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Synthesis of magnetic nanocomposite microparticles for binding of chlorinated organics in contaminated water sources

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Abstract

In this work, the development of novel magnetic nanocomposite microparticles (MNMs) via free radical polymerization for their application in the remediation of contaminated water is presented. Acrylated plant-based polyphenols, curcumin multiacrylate (CMA) and quercetin multiacrylate (QMA), were incorporated as functional monomers to create high affinity binding sites for the capture of polychlorinated biphenyls (PCBs), as a model pollutant. The MNMs were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy, dynamic light scattering, and UV–visible spectroscopy. The affinity of these novel materials for PCB 126 was evaluated and fitted to the nonlinear Langmuir model to determine binding affinities (K_D). The results suggest the presence of the polyphenolic moieties enhances the binding affinity for PCB 126, with K_D values comparable to that of antibodies. This demonstrates that these nanocomposite materials have promising potential as environmental remediation adsorbents for harmful contaminants.

Keywords

Adsorption; Magnetism and Magnetic Properties; Radical Polymerization; Separation Techniques

1 | INTRODUCTION

In recent years, nanotechnology has become one of the fastest growing topics of interest given its potential to greatly improve areas in telecommunications, electronics, manufacturing technologies, health, and environmental remediation. The benefits associated with using nanomaterials result from their large specific surface area and high reactivity, when compared to their bulk counterparts.^[1] Additionally, physical properties of nanomaterials, such as size, porosity, morphology and chemical composition, can be tuned to specifically target molecules of interest, depending on the desired application. This

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SUPPORTING INFORMATION

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combined with a rich surface chemistry modification capacity allows for significant advantages over traditional materials. Nanocomposites are comprised by two or more materials, combining the desired properties from each individual component into the composite system in order to develop more efficient, stable or selective materials.^[2] A subclass of these, magnetic nanocomposite materials, has attracted significant interest in recent years because of their potential application in fields like magnetic resonance imaging, catalysis, biomedicine, and environmental remediation.^[3,4]

Magnetic nanocomposite materials are generally composed of a magnetic nanoparticle embedded within a non-magnetic matrix, commonly made up of polymers, surfactants, or different forms of carbon. These materials combine the properties of an organic matrix with the intrinsic magnetic properties of the nanoparticles, leading to a fast and facile separation method. Magnetic separation is a simple and low-cost method for removing pollutants from contaminated water or slurries, and often times more efficient than more cumbersome methods like centrifugation and membrane filtration. The most commonly used magnetic nanoparticle is iron oxide (IO MNPs) or magnetite (Fe_3O_4), and Fe_3O_4 is super-paramagnetic.^[5,6] More so, these magnetic nanoparticles can be produced with readily available materials through well-known methods, facilitating their scale up process. These magnetic composites have found their main area of application in environmental remediation, specifically their use as adsorbents for organic pollutants, heavy metals, and other emerging contaminants.^[7-9]

Water pollution is a major threat worldwide, which continues to become more complex, difficult, and costly, due to the vast majority of chemicals being discharged into the environment. This is a result of rapid developing economies and technologies, and the inability of regulatory agencies to keep up with the various innovations and their effects in the environment and human health.^[10,11] As harmful contaminants continue to be distributed worldwide, the need to remove them from the environment and increase access to safe drinking water becomes increasingly important. Polychlorinated biphenyls (PCBs) are a group of chlorinated aromatic compounds with a large number of isomers or congeners.^[12] PCBs are some of the most persistent organic pollutants in the environment, despite their production ban in the United States in 1979 and further priority classification in the Stockholm Convention on Persistent Pollutants held in 2001.^[13-15] PCBs are ubiquitous in the environment have low solubility and low volatility, and can bio-accumulate throughout the food chain, making their extraction from soil and water especially challenging.^[13,16,17] The most common remediation techniques employed nowadays consist of using physical caps on contaminated areas or dredging of the area and its deposition on a landfill, both of which can result in further leaching of the contaminant into the environment. Alternatively, they are degraded via incineration of stocks, which can result in incomplete combustion and further environmental exposure.^[18] Recently, dechlorination techniques have been applied to the degradation of PCBs, however they need to be coupled with further oxidation approaches to break the biphenyl ring and, in some cases, formation of more harmful degradation contaminants can occur.^[13,15] There is a need for other remediation techniques for PCBs that limit the production of harmful by-products and reduce the possibility of further contamination to the environment in their application.

Adsorption is a popular method for water treatment due to its simplicity and vast sorbet variety. Features of the adsorbent such as large surface area, porosity, mechanical strength, tunable shape, and morphology, and the presence of a variety of surface functional groups allow for their targeting towards specific contaminants.^[19,20] One way to increase the affinity for hydrophobic molecules, such as PCBs, is by incorporating hydrophobic components into the polymeric matrix of the magnetic nanocomposite. Of particular interest to our group are plant derived polyphenols, curcumin and quercetin, because they are a well-studied group of naturally occurring antioxidants rich in aromatic moieties. The prevalence of aromatic groups has been detected in other molecules that present very high affinities for PCBs, such as the monoclonal antibody S2B1. Through computational analysis, a sterically hindered deep binding pocket rich in aromatic residues from tyrosine and arginine was discovered, demonstrating a high selectivity for nonortho chlorinated PCBs congeners.^[21] This pocket consists of a narrow opening at the top that leads to a shallow pocket where π - π interactions between the antibody and the PCB molecule thrive, and an adjacent deep pocket where π - π interactions and π -cation interactions stabilize the bound aromatic ligand.^[22] These types of interaction have also been observed between water and sediment in the environment, especially with humin and humic matter and PCB molecules.^[19,23] Therefore, the incorporation of aromatic rich molecules, such as plant derived polyphenols, into the polymer matrix of the magnetic nanocomposites will increase the affinity of these materials for PCBs in solution.

The proposed study focuses on the development of magnetic nanocomposite microparticles using free radical polymerization to synthesize PEG-based crosslinked polymers with functional monomers from acrylated plant derived polyphenols and magnetic iron oxide nanoparticles. Both curcumin multiacrylate and quercetin multiacrylate were used in order to enhance the binding affinity of the systems towards PCBs 126, our model contaminant. Binding isotherms were fitted using the Langmuir model obtaining the binding constants and the maximum binding capacities of the synthesized MNM systems.

2 | EXPERIMENTAL

2.1 | Materials

Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ammonium persulfate (APS), N,N,N'-trimethylethylenediamine 97% (TEMED), triethyl amine (TEA), acryloyl chloride, and potassium carbonate (K_2CO_3) were obtained from Sigma Aldrich (St. Louis, MO). Ammonium hydroxide (NH_4OH) was purchased from EMD Chemicals (Gibbstown, NJ). Poly(ethylene glycol) 400 dimethacrylate (PEG400DMA) was obtained from Polysciences Inc. (Warrington, PA). Curcumin was purchased from Chem-Impex International, Inc. (Bensenville, IL) and quercetin was purchased from Cayman Chemicals (Ann Arbor, MI). 3,3',4,4',5-Pentachlorobiphenyl (PCB-126) in isooctane was purchased from Accustandard (New Haven, CT). 5'-fluoro-3,3',4,4',5-pentachlorobiphenyl (F-PCB 126) was purchased from Resolution Systems Inc. (Holland, MI). All solvents (Isooctane, ethanol HPLC grade, tetrahydrofuran (THF); dichloromethane (DCM), acetonitrile (ACN), acetone) were obtained from Fisher Scientific (Hannover Park, IL). All materials were used as received.

2.2 | Iron oxide nanoparticle synthesis

Iron oxide magnetic nanoparticles (IO MNPs) were synthesized via a one-pot coprecipitation method.^[24] In a 3-neck flask a 2:1 M ratio of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, respectively, were dissolved in 40 ml of deionized (DI) water. The flask was sealed purged with nitrogen flow to achieve an inert synthesis environment. Under vigorous stirring and constant N_2 flow, the solution was heated to 85 °C under and, at this point, 5 ml of NH_4OH (30.0% vol/vol) was injected dropwise into the vessel. The reaction was carried out for 1 hr under these conditions. The nanoparticles were then magnetically decanted and washed thrice with DI water. Finally, the particles were resuspended in 45 ml of DI water and dialyzed against water for 24 hr (100 kDa molecular weight cutoff).

2.3 | Curcumin multiacrylate synthesis and purification

Curcumin multiacrylate (CMA) was prepared according to the protocol described by Patil et al.^[25,26] Briefly, curcumin was dissolved in THF at a concentration of 50 mg ml^{-1} . Acryloyl chloride and TEA, both, were added at a 3:1 ratio with respect to curcumin. The reaction mixture was then purged with nitrogen for 20 min and allowed to react overnight. Following, byproduct salts formed during reaction were removed through filtration and the THF was evaporated. The remaining solid was redissolved in DCM and purified by washing three times with K_2CO_3 0.1 M to remove any unreacted acryloyl chloride, and again thrice with HCl (0.1 M) to remove unreacted TEA. Finally, the DCM was evaporated to obtain CMA.

2.4 | Quercetin multiacrylate synthesis and purification

Quercetin multiacrylate (QMA) was prepared according to the method described by Gupta et al.^[27] Briefly, quercetin was dissolved in anhydrous THF at a concentration of 100 mg ml^{-1} . Both acryloyl chloride and K_2CO_3 were added at a 6:1 ratio with respect to quercetin. The reaction vessel was purged with nitrogen for 20 min and allowed to react overnight. The byproduct salts formed were then filtered out from the reaction mixture. The THF was evaporated and the remaining solid was redissolved in DCM. This solution was then purified by washing three times with K_2CO_3 0.1 M to remove unreacted acryloyl chloride. Finally, the DCM was evaporated to obtain QMA.

2.5 | Magnetic nanocomposite microparticle synthesis

In order to make the MNMs, we first synthesized a gel with the desired functionalities in glass templates via free radical polymerization. The functional monomer, CMA or QMA, was dissolved in DMSO and added to the polyethylene glycol 400 dimethacrylate (PEG400DMA) in a 1:9 ratio. The uncoated MNPs (1 wt%), dispersed in DI water, were then incorporated into this mixture, and quickly vortexed to ensure a good dispersion. The initiator was then added to the mixture, closely followed by the accelerator. The mixture was again vortexed and added to the glass template where the polymerization took place. Ammonium persulfate dissolved in ethanol (APS, 2 wt%) was used as the initiator for the reaction, and N,N,N',N'-tetramethylethylenediamine (TEMED, 0.67 wt%) as the accelerator. Once polymerization occurs, the polymer was cut into small pieces and washed once with ethanol, three times with a 50–50% (vol/vol) ACN/DCM solution, twice with a 50–50% (vol/vol) ethanol/DI water solution, and finally once with water. The polymer

pieces were then placed overnight in a freezer at -4°C and then lyophilized for a period of 24 hr to remove any excess solvent (Figure 1).

2.6 | Cryomilling

The polymers were placed in stainless steel vials and cryomilled under liquid nitrogen using a SPEX SamplePrep 6770 Freezer/Mill Cryogenic Grinder. The process began with a 5 min precool, followed by two 10-min cycles at 10 rpm and completed with a 2-min cool down. The microparticles obtained followed a uniform distribution.

2.7 | Microparticle characterization

2.7.1 | Fourier transform infrared (FTIR) spectra—Attenuated total reflectance FTIR (ATR-FTIR) was used to determine the incorporation of the acrylated polyphenols into the polymers with a Varian Inc. 7000e spectrometer. Dried samples were placed on the diamond ATR crystal and the spectrum was obtained between 700 and $4,000\text{ cm}^{-1}$ using 32 scans.

2.7.2 | Thermogravimetric analysis (TGA)—A Netzsch Instruments STA 449A system was used to conduct a TGA of the nanocomposites and quantify the mass percent corresponding to the iron oxide nanoparticles incorporated. Under constant nitrogen flow, approximately 5 mg of the dry sample was heated at a rate of $5^{\circ}\text{C}/\text{min}$ until a temperature of 120°C . The system was kept isothermal for 20 min to vaporize residual solvent and water vapors. Then, the sample continued to be heated at $5^{\circ}\text{C min}^{-1}$ until a temperature of 600°C . The presented mass loss values are normalized to the mass after isothermal heating at 120°C .

2.7.3 | Particle sizing using a micron sizer—A Systat SigmaScan 5.0 software was used to digitally determine the mean size of the microparticle sample and perform the dynamic light scattering analysis of the MNMs in DI water as solvent. The nanocomposite systems were probe sonicated to solubilize at approximately 1 mg/ml. All measurements were conducted in triplicates.

2.7.4 | Scanning electron microscopy—Scanning electron microscopy (SEM) was completed using a Hitachi S4300 microscope in order to observe the particle size. Double-sided adhesive carbon tabs were adhered onto aluminum studs (Ted Pella) and carefully dabbed against a weigh paper containing the dry sample. For all systems, three independent samples were prepared and multiple images were examined for each sample.

2.7.5 | Ultraviolet (UV)–visible spectroscopy—The stability of the nanoparticles was analyzed using a Cary Win 50 probe UV–visible spectrophotometer. The MNMs were suspended in DI water at a concentration of 0.1 mg/g and probe sonicated for 10 min. The samples were placed in a quartz cuvette and their change in absorbance was studied for 12 hr at a wavelength of 540 nm.

2.7.6 | PCB 126 binding studies—The capacity of the MNMs to bind PCB 126 was studied under equilibrium conditions, determined by previous kinetic studies. All

experiments were carried out using 0.1 mg of the microparticle systems (CMA MNMs, QMA MNMs, and PEG MNMs), suspended in a 99:1 DI water to ethanol solvent in 3 ml borosilicate glass vials.

All binding experiments were carried out in batch conditions where 0.1 mg of dry MNMs were weighed into 3 ml borosilicate glass vials and dispersed in DI water. The samples were then spiked using one of the freshly prepared PCB stocks at one for seven different concentrations (0.0003, 0.0005, 0.001, 0.0025, 0.005, 0.0075, 0.01 ppm), all whilst maintaining a 99:1 DI water to ethanol solvent ratio. All samples were bath sonicated for 10 min and then placed in an orbital shaker at 200 rpm and room temperature for 48 hr. After the equilibrium binding study finalizes, the samples are exposed to a static magnet for approximately 20 min to make sure all suspended particles are decanted, as seen in Figure 2. The supernatant containing the unbound PCB was transferred into a new borosilicate glass vial and a 1:1 liquid extraction using isooctane was conducted for a period of 24 hr. Following this, the organic phase, rich in PCB 126, was collected using a Hamilton syringe and deposited directly into a gas chromatography vial. Each sample was then spiked with a known amount of the internal standard, 5'-fluoro-3,3',4,4',5-pentachlorobiphenyl (F-PCB 126). Using an Agilent 6890N gas chromatograph coupled with electron capture detection (CG-ECD), equipped with an Agilent HP-5MS UI column (30 × 0.25 × 0.25), was used to determine the PCB 126 concentration before and after equilibrium binding studies. All studies were carried out in triplicates, as was each sample per study.

Similarly, batch experiments were conducted for microparticles (MPs) prepared following the same synthesis and characterization procedure as the MNMs, however, without the incorporation of the magnetic nanoparticles. These MPs are used as controls during the binding studies to determine the effect the magnetic component has in binding. For this purpose, three systems were evaluated: CMA MPs, QMA MPs, and PEG MPs.

The Langmuir model is the most commonly used model to evaluate the interactions between a molecular adsorbate and a surface site on an adsorbent, and accurately describes many adsorption processes.^[28,29] This model assumes uniform energy for all adsorption sites at localized sites occurring on a homogeneous surface and monolayer adsorption.^[28] The Langmuir model is represented by the following equation:

$$q_e = \frac{B_{\max} K_D C_e}{1 + K_D C_e} \quad (1)$$

where q_e (mg/g) represents the quantity of adsorbate bound at equilibrium, C_e (mg/L) is the equilibrium concentration of the adsorbate, K_D (L/mg) is the adsorption coefficient of the adsorbant related to the energy of adsorption, and $B_{\max}$ (mg/g) is the maximum adsorption capacity of the adsorbent, also known as the equilibrium monolayer capacity.

3 | RESULTS AND DISCUSSION

Magnetic nanocomposite microparticles were prepared via chemically initiated free radical polymerization. FTIR analysis confirms a successful polymerization for all systems. Figure 3 shows the resulting spectra for the MNM systems where characteristic peaks for

PEG400DMA and the functional monomers, CMA and QMA, can be observed. The acrylated polyphenols used in synthesis contain aromatic rings in their structure (Figure 2). Evidence of this functional group in the CMA MNMs is the presence of three peaks between $1,604\text{ cm}^{-1}$ and $1,400\text{ cm}^{-1}$, attributed to symmetric ring vibrations, as well as peaks at $1,026\text{ cm}^{-1}$ and 964.4 cm^{-1} of lesser intensity that correspond to the enol ($\text{C}=\text{O}-\text{C}$) functionality and the benzoate $\text{C}-\text{H}$ vibrations of the aromatic rings, respectively. Likewise, the presence of the benzene rings in the QMA MNMs are confirmed by a broad peak at 1600 cm^{-1} and two shorter peaks at 1432 and $1,404\text{ cm}^{-1}$, corresponding to the aromatic ring vibrations, in addition to the presence of a peak observed at 1122 cm^{-1} attributed to the enol group present. Finally, the presence of peaks at $\sim 1,750$ and $\sim 1,100\text{ cm}^{-1}$ in all the spectra in Figure 3, respectively, corresponding to carbonyl bond ($\text{C}=\text{O}$) stretching and ether bond ($\text{C}-\text{O}-\text{C}$) stretching, demonstrate the presence of PEG400DMA within the MNM systems.

Thermogravimetric analysis has been established as an effective technique to determine inorganic components in a polymer composite. In the case of the synthesized MNMs, the polymer matrix should completely decompose over the temperature range, leaving only the iron oxide magnetic nanoparticles. The TGA curves for the synthesized MNM systems are presented in Figure 4. Here it can be seen that all systems exhibit a single stage thermal decomposition that takes place over a wide range of temperature. The PEG MNMs start to start decompose at a temperature of 218.6°C reaching full decomposition at 420°C . This behavior agrees with what has been reported for the other PEG400 polymers with ranges of decomposition going from 200 to 420°C , with a highest weight loss at 340°C .^[30,31] The total weight loss for the PEG MNMs is of 86.7% , and the remaining 13.3% corresponds to the magnetic nanoparticles in the system. Both the CMA MNMs and QMA MNMs begin to decompose at 285.8°C following an almost identical thermogram until a complete polymer pyrolysis is reached at 420°C . In this thermogram, the biggest weight change is seen at 340°C . This onset in initial decomposition temperature can be explained by the presence of the polyphenol moieties. Patil et al.^[26] studied the thermal stability of the CMA monomer reporting the biggest decomposition at around 350°C , which is akin to the temperature observed in the CMA MNMs TGA curve. Similarly, within the temperature range of the QMA MNMs thermogram, previous published studies for quercetin and polyquercetin systems have reported a maximum weight change at a temperature of 340°C which is in accordance to what is observed here.^[27,32] The final weight loss for the CMA MNMs was of 89.6% and for the QMA MNMs of 90.2% , meaning the iron oxide nanoparticles represent 10.4 and 9.8% of the respective systems. Overall, the synthesis and further processing to obtain the MNM systems produces microparticles with an approximately $90:10$ polymer network to magnetic nanoparticle composition.

The loading of magnetic nanoparticles into the MNMs needs to be enough to enable the MNMs to be pulled out of a dispersed solution upon exposure to a static magnetic field. Figure 5 shows how the MNMs dispersed in water forming an opaque solution are rapidly decanted when exposed to a magnetic field, resulting in a transparent solution and the MNMs collected on the side of the magnet.

The hydrodynamic size of the microparticles was determined using a Systat SigmaScan 5.0 software to digitally determine the mean size of the microparticle sample suspended in DI water at a concentration of 1 mg mL^{-1} . The average size for the MNM systems is reported as an average with the variability in particle size within the cryomilling processes being quantified by the polydispersity index (PDI) presented in Table 1. All the MNM systems presented a uniform distribution with a size of around $20 \mu\text{m}$. The variation in size between the systems comes from the cryomilling process where the polymer films are milled into a fine powder. Because of the aggressiveness of the milling process, the resulting MNMs have random shapes and nonuniform surfaces, as can be seen in the SEM images (Figure 6). The average diameter for the MNM systems as determined from the SEM images is approximately $10 \mu\text{m}$, even though some particles can be seen to be larger or smaller in the images.

Furthermore, the stability of the MNM systems in an aqueous environment plays an important role during the binding process. In order to maximize the surface interactions between the MNMs and the pollutant, it is necessary to make sure no further aggregates form in solution. The stability of the MNM systems in DI water was studied for a period of 12 hr after an initial 10-min probe sonication. It can be seen from Figure 7 that all the MNM systems fall out of solution within the first hour. Consequently, it is necessary to introduce some mechanical agitation into the system during the binding studies and for their ultimate application as environmental adsorbents, in order to avoid microparticle aggregation or sedimentation of the MNMs and, hence, maximize pollutant binding.

The binding capacity of the MNM systems towards PCB 126 was studied at equilibrium conditions, room temperature and under constant shaking. The equilibrium time for the study was of 48 hr, as determined by previous kinetic studies where the contact time ranged from 30 min to 1 week. The binding isotherm was obtained for all the systems was obtained using a loading of 0.1 mg/ml and seven different PCB 126 concentrations, from 0.003 to 0.1 ppm . The adsorption isotherms for the MNM systems are presented in Figure 8a. For all systems, as the concentration of the free PCB in solution increases, the amount of PCB bound per total mass of adsorbent increases as well until a plateau is reached. This plateau is also known as the equilibrium monolayer capacity.^[33] In order to understand the behavior of the synthesized microparticles, the Langmuir model is used to fit the experimental data and obtain the maximum adsorption capacity (B_{max}) and Langmuir adsorption coefficients (K_D) for each system (presented in Table 2). According to the values of nonlinear R^2 presented in Table 2, the Langmuir model provides a good fit to describe the systems and suggests the adsorption process is homogeneous and occurs as a monolayer, implying there is no interactions between PCB molecules bound at the surface of the MNMs. The binding isotherm for both CMA MNMs and QMA MNMs behaves almost identically, showing higher binding at all concentrations when compared to the PEG MNMs. Previous studies have demonstrated that the sorption of hydrophobic organic chemicals, like PCBs, show strong absorption to aromatic-carbon-based materials as a result of hydrophobic interactions and, most importantly, π - π interactions at the aromatic surface.^[34,35] Moreover, PCB 126 is a planar molecule, which can closely approach the sorption sites of the adsorbent material allowing for the formation of favorable π -cloud interaction between the aromatic groups present in the adsorbent and those in the sorbate molecules.^[36,37] Hence, the presence of the

acrylated polyphenol, rich in aromatic groups, in the CMA MNMs and QMA MNMs appears to enhance binding for PCB 126.

The binding isotherms from Figure 8a show some variability between in the concentration of free PCB in solution. This comes from to the preparation of 12 independent samples per concentration proceeding from three different microparticle batches. At the lower concentrations, all the MNM systems behave very similarly, having a rapid increase for PCB bound and continue to increase until a maximum capacity is reached. At this point, the PEG MNMs visibly are saturated at a lower amount of PCB bound. This can be confirmed by the scatter plots presented in the supportive information (Data S1), where confidence intervals for each individual initial concentration are shown, demonstrating than only at the highest concentration of the present study (0.1 ppm), the PEG MNMs behave significantly differently from the other two MNM systems.

As mentioned above, the maximum binding capacity of the presented MNMs appears to be enhanced by the presence of the acrylated polyphenol moieties. From the confidence intervals presented in Table 2, obtained from the nonlinear models in JMP statistical software, it is clear that the value for $B_{\max}$ for the PEG MNMs (0.74 mg/g) is significantly lower than those for the CMA MNMs (0.96 mg/g) and QMA MNMs (1.02 mg/g). This can again be explained by the ability of the aromatic moieties present in the CMA MNMs and QMA MNMs to form π - π interactions at the surface with the PCB molecules, resulting in a higher binding capacity towards PCB compared to the PEG MNMs, where only hydrophobic interactions can occur. There is no significant difference in the binding capacity between either the CMA MNMs or the QMA MNMs, both having a maximum binding capacity for PCB 126 of approximately 1 mg/g. These values are within error of reported saturation capacities for other engineered microplastics and magnetic composites developed for the adsorption of organic pollutants.^[33,38] However, the $B_{\max}$ of all the MNM systems are lower than those reported for other carbon-based materials, specifically a couple orders of magnitude lower than activated carbon.^[39,40] The Langmuir adsorption coefficients obtained for the CMA MNMs, QMA MNMs, and PEG MNMs are 1.20, 1.28, and 1.84 nM, respectively. These K_D values are all in the same order of magnitude as what has been reported for the monoclonal antibody S2B1 binding to PCB 126 (2.5 ± 0.01 nM), demonstrating the high affinity of the synthesized MNMs for this contaminant.^[41] Moreover, the obtained Langmuir constant values are lower than values found in literature specifically for PCB 126 being adsorbed by activated carbon (6.12 nM), the gold standard for nonspecific adsorption of organic contaminants, and micron sized charcoal (15.2 nM), another commonly used material for pollutant remediation.^[42,43] This further demonstrates the applicability of the newly synthesized MNMs as adsorbent materials with the possibility to outcompete current remediation materials in the adsorption of specific contaminants, like PCBs.

In order to determine if the presence of the magnetic nanoparticles within the polymeric matrix of the MNM systems will have an effect on affinity, a set of microparticles (MPs) was synthesized without this magnetic component. Here, a smaller K_d value represents a greater binding affinity of the microparticle systems for PCB 126. The synthesis process followed was the same as previously described for the MNMs. The binding studies were conducted in

the same manner, with the exception of the magnetic decantation step due to the absence of magnetic nanoparticles within the MPs. In this case, the MPs were left to sediment out of solution and a sample of the supernatant was taken from the top of the vials. The results for the binding isotherms are shown in Figure 8b. It can be seen that the CMA MPs and QMA MPs follow a similar behavior, reaching a maximum amount of PCB bound per total mass close to 1 mg/g, almost the same as what was observed for their corresponding MNM systems. From the confidence intervals shown in Table 2, it can be seen that all for polyphenol containing systems have maximum binding capacities within error of each other, which suggest the presence of the magnetic nanoparticles does not negatively affect the capacity of the MNM or MP systems for PCB 126 at the studied conditions. Regarding the PEG MPs, the binding isotherm does increase as the concentration of free PCB in solution increases, as does the other two MP systems, but reaches a lower maximum binding capacity at 0.6 mg/g. This behavior is similar to what is observed for the PEG MNMs, however, the maximum binding capacity for this system is in fact greater and statistically different to the PEG MPs, as determined from the confidence intervals shown in Table 2. In this case, the magnetic nanoparticles appear to be increasing the maximum binding capacity of the PEG MNMs by providing additional surface area for binding to occur, and reducing the possible hydrophilic interactions the PEG polymer may be having with the water molecules in solution.^[44] Examining the K_D values of the MP systems presented in Table 2, all fall within the confidence intervals of each other and the MNM systems, demonstrating they are not adversely affected by the presence of the magnetic nanoparticles in the material.

Taking a closer look at the Langmuir constant for PCB 126 of all the synthesized systems in this work, from lowest affinity to highest, the order is as follows: PEG MNPs < PEG MPs < QMA MNMs < CMA MNMs < QMA MPs = CMA MPs. The PEG systems present a lower affinity for PCB 126 in the aqueous solution most likely due to the hydrophilic nature of the PEG400DMA, therefore impeding interactions with the hydrophobic PCB 126 molecules.^[45] The CMA and QMA containing systems exhibit a higher binding affinity for the PCB molecule, which can be explained on the basis of the presence of π - π stacking interaction between the aromatic rings in the adsorbate and the adsorbant. This result demonstrates the important role the incorporation of the functional monomers, CMA and QMA, imparts into the microparticle systems by increasing the affinity of the material via the introduction of π -electron rich sites that allow for π -electron coupling/stacking, and lead to an overall increase in hydrophobicity.

Recently, our group developed nanoadsorbent materials containing these functional acrylated monomers, CMA and QMA, to be used in environmental remediation.^[45] Briefly, the core-shell systems consisting of a magnetite nanoparticle core was coated using a grafting from approach (atom transfer radical polymerization) with PEG400DMA and either CMA or QMA. The adsorption for PCB 126 for these magnetic nanoparticles was subsequently analyzed and fit to the Langmuir model. From the data in Table 2, it can be seen that the CMA MNPs and QMA MNPs have higher affinity for PCB 126, than the PEG MNPs, as is the case with the MNM and MP systems in this work. However, by examining the confidence intervals, it becomes evident that the K_D values for the CMA MNMs, QMA MNMs, CMA MPs, and QMA MPs indicate a greater affinity for PCB 126. This result seems counter intuitive given that it is expected that the nano-sized MNPs with an average

size 240 nm compared to an average size of 18 μm for the MNM and MP systems, would translate into a higher surface where adsorption of the contaminant molecule can occur. However, the amount of functional polymer consisting of PEG and CMA/QMA present in the MNP systems represents only 10 wt% of the total mass in comparison to 90 wt% in the MNMs and 100% in the MPs. Given this considerable difference in composition, it is possible that the available sites for a combination of π – π interactions, primarily, and hydrophobic interactions at the particle surface are significantly reduced ensuing a lower affinity for PCB 126 at the studied conditions. These results provide significant promise for the use of our magnetic nanocomposite microparticle systems to be used as high affinity adsorbents for specific harmful contaminants in the remediation of contaminates sites.

4 | CONCLUSIONS

This work presents the promising application of the synthesized magnetic nanocomposite microparticles as high affinity adsorbents for harmful organic pollutants in environmental remediation. The synthesized MNMs incorporated curcumin multiacrylate or quercetin multiacrylate in order to provide the microparticles with π –electron rich sites and, hence, enhance the pollutant binding capacity. The magnetic nanoparticles served as a means of magnetic separation throughout the binding process and do not adversely affect the binding properties of the MNM systems. The Langmuir model adequately fit the adsorption data, providing information about the maximum binding capacity of the systems and their binding coefficients. The saturation capacity proved to be consistent to available literature of other engineered polymer based micro-adsorbents used for organic contaminants but lower than reported values for carbon-based materials. It was demonstrated that the synthesized MNMs possess a higher binding affinity for PCB 126 than activated carbon and charcoal, which are the most commonly used materials for capture of organic pollutants. Additionally, the incorporation of a small amount (10 mol%) of the functional monomer, CMA or QMA, into the microparticles resulted in an increase in affinity due to the ability to form π – π interactions, resulting in affinities comparable to those observed in antibodies. Finally, the MNM systems combine the increased affinity provided by these plant derived monomers with the magnetic separation capabilities of the magnetic nanoparticles, and they offer a unique advantage for their use in the environment: micron size allows for an easier manipulation and control of their fate in comparison to nanoparticles. Overall, we have developed novel nanocomposite materials with high affinities for PCBs that show promising potential for use as environmental remediation adsorbents for harmful contaminants.

Supplementary Material

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FIGURE 1.

Schematic representation of the overall synthesis of magnetic nanocomposite polymers and their cryomilling to obtain magnetic nanocomposite microparticles (MNMs)

FIGURE 2.
Schematic representation of the binding studies conducted with PCB 126 in a 99:1 DI water ethanol solvent

FIGURE 3.

FTIR spectra of the synthesized magnetic nanocomposite microparticles. (a) CMA MNMs, (b) QMA MNMs, and (c) PEG MNMs

FIGURE 4.
Mass loss profile with increasing temperature of the synthesized magnetic nanocomposite microparticles

FIGURE 5.
Suspended solution of CMA MNMs in water (left) and capture of CMA MNMs upon exposure to a static magnetic field (right)

FIGURE 6.
SEM images of (a) CMA MNMs, (b) QMA MNMs, and (c) PEG MNMs

FIGURE 7. Normalized absorbance (at 540 nm) of the MNMs in DI water for 12 hours using UV-visible spectroscopy

FIGURE 8.

Room temperature adsorption isotherms for PCB 126 of the (a) MNM systems and (b) MP systems. PCB 126 initial concentrations from 0.003 to 0.1 ppm fitted using the Langmuir model

TABLE 1

Size analysis from SEM images and hydrodynamic size analysis via dynamic light scattering of the synthesized MNMs

MNM system	SEM diameter (μm)	Hydrodynamic size (μm)	PDI
CMA MNMs	10 ± 1.6	20.6 ± 0.4	0.27
QMA MNMs	11 ± 1.5	15.3 ± 0.6	0.31
PEG MNMs	10 ± 2.0	18.2 ± 0.2	0.22

TABLE 2

Langmuir binding constants for the binding isotherm of PCB 126 for the microparticle systems synthesized ($n = 12$ independent samples)

System ID	K_d (nM)	95% CI	$B_{\max}$ (mg g ⁻¹)	95% CI	R_2
CMA MNMs	1.20	0.98–1.47	0.96	0.94–1.01	0.983
QMA MNMs	1.28	1.05–1.55	1.02	0.94–1.04	0.995
PEG MNMs	1.84	1.72–1.97	0.74	0.71–0.79	0.949
CMA MPs ^{aa}	1.06	0.86–1.30	0.96	0.89–1.04	0.999
QMA MPs ^{aa}	1.06	0.88–1.28	0.97	0.91–1.04	0.986
PEG MPs ^{aa}	1.71	1.24–2.32	0.60	0.57–0.64	0.999
CMA MNPs ^{bb}	2.72	2.50–3.00	1.06	1.02–1.09	0.993
QMA MNPs ^{bb}	5.88	5.58–6.24	1.06	1.02–1.10	0.956
PEG MNPs ^{cb, bc}	8.42	6.54–14.24	1.91	0.98–2.75	0.980

^a $n = 9$ independent samples.

^b Values reproduced from Reference 45 with permission from the authors.

^c $n = 15$ independent samples.