Nanosecond-Pulsed Dielectric Barrier Discharge Regeneration Granular Activated Carbon in Water Filtration Applications

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Abstract: At present, there are no commercially available treatment technologies that can destructively remove per- and polyfluoroalkyl substances (PFAS) from filter material, such as granular activate carbon (GAC). Nonthermal plasma has demonstrated promising results in both (1) improving adsorption characteristics via producing amine chemical groups on the surface of GAC and (2) destructively mineralizing adsorbed PFASs to regenerate spent GAC. Drexel University is currently investigating an innovative GAC regeneration method using a dielectric barrier discharge to treat the surface for regeneration and adsorption improvement.

Keywords: Non-equilibrium plasma, DBD, granular activated carbon, water treatment, contaminant removal, surface amination

PFASs as emerging contaminants

Perfluoroalkyl substances (PFASs) have been used extensively in industrial products, as they exhibit useful physical and chemical properties including hydrophobicity and oleophobicity [1-4], but they also represent a potential human and ecosystem health risk including reproductive, developmental, and carcinogenic effects [5-8]. Due to growing evidence suggesting PFASs are persistent, bioaccumulative, and toxic [1, 5-7, 9, 10], many US and international governing bodies have begun to establish regulations and advisory levels for select species of this emergent contaminant. New regulations and advisory levels for PFOA and PFOS have resulted in increased wastewater treatment costs or inadequate wastewater treatment practices. Treatment technologies are needed that can achieve levels under 70 parts-per-trillion. Presently, there are insufficient treatment technologies that can destructively remove PFASs.

Current water treatment solution

Most water treatment plants today do not utilize filtration methods capable of removing PFAS species from water due to regulations not yet in effect. Therefore, the predominant bulk water filtration method resides in sand filtration, as it comes with very low associated costs. Upon establishment of these regulations requiring effective PFAS removal from water, activated carbon filtration is the most practical method in terms of PFAS removal and affordability, yet it still adds significant operational costs.

Due to the lack of demonstrated treatment technologies capable of mineralization of PFOS and PFOA, removal of these compounds from contaminated wastewater has been limited to adsorption by activated carbon (AC), membrane filtration, or ion exchange resin (IX), with AC being the most affordable while maintaining its effectiveness. PFOA and PFOS belong to a subset of PFASs referred to as perfluoroalkyl acids (PFAAs), which have negatively charged head groups at near neutral pH and a hydrophobic perfluorinated tail. Since the surface of AC are generally non-polar, granular activated carbon (GAC) is often used to remove hydrophobic pollutants from water. GAC is regenerable and tends to be used more in water filtration.

GAC regeneration

Thermal regeneration of activated carbon is currently the most effective at removing PFAS chemical species from the surface, however, this process is highly energy inefficient and suffers from a carbon mass loss of 15% [11].

The use of corona pulsed plasma discharges has recently been shown to rapidly mineralize a significant amount of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) in groundwater into carbon dioxide (CO_2) and fluoride ions (F^-) [12]; however, pulsed corona is difficult to scale up primarily because its power output is relatively low (on the order of mW/cm^3) and, for this reason, we are investigating DBD plasma with power outputs on the order of 1 W/cm^3 (experimental set-up shown in Figure 1), requiring only one thousandth of the

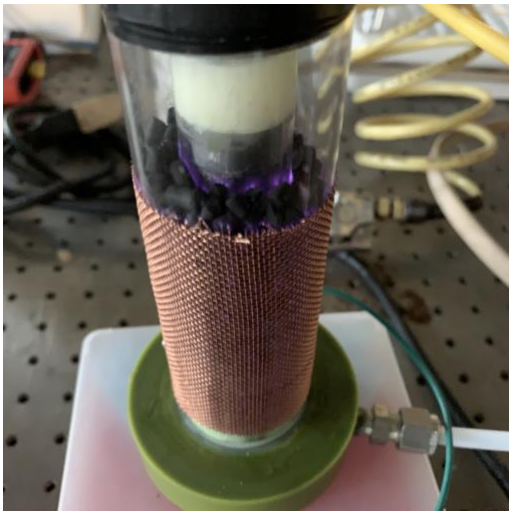

Figure 1. Single chamber DBD plasma GAC regeneration system during testing.

footprint required by corona discharge. DBD plasma can create more energetic reactive species/conditions that have been commercialized to oxidatively degrade gaseous PFCs (*e.g.*, C_2F_6, CF_4, NF_3) in other applications [13, 14]. These previously validated examples support DBD plasma's promise as an effective technology for PFAS degradation along the surface of saturated activated carbon.

GAC amination

The extent of PFOS and PFOA uptake by GAC has recently been shown to be positively correlated with surface basicity [15]. Surface modification of ACs to increase basicity of their surface chemistry by using ammonia gas at elevated temperatures (700°C) led to enhanced adsorption of PFOA and PFOS [16]. This ammonia gas treatment causes surface amination (i.e., the formation of NH_2 and NH functional groups on the carbon surface). Non-thermal DBD plasma can use a mixture of nitrogen and hydrogen (N_2/H_2) gas to introduce amine and amide groups to the surface of GAC. This approach can follow the in-air regenerative DBD plasma treatment to rapidly mineralize adsorbed PFOA/PFOS and then introduce amine groups to regenerate and improve the GAC for reuse with higher adsorption rates than untreated GAC.

Challenges associated with GAC plasma regeneration and amination

The major technical challenges associated with bringing this technology to market is demonstrating the proof-of-concept and feasibility of using non-thermal plasma technology to achieve surface amination on GAC and to oxidatively mineralize PFOA and PFOS adsorbed on the surface of GAC to regenerate it. To date, no one has used plasma treatment with N_2/H_2 gas to introduce amino groups to the surface of GAC. There has, however, been demonstrated use of microwave-excited ammonia/argon (NH_3/Ar) surface-wave plasma for surface amination of multiwall carbon nanotubes [17]. The surface of many biopolymers (e.g., polystyrene, polyethylene, polycarbonates) have been functionalized with amino groups using low-pressure plasma processes, such as microwave and radiofrequency plasma using either NH_3 gas or N_2/H_2 mixtures of gas (see references in [18]). In our research, we are investigating the capacity to synthesize amino groups on the surface of GAC utilizing a DBD plasma technology.

Additionally, it is well-known that activated carbon, especially when wet, can be highly conductive and thus disrupt the generation of plasma discharges. In order to avoid this, the operation and design of our plasma absorber system may be altered to allow for fluidization of the bed to reduce its conductive interference during plasma-assisted regeneration of the GAC.

Despite the challenges described above, the concept of using plasma technology to enhance GAC adsorption and for on-site/*in situ* regeneration the GAC is innovative and groundbreaking. The majority of currently available PFOS/PFOA absorbing methods that compete with our proposed technology do not have the capability to be reused/regenerated. That is, once the material has absorbed contaminants to its capacity, it must be disposed of. This proves disadvantageous to regenerable filtration systems as disposal requires additional resources that accumulate into a higher operation cost. Even processes that use off-site regeneration, must deal with liability concerns and transportation costs associated that increase operation costs. The potential for on-site regeneration using plasma has the potential to reduce the environmental concerns and operational costs associated with using GAC to remove PFOA and PFOS from water.

Discussion

The small-scale system set-up shown in Figure 1 has provided us with initial data allow us to make steps towards feasibility verification of this technology and

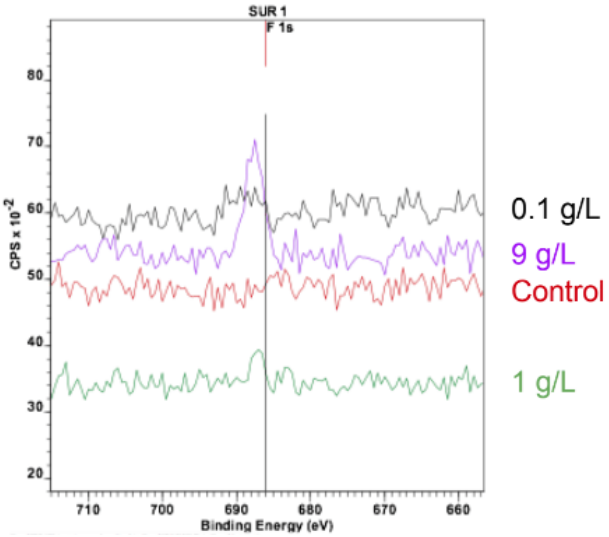

Figure 3. XPS spectra showing fluorine concentration progress for all four GAC samples.

we continue to optimize the system and analyze its resulting data to develop a larger scale system capable of answering industrial needs. XPS (Figure 2) and FTIR (Figure 3) spectroscopic scans are able to detect atomic fluorine and C-F bonds respectively, however, due to the complexity of these processes, detection precision is anticipated to improve as we continue to refine these analytical methods. Preliminary efforts towards the validation of non-equilibrium plasma are promising and further data will be presented at ISPC 24.

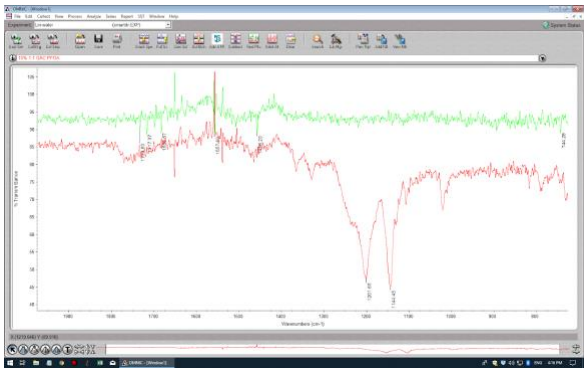

Figure 2. FTIR spectrum comparison of 10% control GAC in KBr (green) and 10% 1:1 GAC / PFOA in KBr (red).

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