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# Cost-effective hybrid adsorbent facilely prepared with dye waste and calcium fluoride for adsorption of organic contaminants

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ABSTRACT

A new sorbent material, calcium fluoride-acid red 138 (AR138), was synthesized and characterized by various methods. The hybrid adsorbent for adsorption of PCBs corresponded to the octanol–water partition law, and their partition coefficients were calculated to be 5,836.8 mg kg$^{-1}$ for PCB029, 8,311.9 mg kg$^{-1}$ for PCB101, and 20,815 mg kg$^{-1}$ for PCB180, respectively. When the hybrid adsorbent was used in the treatment of a polluted ground water sample, the removal of PCB concentrations was satisfactory. All the reactants used in the synthesis of the adsorbent material are easily available and are harmless to the environment. Also, the AR138 reactant may reuse a concentrated AR138-producing wastewater instead. Therefore, this work has developed a simple, eco-friendly, and "waste treat waste" method for the large-scale production of a cost-effective sorbent.

*Keywords:* Hybrid sorbent; Polychlorinated biphenyls; Water treatment; Adsorption

## 1. Introduction

Polychlorinated biphenyls (PCBs) are an organic pollutant group manufactured for use in industry since the 1930s, but their use was banned in the 1970s due to their accumulation and toxicity on human and wildlife health [1–6]. However, it has been known for years that PCBs from industrial products and waste remain in the environment for long periods of time due to their high chemical and thermal stability. Various contaminants including PCBs may be leaching into the water environment [7]. Therefore, it is necessary to develop treatment technologies for the remediation of these compounds.

The primary measure is to strengthen the pollution source control, implement wastewater treatment, and reduce emissions of pollutants so as to solve the water body pollution. The conventional treatment techniques such as flocculation, adsorption, ion exchange, membrane filtration, oxidation, electrolysis, and so on have been applied extensively to treatment of wastewaters [8–11]. For example, due to the advantages of low investment, less energy demand, and easy handling of photochemical oxidation processes for organic pollutants, some hazardous dye wastewaters were efficiently treated by photodegradation [12–16]. However, some of these techniques often have serious limitations [17–21]. It is essential for the joint use of a variety of techniques to achieve the discharge requirement of organic wastewater, and this will greatly increase the process cost and secondary pollution may appear. As an environmentally friendly approach to treat wastewater, the "using waste treat waste" is always what people have

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ever expected while the waste reuse is an optimal selection [22–24]. Recently, Gupta et al. developed many low cost adsorbents for the removal of toxic pollutants from waste waters with waste materials [25–28].

The low solubility and hydrophobic nature of the chlorinated biphenyls make them relatively easy to adsorb from aqueous solution. The purpose of this work was to study the feasibility of eliminating PCBs from polluted ground water. Utilization of industrial wastes for the treatment of polluted water could be helpful not only to environment in solving the industrial wastewater disposal problem, but also the economy. Recently, there has been a great interest in the design and synthesis of inorganic–organic hybrid materials to achieve specific properties [29–31], due to their structural versatility and multifunctional properties [32,33]. However, inorganic/organic hybridization is seldom considered for pollution control, e.g. treating industrial wastewater and polluted ground water. Therefore, a new-style highly effective sorbent was developed by the hybridization of AR138 into $CaF_2$. The skeleton reactants are low-cost, easily available, and harmless to environment and the AR138 reactant may reuse a concentrated AR138-producing wastewater instead. The removal of PCBs by treating the polluted ground water indicated that the sorbent had a high adsorption capacity for PCBs. The adsorption of PCBs corresponded to the octanol–water partition law. Therefore, the developed method has been found to be easy, versatile, and economical because of its easy operation, simple design, and low investment costs.

## 2. Experimental section

### 2.1. Apparatus and materials

A photodiode array spectrometer (Model S4100, Scinco, Korea) with the Labpro plus software (Firmware Version 060105) was used to determine the concentration of color compounds. Infrared (IR) spectra of the hybrid powder were measured by an infrared spectrometer system (Model Equinoxss/hyperion 2000, Bruker Co., Germany). Scanning electronic microscopy (SEM) (Model Quanta 200 FEG, FEI Co., USA) was used to measure the size and shape of the materials. Microstructure of the materials was studied with a high resolution transmission electronic microscopy (HRTEM) (Model Tecnai G$^2$ F20 S-Twin, FEI Co., USA) (120 KV, 2.4 Å resolution). The thermal gravity analysis (TGA) of the material powder was carried out with a thermogravimetry (Model TAQ 600, USA). A high performance liquid chromatography (HPLC) (Model L-2000, Hitachi, Japan) was used to determine PCBs with a diode array detector (DAD) (Model L-2455) and an inverse-phase column (C18, Model Allsphere ODS-2 5μ, 250 mm × 4.6 mm, Alltech Associates, Inc., USA).

The acid red 138 (AR138) containing two negative sulfonic acid groups and a long hydrophobic alkyl chain) reagent (content >98%) purchased from Sigma and AR138-producing wastewater (pH 8.0) containing 0.08% AR138 provided by Jinhua Shuanghong Chemical Plant (Zhejiang, China) were used to prepare the hybrid material. Calcium chloride was purchased from Sinopharm Chemical Reagents (Shanghai, China). NaF was purchased from Shanghai Medical Group. PCB-polluted water containing 2 ppm PCB029, PCB101, and PCB180 was prepared with the Taihu Lake water.

### 2.2. Preparation and measurement of the materials

Into an AR138 solution (1.5 mmol/L) prepared with the AR138 reagent or the AR138-producing wastewater mixed with 0.120 mol/L NaF, 200 ml of 0.040 mol/L $CaCl_2$ was added slowly under stirring. The reaction liquid was stewed for precipitating the suspended substances, and then the precipitate was washed three times with 2000 ml of deionized water. The final suspending substance liquid with the $CaF_2$/AR138 (CFA) material was formed. The microstructure of the material was measured by the TGA, X-ray diffraction (XRD), IR, SEM, and HRTEM.

### 2.3. Adsorption of organic compounds

In order to clarify the adsorption of hydrophobic organic contaminants on the CFA sorbent, PCB029, PCB101, and PCB180 were selected. A known weight of CFA was added to 10 mL of each PCB solution in various concentrations and each liquid was mixed for 15 min. Then, the concentrations of PCBs in the supernatants were determined by HPLC coupled with a DAD at 210 nm for PCBs. The optimized mobile phases were the methanol–phosphate buffer (pH 7.0) (v/v: 95:5) with the flow rate at 1.0 mL/min (isocratic mode) for PCBs. The retention time is 3.75 min for PCB029, 4.21 min for PCB101, and 7.10 min for PCB180. All injections (20.0 μL) were performed manually. Their $K_{pw}$ values were calculated, and the relationship between the $K_{ow}$ and $K_{pw}$ of the contaminants was established.

### 2.4. Treatment and restoration of polluted waters

A polluted water sample containing PCB029, PCB101, and PCB180 wastewater was treated by adding the adsorbents (0.08, 0.12, 0.16, 0.20, 0.24, and 0.30 mL of 5.0% CFA liquid) in 10.00 mL polluted water. After mixing for 15 min, the concentrations of PCBs in the supernatants were determined by HPLC.

## 3. Results and discussion

### 3.1. Formation and characterization of the $CaF_2$/AR138 hybrid material

According to the experimental result (Fig. 1), the hybridization of AR138 into $CaF_2$ particles remained maximal when the molar ratio of $F^-$ to $Ca^{2+}$ is approximately 3 and pH over 2. Hence, the preparation of the hybrid material was carried out in neutral media. According to the optimal conditions, a suspending solid (SS) liquid containing CFA was synthesized.

From the SEM and HRTEM images (Fig. 2), the $CaF_2$-only particles are stacked like the square shape with the mutual adhesion, most of which are about 100–200 nm (Fig. 2A–C). This is attributed to the dense packing of $CaF_2$ layers. The CFA particles are global in 100–150 nm of size with the clear particle borderline (Fig. 2E–G). Therefore, the participation of AR138 inhibited the self-stacking of $CaF_2$. Without doubt, the addition of AR138 plays an important role in controlling the size and morphology of the material. From electron diffraction X-ray scanning (EDX) of the $CaF_2$ and CFA materials (Fig. 2D and H), AR138 resulted in a polycrystal formation, i.e. AR138 was occluded in $CaF_2$. However, from the XRD data of $CaF_2$ and CFA (Fig. 3C), AR138 has not altered the crystallization process of $CaF_2$, i.e. AR138 was captured via the affinity between $CaF_2$ and $-SO_3^-$ groups of the AR138 [34,35]. The IR spectrum (Fig. 3A) revealed the difference in composition between the $CaF_2$ and the CFA materials. The $CaF_2$ has characteristic vibration bands—strong peaks at 2,954 and 2,923 $cm^{-1}$, peaks at 1,463 and 1,377 $cm^{-1}$, and weak peak at 722 $cm^{-1}$ (Fig. 3A). In the hybrid material, the characteristic vibration peaks of AR138 (Fig. 3A) were found at 3,000–3,600 $cm^{-1}$ of O–H and N–H, 1,650 $cm^{-1}$ of C=O, 1,500 $cm^{-1}$ of N=N and the $\upsilon(-SO_3^-)$ peak at 1,230 and 1,100 $cm^{-1}$ [36]. It convinced the hybridization of AR138 into the calcium flouride growing. From TGA of the AR138-only, $CaF_2$-only, and CFA hybrid materials (Fig. 3B), AR138 appears to undergo a strong thermal decomposition between 250 and 600℃. The weight loss of AR138 is 26% around 250℃ and 27% around 400℃. The former may be due to the volatilization of alkyl chain $-C_{12}H_{25}$ and the latter due to the decomposition of azo naphtholamide [37–39].

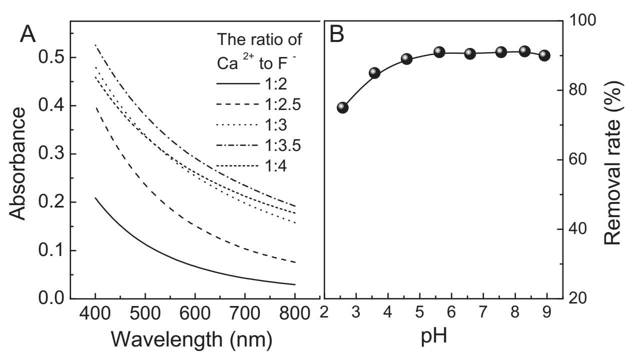


Fig. 1. A-the optimum dosages of $F^-$ addition in the process of becoming $CaF_2$ in the presence of 0.040 mol/L $Ca^{2+}$; B-Effect of pH on assembly aggregation of CFA. (0.120 mol/L $F^-$, 0.040 mol/L $Ca^{2+}$, 1.5 mmol/L AR138).

### 3.2. Interactions of PCBs with the materials

AR138 contains a long alkyl chain, $-C_{12}H_{25}$ group, which may expose on the outside surface of the hybrid material. The hydrophobic shell formed will adsorb lipophilic organic substances e.g. persistent organic pollutants (POPs). Recently, it has been reported that POPs, which can be detected in a variety of surface waters [40–43], have an impact on human and animal systems – including carcinogenic, teratogenic, and mutagenic toxicity [44,45]. They are also endocrine disruptors [46]. POPs are highly resistant in the aquatic environment. So, their industrial use in many industrialized countries has been restricted since the 1970s. These compounds have also been considered for inclusion in the priority pollutant list of the State Environmental Protection Administration in China [47]. As a category of POPs, the adsorptions of three PCBs: PCB029, PCB101, and PCB180 were investigated on CFA adsorbent.

From the curves in Fig. 4, the adsorption of PCBs on the CFA absorbent accorded with the octanol–water partition law, i.e. hydrophobic interaction occurred between the long alkyl chain of AR138 and PCBs. According to the line slopes, the partition coefficients ($K_{pw}$) of PCBs were calculated to be 5836.8 mg/kg for PCB029, 8311.9 mg/kg for PCB101, and 20,815 mg/kg for PCB180, respectively (Fig. 4). The $K_{pw}$ values of PCB029, PCB101, and PCB180 are in direct proportion to their $K_{ow}$ ($\log K_{ow} = 5.81$ for PCB029, 6.50 for PCB101, and 7.21 for PCB180) [48,49]. The $K_{pw}$ is the almost direct ratio to the corresponding $K_{ow}$ with 0.608 of slope (Fig. 5), i.e. 6 g of the CFA played the role equivalent to 1 g of octanol in the removal of POPs.

### 3.3. Effect of temperature and time

The influence of time and temperature on PCB101 by CFA was investigated at five different temperatures (namely, 10, 20, 30, 40, and 50℃) from 0 to 30 min at an initial PCB concentration of 1.2 mg/L. With an increase in temperature from 10 to 50℃, the removal efficiency of PCB101 by CFA increased from 87.6 to 92.0%. These increases might be due to

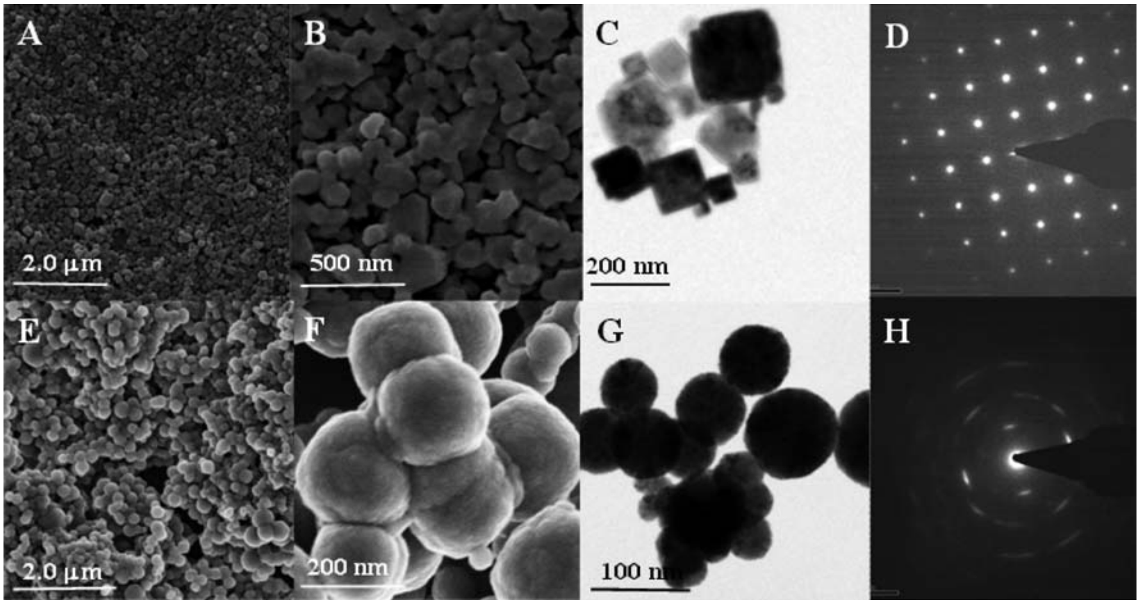


Fig. 2. SEM images of $CaF_2$-only (A, B) and CFA hybrid particles (E, F), HRTEM of $CaF_2$-only (C), CFA hybrid particles (G) and EDX images of $CaF_2$-only (D) and CFA hybrid particles (H).

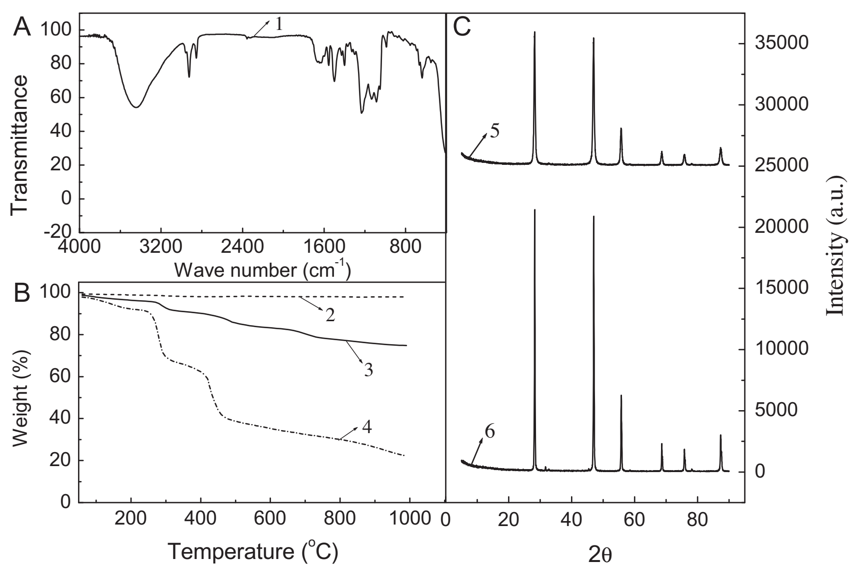


Fig. 3. A-IR spectra of CFA (curve 1), B-different particles TGA for $CaF_2$-only (curve 2), CFA (curve 3) and AR138-only (curve 4) and C-XRD of $CaF_2$-only (curve 5) and CFA (curve 6).

increased mobility of the PCBs and a higher availability of active surface sites at higher temperatures [50]. This result indicates that higher temperatures slightly favor the removal of PCBs by adsorption onto CFA. In addition, from the curves in Fig. 6, the effect of time and temperature on the adsorption of PCB101 indicated that the saturation adsorption is complete in 5 min and that temperature has no obvious effect between 10 and 50°C.

### 3.4. Application in polluted water treatment

Recycle and reuse of waste has caught people's attention more and more [51,52]. A more practical hybrid material was prepared with an AR138-producing wastewater instead of AR138 reagent. With the same determination method, it contains similar mole number of AR138 to that prepared with the above AR138 reagent. A polluted water sample with PCBs was treated by the CFA adsorbent. From the curves in

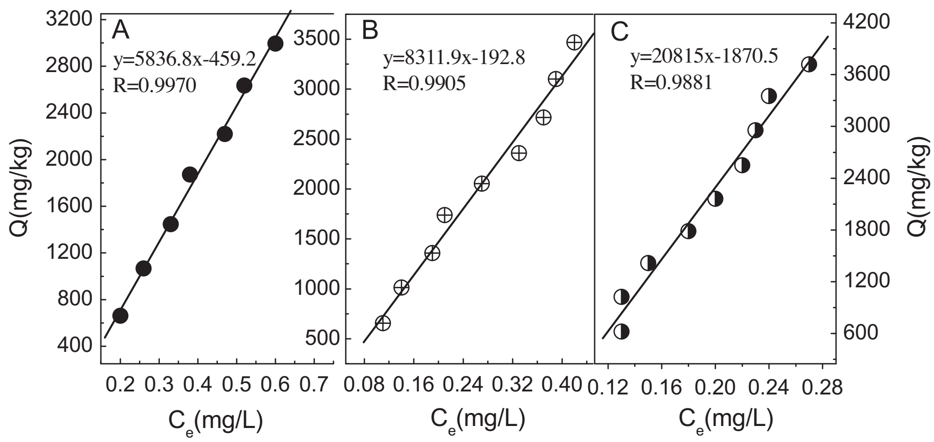


Fig. 4. Adsorptions of PCB029 (A), PCB101 (B), and PCB180 (C) 0.06% CFA was added.

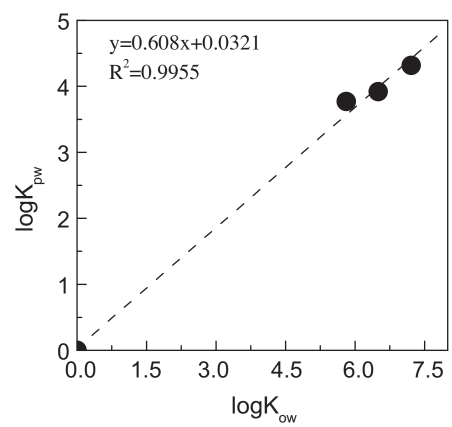


Fig. 5. The correlation between $K_{pw}$ and $K_{ow}$.

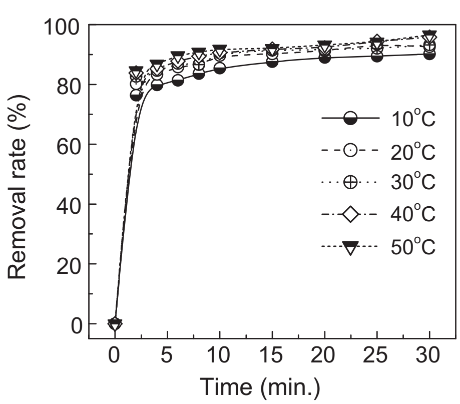


Fig. 6. Effect of temperature and time on the removal rate of PCB101 absorbed by 0.05% CFA hybrid particles.

Fig. 7, the removal rates of PCBs in the polluted water containing PCB029, PCB101 and PCB180 increased with increase of the adsorbent. The removal rates are 86% for PCB029, 89% for PCB101, and 94% for PCB180 when 10.0 mg of the CFA adsorbent is added in 10.0 mL of the polluted water (0.1% CFA). Therefore, the co-existence of organic contaminants does not affect their simultaneous removals from the polluted water. Without doubt, the CFA is a good sorbent for adsorption of PCBs in the polluted water.

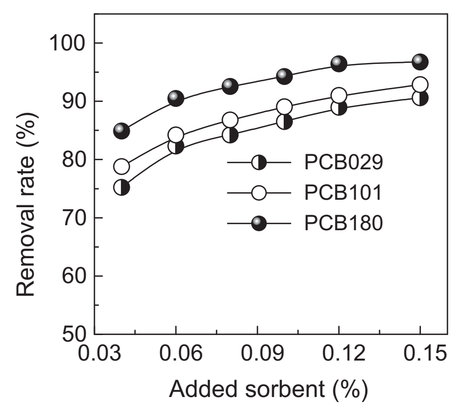


Fig. 7. The removal rate of PCBs in the polluted water treated with CFA sorbent.

## 4. Conclusion

A new-style highly effective material was prepared by the hybridization of AR138 into calcium fluoride and characterized structurally by various instruments. The adsorption of PCBs corresponded to the lipid–water partition law via hydrophobic stacking. The CFA adsorbent was used to treat polluted ground waters with satisfactory results. The skeleton reactants are low-cost, easily available, and harmless to the environment; additionally, the AR138 reactant may reuse a concentrated AR138-producing wastewater instead. Therefore, this work has developed a simple, eco-friendly, and cost-effective sorbent for organic contaminants in ground water. It will be very significant for environmental conservation and the protection of the health of the people.

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