollutants [14,15]. Additionally, photocatalytic technology due to the advantages of low energy and raw material consumption, simple process, no secondary pollution, so it is a promising environmentally friendly water treatment method. However, conventional photocatalysts are prone to electron hole recombination, which affects the photocatalytic efficiency [16,17]. Although the above degradation methods, including biotechnological and advanced oxidation techniques, can effectively remove environmental hormone contaminants to a high degree, most of the treatment concentrations in these literature reported are relatively high (mg/L). According to the pollution distribution of environmental hormones can know, the concentration lower limit in many water bodies reaches nanogram per liter. It should be pointed out that the adsorption method is more suitable for advanced treatment aiming at the characteristic of low pollution concentration of environmental hormone in water [18–20]. However, treatment of environmental hormone micro-contaminated water by adsorption method is still uncommon due to the low adsorption capacity and regeneration problem of the adsorbent. Also for such low concentrations, these degradation methods will be limited by adsorption and desorption equilibrium, and cannot reach the purpose of rapid and efficient removal [21]. However, this low concentration level of environmental hormones can still cause serious biological effects, so it is necessary to develop new control methods for the removal of low concentrations of environmental hormones in micropolluted water bodies.

In view of the current single treatment method for low concentration of environmental hormone pollution water treatment effect is not satisfactory, herein $AgIn_5S_8$ and g-C_3N_4 were combined to prepare photocatalyst to increase the adsorption capacity while improving the photocatalytic efficiency. Moreover, the prepared composite photosynthetic catalyst combined with a modified mesoporous carbon adsorbent was applied for the adsorption and photodegradation removal of trace environmental hormones in wastewater. In the composite treatment process of adsorption and photocatalysis, catalytic oxidation can be used to decompose the adsorbed environmental hormones, and then regenerate the adsorption site of the adsorbent in situ, to further improve its adsorption performance. This composite treatment process achieved efficient removal of trace environmental hormones and recycling of materials, and reduced secondary contamination. Accordingly, the paper proposes a new idea of efficient treatment of environmental hormone micropolluted water.

2. Materials and methods

2.1. Materials

All the synthetic raw materials of composite photocatalyst ($AgIn_5S_8$/g-C_3N_4) and were analytical grade and purchased from Sigma-Aldrich (Room 1705, 17th Floor, Renheng Land Plaza, No. 1, Section 2, Renmin South Road, Jinjiang District, Chengdu, China). The reagents used in the synthesis experiment include melamine, dilute nitric acid, $AgNO_3$, $In(NO_3)_3·5H_2O$, ethylene glycol, thioacetamide. Additionally, reagents and solvents related to water quality analysis were purchased from Chongqing Chuandong Chemical Industry Co., Ltd., Chongqing, China. The modified mesoporous carbon adsorbent (specific surface of 800 m^2/g, hole volume of 1.1 cm^3/g, aperture of 3.9 nm) and three environmental hormones used in the study was purchased from Aladdin (No. 809, Chuhua Branch Road, Fengxian District, Shanghai, China). All reagents were used in the study without further purification.

2.2. Synthesis of $AgIn_5S_8$/g-C_3N_4

2.2.1. Preparation of g-C_3N_4

15.0 g of analytical pure melamine is placed in a silicon crucible, and then it is placed in a muffle furnace for heat treatment at 500°C for 3 h. Disperse the light yellow powder after heat treatment in dilute nitric acid and ultrasonic for 15 min. Finally, the product is fully washed with deionized water. After washing, the product is placed in a vacuum drying oven, dried overnight at 60°C and stored for standby.

2.2.2. Preparation of $AgIn_5S_8$

0.1 mmol $AgNO_3$ and 0.5 mmol $In(NO_3)_3·5H_2O$ were mixed in 20 mL ethylene glycol, and then the mixed solution of thioacetamide and ethylene glycol (0.8 mmol thioacetamide and 10 mL ethylene glycol) was added. The mixture was stirred and mixed evenly at room temperature. The mixture was sealed in the reactor and reacted at 180°C for 24 h. The reactor was taken out and cooled to room temperature. The precipitate in the reactor was washed with distilled water, and dried to constant weight at 70°C in vacuum.

2.2.3. Preparation of $AgIn_5S_8/g\text{-}C_3N_4$

1.0 g $g\text{-}C_3N_4$ was ultrasonically dispersed in ethanol aqueous solution for 1 h (ethanol: water = 2:1), $AgIn_5S_8$ nanoparticles were added (the mass fraction of $g\text{-}C_3N_4$ was controlled at 25%) and the mixture was continuously stirred for 12 h. Then the produced precipitate was centrifuged and dried overnight in a vacuum drying oven at 70°C. The dried product was the target photocatalyst.

2.3. Photocatalytic properties evaluation of $AgIn_5S_8/g\text{-}C_3N_4$

50 mL predetermined mass concentration bisphenol environmental hormones wastewater was added into the photo-reactor, and then added predetermined quality $AgIn_5S_8/g\text{-}C_3N_4$ photocatalysts to perform the photocatalytic degradation experiments. Before light, a dark adsorption–desorption reaction (10 min) was performed to achieve a balance between the catalyst and the bisphenol A (BPA) solution. After a certain light time, 2 mL of the degradation solution was centrifuged and the supernatant was taken for liquid chromatography to calculate the bisphenol environmental hormones degradation efficiency.

2.4. Adsorption properties evaluation of nitrogen doped ordered mesoporous carbon

Bisphenol contaminated wastewater at a predetermined mass concentration and volume was placed in a 100 mL beaker, and a predetermined quality of nitrogen doped ordered mesoporous (NMC) adsorbed material was added to the beaker. Controlling the final liquid volume in the beaker was 50.0 mL, the adsorbent concentration was 50.0 mg/L and the initial pH was 6.0–7.0, and at room temperature to conduct the adsorption experiment. Start timing after the adsorbent is added, and took samples at the expected time to conduct centrifugation to remove the adsorbent, and take the supernatant to determine the content of bisphenol environmental hormones by UV-Vis spectrophotometer and high-efficiency liquid chromatography (HPLC).

2.5. Conjugation treatment of environmental hormone micro-contaminated water

2.5.1. Batch treatment

50 mL BPA wastewater at a predetermined mass concentration (0.2 mg/L) was measured in the optical reactor, and the NMC (mass concentration of 50.0 mg/L) and 0.1 g $AgIn_5S_8/g\text{-}C_3N_4$ were added to conduct the coupling treatment experiment. The final liquid volume of the photoreactor was 50.0 mL, with an initial pH of 6.0–7.0. Before light, a dark adsorption–desorption reaction (10 min) was performed to achieve a balance between the adsorbent and the BPA solution. After a certain light time, 2 mL of the degradation solution was centrifuged and the supernatant was taken for liquid chromatography to calculate the BPA degradation efficiency.

2.5.2. Continuous treatment

The removal efficiency of $NMC/AgIn_5S_8/g\text{-}C_3N_4$ to BPA was investigated by using the fluidized bed photocatalytic reaction device. The schematic diagram of the fluidized bed is shown in Fig. 1. The fluidized bed photocatalytic reaction device was an overall light avoidance, while the thermostatic water circulation device was used to stabilize the photocatalytic system at 25°C with pH of 6.0~7.0. The effective volume of the reaction vessel was 50.0 mL, the incoming water flow rate was 1.42 mL/min, and the incoming water BPA concentration was 0.2 mg/L. When 0.1 g $AgIn_5S_8/g\text{-}C_3N_4$ was added to the 50 mL BPA solution and the NMC mass concentration was 50.0 mg/L, after 10 min adsorption, the light source was turned on for the photocatalytic degradation reaction. Sampling was then performed

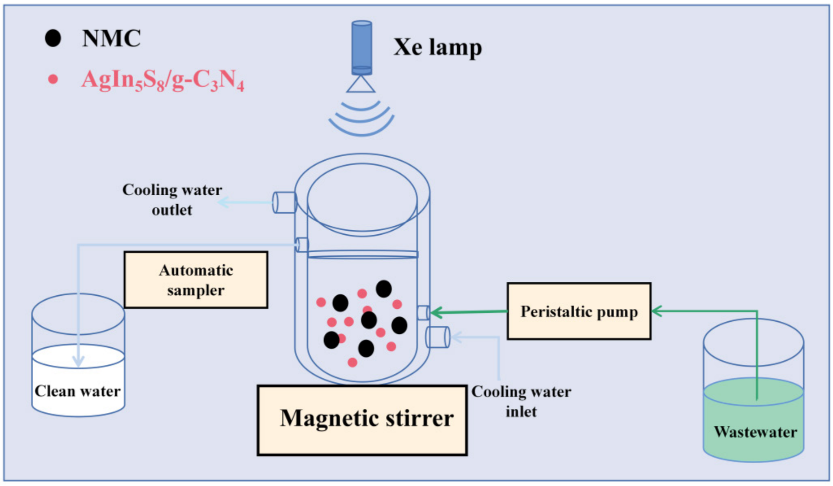

Fig. 1. Schematic diagram of fluidized bed photocatalytic reactor.

in the automatic sampling device at the outlet and at the set time point using a 1 mL syringe, then the concentration of water BPA was detected on the HPLC after 0.22 m glass fiber needle filter filtration.

3. Results and discussion

3.1. Photocatalytic properties evaluation of $AgIn_5S_8/g\text{-}C_3N_4$

As seen from Fig. 2a, the BPA shows little degradation in the presence of any photocatalyst. Furthermore, due to the rapid electron hole pair recombination in the pure catalyst, the degradation rate of BPA was also quite low when $g\text{-}C_3N_4$ or $AgIn_5S_8$ alone as visible photoactive photocatalyst, only about 15% and 25%, respectively. In contrast, when $g\text{-}C_3N_4$ was recombined with $AgIn_5S_8$, the formed composite photocatalyst had significantly improved the degradation rate of BPA. In a series of synthetic composites, the $AgIn_5S_8/g\text{-}C_3N_4$ (25%) photocatalyst exhibited the highest photocatalytic activity, with 82% of the BPA being degraded within 35 min under visible light irradiation. In the photocatalytic degradation experiments of the three bisphenol environmental hormones, $AgIn_5S_8/g\text{-}C_3N_4$ (25%) showed the highest 35min degradation rate of bisphenol F (BPF), with an average degradation rate of 85% (Fig. 2b). In addition, the project also investigated the kinetics of the BPA degradation reaction (Fig. 2c). As seen from Fig. 2c, this degradation matches the quasi-primary reaction kinetics and follows the Langmuir–Hinshelwood equation model. The rate constants of the $AgIn_5S_8/g\text{-}C_3N_4$ (25%) composite are much higher under visible light irradiation than those obtained with either $AgIn_5S_8$ or $g\text{-}C_3N_4$ as a photocatalyst. The results showed that the visible photocatalytic mechanism of $AgIn_5S_8/g\text{-}C_3N_4$ (25%) composite was consistent with that of the reported $g\text{-}C_3N_4$ based photocatalyst [22–24].

Ammonium oxalate (AO), isopropanol (IPA) and phenylquinone (BQ) were used as h^+, OH^- and $^{\bullet}O_2$ scavenger, respectively, to investigate the catalytic degradation mechanism of BPA by $AgIn_5S_8/g\text{-}C_3N_4$. As seen from Fig. 3, IPA has little effect on the BPA degradation rate, indicating

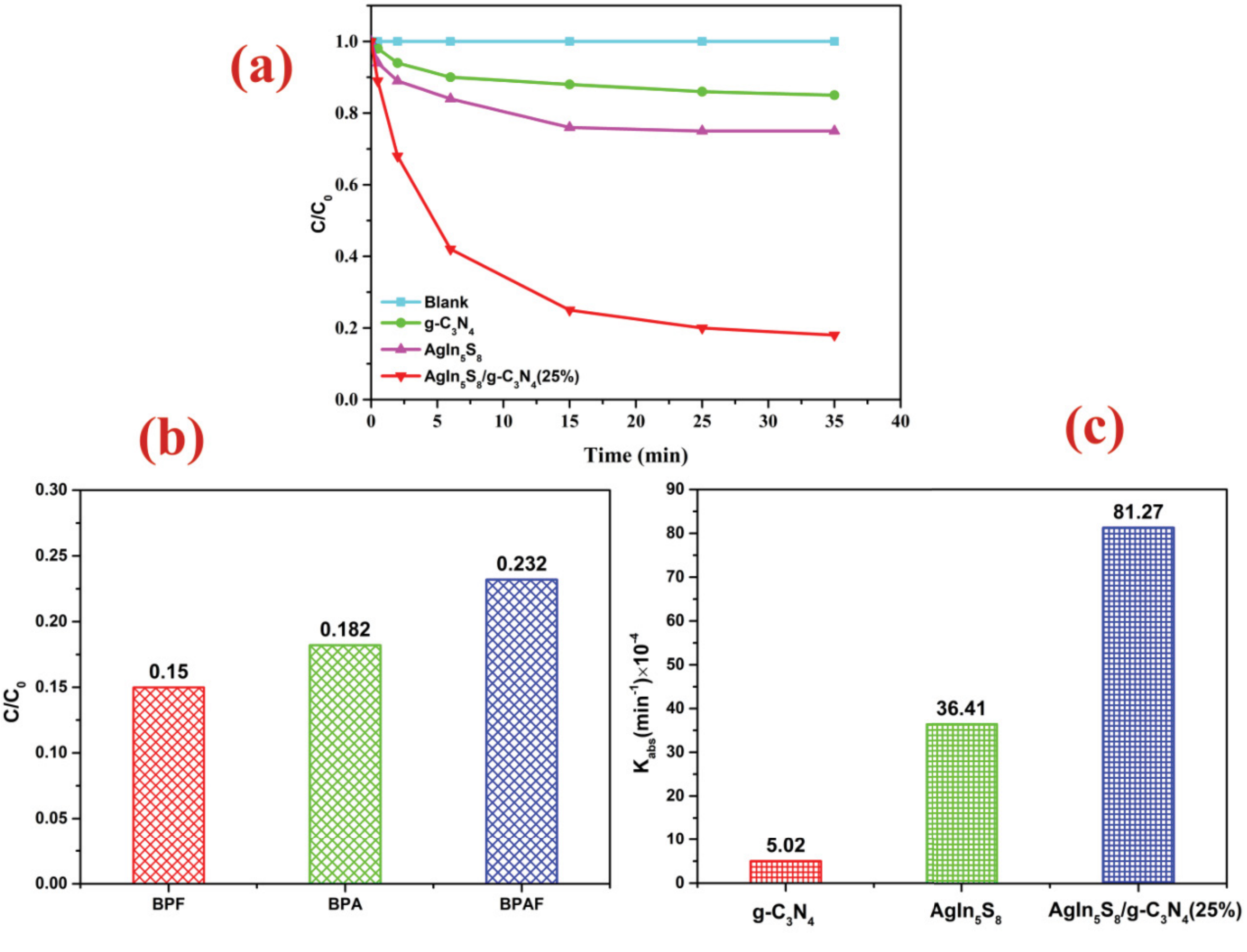

Fig. 2. Evaluation of the photocatalytic properties of $AgIn_5S_8/g\text{-}C_3N_4$ on bisphenol environmental hormones under 35-min visible light exposure. (a) Photocatalytic degradation of BPA by different reagents, (b) photodegradation of the three bisphenol environmental hormones by $AgIn_5S_8/g\text{-}C_3N_4$, and (c) kinetics of the photocatalytic degradation reaction of $AgIn_5S_8/g\text{-}C_3N_4$ for BPF.

that OH^- is not the major active factor in the photodegradation process. However, when using AO and BQ, it was observed that the degradation rate of BPA decreased from 82% to 36% and 27% after the 35 min degradation reaction, respectively. Therefore, we could argue that BPA degradation occurs from the formation of h^+ and $^{\bullet}O_2$, and that h^+ and $^{\bullet}O_2$ are the main active factors in BPA photodegradation.

3.2. Adsorption properties evaluation of NMC

In this paper, polluted water containing bisphenol environmental hormones was taken as the treatment object, and the adsorption kinetics of bisphenol environmental hormones by NMC was investigated, so as to obtain the equilibrium adsorption capacity of NMC for various environmental hormones, and evaluate the adsorption performance for environmental hormones. Meanwhile, in order to comprehensively investigate the adsorption capacity and adsorption rate of NMC adsorption materials for bisphenol environmental hormone, this paper investigate the adsorption behavior of the adsorption materials to high and low concentrations of bisphenol environmental hormone wastewater. The bisphenol environmental hormones selected were BPA, BPF and bisphenol AF (BPAF), respectively, and the concentrations of environmental hormones in low concentration wastewater and high concentration wastewater were 0.2 and 40 mg/L. The residue of bisphenol environmental hormone were determined at 0.5, 2, 6, 15, 20 and 35 min after the adsorption started, respectively. The experimental results are shown in Fig. 4.

As can be seen from Fig. 4, the adsorption rate of NMC to bisphenol environmental hormones is relatively fast within 1min of the beginning, and each adsorption amount is basically stable after 2 min, and the adsorption–desorption is in a dynamic equilibrium. As can be seen from the figure, the equilibrium adsorption of NMC to the three environmental hormones is BPA: 2.88 mg/g, BPF: 2.89 mg/g, BPAF: 2.61 mg/g. At high concentration, the adsorption amounts are BPA: 350 mg/g, BPF: 2.81 mg/g and BPAF: 348 mg/g. NMC to the different diphenolic environmental hormones have different adsorption amounts may result from the different molecular sizes of the diphenolic environmental hormones. Under this experimental conditions, the highest adsorption removal rate of the three low concentrations diphenolic environmental hormones was 72.3% (BPA), 72% (BPF) and 65.3% (BPAF), while the removal rate was significantly lower at higher concentrations, and thus, NMC is more suitable for the adsorption removal of low concentrations of diphenolic environmental hormones.

3.3. Conjugation treatment of environmental micro-contaminated water

3.3.1. Batch treatment

As shown from Fig. 5, in the couple use of NMC and $AgIn_5S_8/g-C_3N_4$ the BPA removal rate was significantly increased compared with those in use one of the two material (the removal rate were 72% of NMC, 82% of $AgIn_5S_8/g-C_3N_4$, and about 94.8% of NMC/$AgIn_5S_8/g-C_3N_4$). Also can be

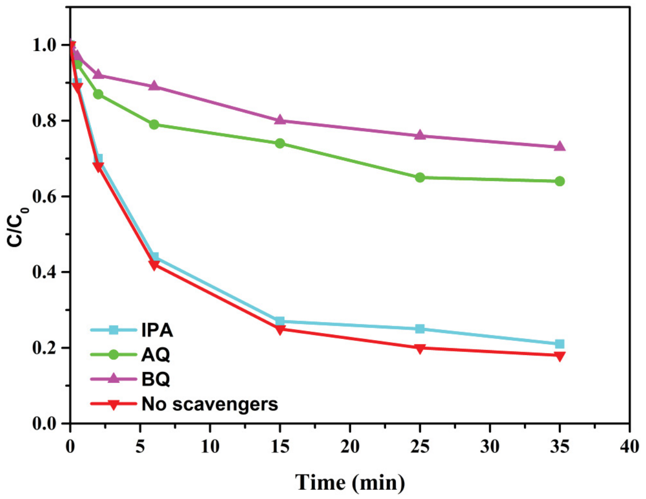

Fig. 3. The photocatalytic activity of $AgIn_5S_8/g-C_3N_4$ for BPA in the presence of different scavengers with 35 min visible light irradiation.

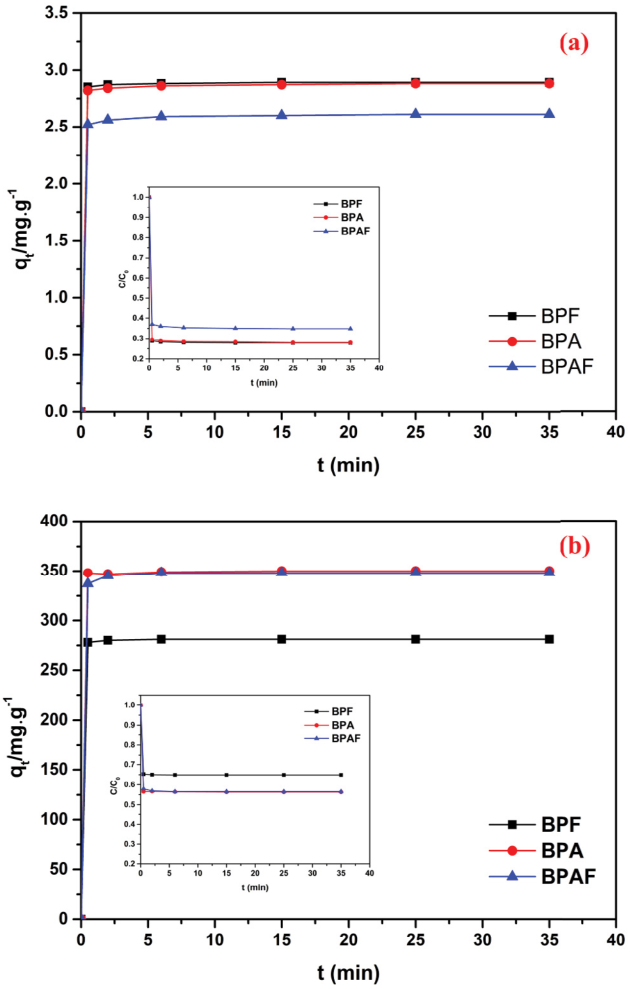

Fig. 4. Adsorption kinetics of bisphenol environmental hormones on NMC (a) initial concentration was 0.2 mg/L and (b) initial concentration was 40.0 mg/L.

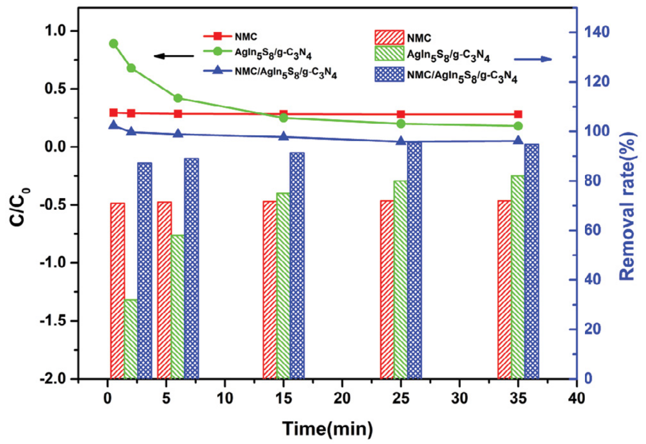

Fig. 5. BPA removal effect by NMC, $AgIn_5S_8/g\text{-}C_3N_4$ and $NMC/AgIn_5S_8/g\text{-}C_3N_4$

seen that, when using the two materials alone, the effect of using the adsorbent was obviously better in the first 10 min of the treatment, and when the treatment time was more than 15 min, the photocatalytic effect was better than the adsorption effect. It can be speculated that the removal of BPA in the first 10 min of composite application was mainly the adsorption effect of NMC, as the BPA adsorption on the NMC gradually reached the equilibrium, photocatalysis began to play a major role. At this time, the photocatalysis simultaneously degraded the BPA in the solution and the BPA already adsorbed to the NMC, and thus, regenerated the adsorption site of the adsorbent in situ, further improving the adsorption performance of the NMC. The synergy of the two effects caused a significant increase in the removal rate of BPA. Adsorption–photocatalytic degradation composite treatment method compared with a single adsorption method, the advantage is that the pollutants adsorbed on the adsorbent can be timely and effectively photodegraded and restore the original pore of the adsorbent, and maintain its adsorption performance. Therefore, the adsorption–photocatalytic degradation composite treatment method studied in this project is characterized by high treatment efficiency, simple process and energy saving, and has good practical engineering application prospects.

In this section, composite application was used to treat simulated wastewater containing BPA (the initial concentration was 0.2 mg/L), and this experiment was performed for four times to investigate the recycling performance of the materials and evaluate the stability of the composite treatment method. The experimental results are shown in Fig. 6. It can be seen from Fig. 6 that after four cycles of recycling, the removal rate of BPA was only slightly reduced (94.8% ~ 93.2%), indicating that the reuse rate of the two materials was high and the stability of composite treatment was also excellent.

3.3.2. Continuous treatment

The experimental results of adsorption–photocatalysis in the continuous flow experiments of the fluidized bed are shown in Fig. 7. As can be seen from the figure, when the dark adsorption was performed, the fluidized bed reached the adsorption equilibrium at about 5 min, the BPA removal rate was 73.6%, and the equilibrium removal rate of BPA was rapidly increased to 97.3% after turning on the light source for photocatalysis. When adsorption and photocatalysis proceed simultaneously, the removal of BPA by the fluidized bed reached equilibrium at about 10 min and the equilibrium removal rate was 96.9%, significantly higher than prior adsorption, indicating that $NMC/AgIn_5S_8/g\text{-}C_3N_4$ also exhibited good adsorption–photocatalytic synergy under continuous flow conditions of the fluidized bed. The highest removal rate of BPA in the dark-free adsorption experiment was about 98.1%. Single methods reported in the literature to treat low concentration of BPA contaminated water has either insufficient removal rate or longer treatment time [25–30]. Therefore, in contrast, the coupling process had the advantages of high processing efficiency and short processing time. Based on the experimental results of batch reaction and continuous flow reaction, it is speculated that the

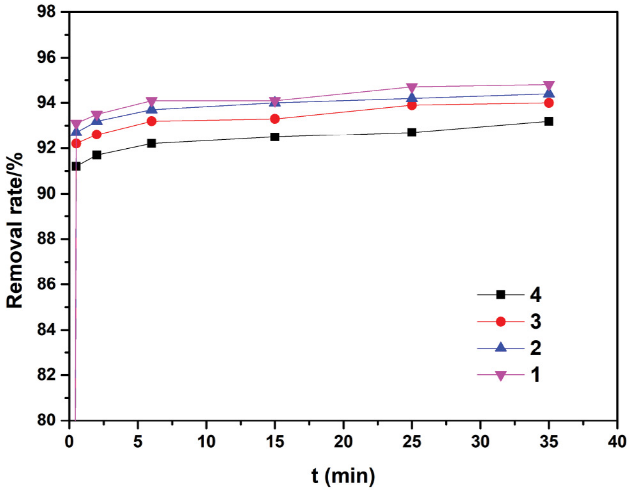

Fig. 6. Recycling performance evaluation.

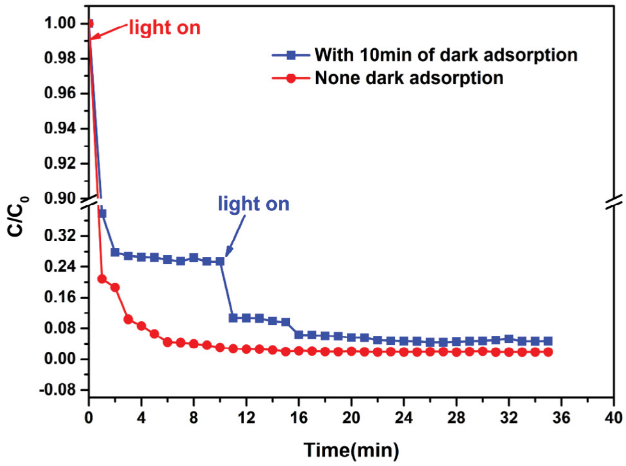

Fig. 7. Effect of dark adsorption on the BPA removal effect in continuous treatment.

possible adsorption–photocatalytic synergy mechanism of this system was that the large adsorption sites were not saturated when the adsorption just began, with the fastest adsorption dynamics. Whereas, with the gradual saturation of the adsorption site, the adsorption kinetic rate decreased significantly. The adsorption site was mostly saturated, in the presence of pre-saturated adsorption steps under dark conditions. At this time, the synergy between photocatalysis and adsorption was greatly reduced. When without the adsorption saturation process under dark conditions and directly for photocatalytic reaction process, because a large number of adsorption sites did not reach the saturation state, and the photocatalytic process constantly decompose the just adsorption BPA into easy intermediates or mineralization products, so that the adsorption site was always in the unsaturated state, and the NMC always maintain a high adsorption rate, thus showing a strong adsorption–photocatalytic synergy. The above inferences are consistent with the results of static batch adsorption–photocatalytic experiments and dynamic fluidized bed adsorption–photocatalytic experiments.

4. Conclusion

The rapid and effective removal of trace environmental hormones in water has always been a difficult problem in the field of water pollution control. It is of great practical significance to study the targeted and efficient treatment process of this kind of wastewater. In this study, metal-doped g-C_3N_4 composite photocatalysts was synthesized and was coupled with nitrogen doped ordered mesoporous carbon to treat water contaminated by environmental hormone micropollutants. Experimental results show that $AgIn_5S_8$/g-C_3N_4 had good photocatalytic degradation performance for BPA and good recycling performance, and its removal rate of 0.2 mg/L of BPA solution could still reach over 80% after 5 cycles. Under the photocatalysis action of $AgIn_5S_8$/g-C_3N_4, the adsorption site of NMC can be regenerated in time, making it has a good cycle removal efficiency for BPA. NMC/$AgIn_5S_8$/g-C_3N_4 showed significant adsorption–photocatalytic synergy in both batch experiments and fluidized bed experiments. The photocatalysis effect of $AgIn_5S_8$/g-C_3N_4 promotes the adsorption site recovery of NMC, and the adsorption effect of NMC enhances the driving force of the photocatalytic degradation of BPA. Under the batch experimental conditions, NMC/$AgIn_5S_8$/g-C_3N_4 could remove 94.8% of BPA (0.2 mg/L) within 35 min. In addition, NMC/$AgIn_5S_8$/g-C_3N_4 system could maintain a removal rate of 98.1% for BPA (0.2 mg/L) in the fluidized bed.

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