Review

Designing clay-polymer nanocomposite sorbents for water treatment: A review and meta-analysis of the past decade

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A R T I C L E   I N F O

A B S T R A C T

Clay-polymer nanocomposites (CPNs) have been studied for two decades as sorbents for water pollutants, but their applicability remains limited. Our aim in this review is to present the latest progress in CPN research using a meta-analysis approach and identify key steps necessary to bridge the gap between basic research and CPN application. Based on results extracted from 99 research articles on CPNs and 8 review articles on other widely studies sorbents, CPNs had higher adsorption capacities for several inorganic and organic pollutant classes (including heavy metals, oxyanions, and dyes, $n = 308$ observations). We applied principal component analysis, analysis of variance, and multiple linear regressions to test how CPN and pollutant properties correlated with Langmuir adsorption model coefficients. While adsorption was, surprisingly, not influenced by mineral properties, it was influenced by CPN fabrication method, polymer functional groups, and pollutant properties. For example, among the pollutant classes, heavy metals had the highest adsorption capacity but the lowest adsorption affinity. On the other hand, dyes had high adsorption affinities, as reflected by the linear correlation between adsorption affinity and pollutant molecular weight. Scaling from 'basic research' to 'technological application' requires testing CPN performance in real water, application in columns, comparison to commercial sorbents, regeneration, and cost evaluation. However, our survey indicates that of the 158 observations, only 20 compared the CPN's performance to that of a commercial sorbent. We anticipate that this review will promote the design of smart and functional CPNs, which can then evolve into an effective water treatment technology.

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1. Introduction

Water resources often contain an array of pollutants that pose public health and environmental concerns (Schwarzenbach et al., 2010). Removing organic and inorganic pollutants from water is often achieved by adsorbing them to activated carbon, ion exchange resins, and oxides (Driehaus et al., 1998; Fu and Wang, 2011; Kumar et al., 2019; Worch, 2012). However, each of these sorbents has various critical shortcomings such as reduced effectiveness in the presence of background electrolytes and organic matter (Dixit et al., 2018; Quinlivan et al., 2005), low pollutant specificity (Ling et al., 2017), high operating costs (Alhashimi and Aktas, 2017), and energy intensive regeneration (Foo and Hameed, 2012). Therefore, in recent decades there has been enormous interest in tailoring sorbents to provide efficient,

inexpensive, and pollutant-specific alternatives to conventional sorbents (Kyzas and Matis, 2015).

Clay-polymer nanocomposites (CPNs) are a broad group of materials designed using many combinations of clay minerals and polymers. Originally, clay minerals were dispersed into individual layers and incorporated into the polymer phase, typically at less than 5 wt%, to enhance polymer properties (Chen et al., 2008). Clay minerals such as smectites have layers that are approximately 1 nm thick and a diameter of up to several microns. The Young's modulus in the layer direction is 50 to 400 times higher than that of a typical polymer, thus the composite material has improved properties such as Young's modulus, tensile strength, fire retardancy, barrier resistance, and ion conductivity (Chen et al., 2008). Clay minerals often bare a negative charge resulting from isomorphous substitution, and have the capacity to adsorb positively charged pollutants, such as heavy metals and cationic dyes, via exchange of their counter cation. More recently, CPNs have been studied as materials for pollutant removal from water in membrane, flocculation, oxidation, and adsorption processes. By

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combining the valuable properties of the mineral component (low cost, low toxicity, mechanical stability, and large surface area) with those of the polymeric components (high adsorption efficiencies, diverse functional group chemistry, enhanced swelling, and surface area) CPNs can be tailored to target specific pollutants with enhanced adsorption performance, compared to bare clay minerals. The field has rapidly evolved since Breen and Watson first reported a CPN sorbent, composed of a polycation adsorbed to a smectite mineral (Breen and Watson, 1998). Recent studies have reported smart, multi-component composite sorbents based on multiple polymers and modifiers that are characterized using advanced techniques (Gardi and Mishael, 2018; Hatami et al., 2020; Lv et al., 2020; Ma et al., 2017; Rethinasabapathy et al., 2018; Sarkar et al., 2018) and employed for the removal of an array of pollutants (Ray et al., 2019).

Recent literature reviews on CPNs have qualitatively discussed CPN "building blocks" (clays and polymers), fabrication methods, and properties (e.g., surface area and charge), compiled adsorption results from relevant studies, and suggested future challenges and research directions (Han et al., 2019; Kar et al., 2019; Mukhopadhyay et al., 2020; Srinivasan, 2011; Unuabonah and Taubert, 2014). Such literature reviews are instrumental for summarizing recent progress in a given discipline, but they cannot quantitatively synthesize and interpret large-scale datasets and results across studies. In contrast, meta-analyses are aimed at determining overall trends by statistically analyzing data from several independent studies of the same subject. Meta-analyses are adept at summarizing and synthesizing diverse studies (Meng et al., 2016; Meyer et al., 2019; Wolfram et al., 2018). A key benefit of analyzing numerous studies is the aggregation of information that leads to a higher statistical power and more robust estimates than are possible from any individual study. Meta-analyses have been implemented to identify universal trends in topics central to water research such as phosphorous removal from lake waters (Spears et al. 2016), decay rates of viruses and coliphages in surface waters (Beohm et al. 2019), and contaminant removal by conventional and emerging media for urban stormwater treatment (Okaikue-Woodi et al. 2020). However, only a handful of meta-analyses have been performed on sorbents in general (Alhashimi and Aktas, 2017; Benstoem et al., 2017; Mejias Carpio et al., 2018), and none have been performed on clay-based sorbents.

Here, we present a quantitative meta-analysis of the data published on CPNs in the last decade. From a basic science perspective it is important to identify how CPN and pollutant properties influence adsorption performance (Kar et al., 2019), but a meta-analysis can reveal more general trends based on numerous observations. Translating CPN laboratory-based data into technology-based processes is complex (Mukhopadhyay et al., 2020) and seldom addressed (Gardi et al., 2015; Kumar et al., 2012; Ray et al., 2019). This review highlights the key steps necessary to bridge CPN laboratory-scale performance to technological applicability, which is a crucial stage towards commercialization of CPNs, or any other sorbent.

Accordingly, we collected sorbent, pollutant, and adsorption data from 397 observations, published in 99 original research articles and 8 review articles. We analyzed the adsorption performance of CPNs for different pollutants using principal component analysis (PCA), analysis of variance (ANOVA), and stepwise multiple linear regression (MLR).

The aims of this review were to: 1) compile a database consisting of information from CPN studies of the past decade to quantify the number of studies reporting different clays and polymers, modes of CPN fabrication, pollutants, and adsorption models, 2) analyze the linkages between CPN properties, pollutant chemistry, and adsorption performance, 3) highlight the necessary steps to benchmark novel CPNs in realistic wa-

ter treatment scenarios, and 4) identify underexplored research opportunities.

2. Methods

The workflow and methodology of this Review is depicted in Fig. 1.

2.1. Literature review

We identified potentially relevant studies ($n = 548$) using the search string (clay OR clay mineral) AND (polymer OR composite OR nanocomposite) AND (water OR wastewater) AND (adsorption OR sorption OR removal) AND (pollutant OR contaminant) occurring in the title, abstract, and/or keywords of articles published in the years 2008–2019 using the Web of Science Core Collection and Google Scholar. Our search cutoff date was 14.9.2019, and our selection criteria (below) yielded 99 articles and 158 experimental observations (Fig. S1). We verified that each article reported original, quantitative data for pollutant adsorption from an aqueous matrix to a composite material consisting of, at the least, a clay mineral or iron (Fe) oxide functionalized with a synthetic or natural polymer. Studies on CPNs based on an unidentified mixture of clay minerals were excluded. Only studies that reported Langmuir adsorption capacity (Q_{max}) and affinity (K_L) or Freundlich model coefficients (n and K_F) (see below), based on replicated adsorption isotherms, were included. Separately, Google Scholar was searched for review articles on widely studied sorbents that compiled published data of pollutant adsorption. We chose commonly studied pollutants for which we could extract $n \geq 10$ observations from at least four additional sorbents and extracted their Q_{max} values. K_L values were often not reported in these reviews and therefore not included. While we acknowledge that a few sorbents included in our meta-analysis may not meet the accepted definition of a nanomaterial, the vast majority of them do. We chose to classify all sorbents reviewed here as CPNs to continue the terminology used in recent reviews and papers (Kar et al., 2019; Mukhopadhyay et al., 2020; Unuabonah and Taubert, 2014).

2.2. Data extraction

Information about the CPN, the targeted pollutant, adsorption metrics, and other information were extracted from every experimental observation in each study. 33 of the 99 studies contained more than one experimental observation (e.g., one CPN tested for more than one pollutant). CPN information included clay mineral and polymer type and CPN fabrication method (adsorption, cross-linking, *in-situ* polymerization, or grafting). Montmorillonite and bentonite were collectively classified as smectites, while attapulgite, sepiolite, and palygorskite were classified as palygorskites. Active adsorption sites, termed "functional groups" were inferred from *a priori* knowledge about polymer chemistry, experimental results (e.g., effect of solution chemistry on adsorption, evidence of cation or anion exchange, or spectroscopic findings) and based on the discussion in each study. Where relevant, the pH of the adsorption system was used to help assign functional groups. For example, carboxyl groups were assigned as a CPN functional group when the pH was higher than its typical pKa (~4.5). We recorded, where available, CPN surface charge ($n = 68$ observations) inferred from electrophoretic mobility (Zadaka et al., 2010) or potentiometric titration (Pereira et al., 2017) measurements, and BET surface area ($n = 62$ observations) (Dogan et al., 2006). We recorded, where available, CPN polymer (or organic component) content ($n = 50$ observations). CPN polymer content was mostly determined using thermogravimetric or elemental analysis of the
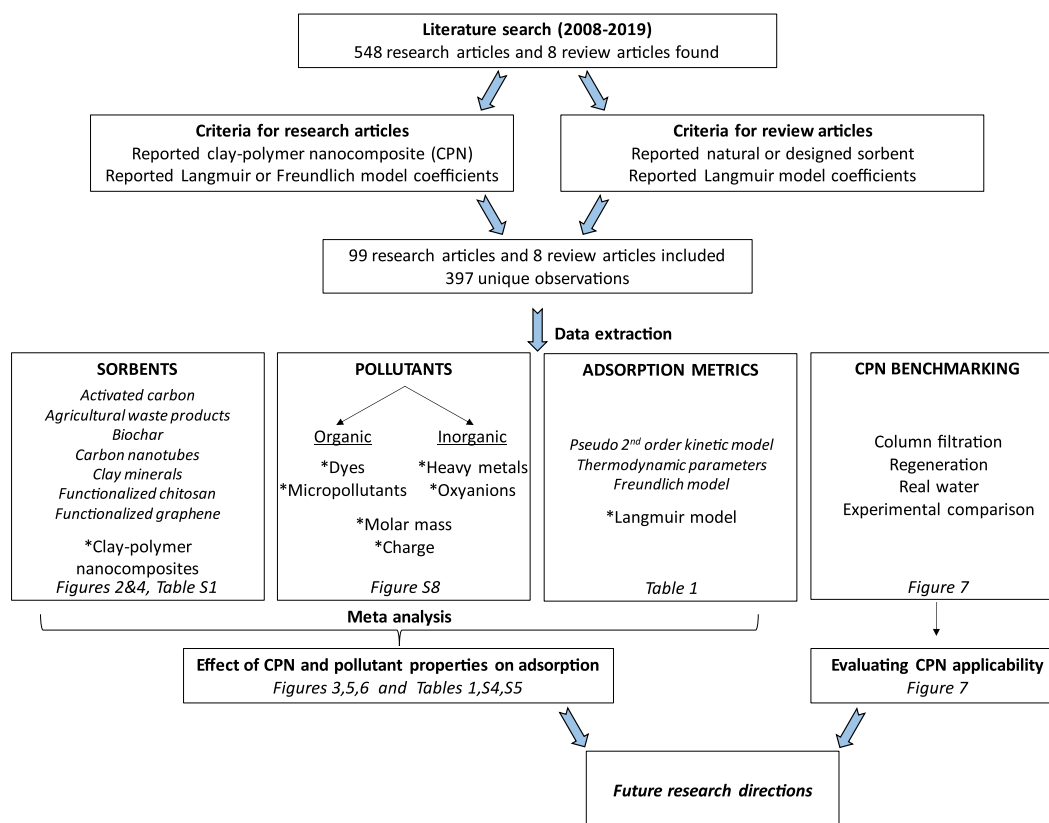
Fig. 1. Flowchart of the Critical Review. Parameters included in formal statistical analyses are depicted with a *.

solid phase, or in the case of CPN fabrication using direct polymer adsorption, by measuring the non-adsorbed polymer concentration. However, thermogravimetric analysis results were only included if they accounted for mass loss from CPN dehydration and other structural decomposition of the clay mineral as described by Ray et al. (Ray et al., 2019).

Organic and inorganic pollutants were binned into four classes: dyes ($n = 53$), micropollutants ($n = 23$), heavy metals ($n = 65$), and oxyanions ($n = 17$). Studies on the adsorption of other inorganic ions, including fluoride ($n = 4$), cesium ($n = 1$), and ammonium ($n = 1$) were excluded due to insufficient sample size. Pollutant information included molecular weight (M_w) and charge (negative, neutral, or positive) at the pH value of the adsorption experiment. We excluded studies on substances lacking a definitive M_w, such as dissolved organic matter.

CPN adsorption performance was evaluated by analyzing adsorption isotherm coefficients. An adsorption isotherm is a curve describing the retention of a substance, at equilibrium, on a solid particle. Data from adsorption isotherms are typically fit to Langmuir and Freundlich models. The Langmuir isotherm equation was developed to model homogenous, monolayer adsorption of gas to a solid surface (Foo and Hameed, 2010), but is the most widely used model to interpret adsorption from aqueous media. The Langmuir adsorption capacity (Q_{max}) reflects the maximum amount of adsorbed pollutants per unit mass sorbent, and the Langmuir adsorption coefficient (K_L) quantifies the affinity of a pollutant to the sorbent surface. Across the entire database, CPNs had median Q_{max} and K_L values of 0.55 mmol/g, and 29.64 L/mmol, respectively. The Freundlich isotherm equation is a power function; while lacking a thermodynamic basis, it is often used to fit adsorption data to heterogenous adsorption sites (Foo and Hameed, 2010). Freundlich coefficients include the dimensionless n, and the Freundlich constant (K_F), which relays information on the extent of adsorption, though

it does not predict adsorption capacity (Foo and Hameed, 2010). In cases where Langmuir and Freundlich models were applied to the same adsorption isotherm, we extracted the coefficients that provided a better fit for the data.

Adsorption coefficients were converted to molar basis using pollutant M_w, as necessary. We used the reported pH in the adsorption experiment to determine the M_w of oxyanions, which varies with pH. Thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0), which can be calculated from adsorption isotherms measured at several temperatures, and the pseudo-second-order kinetic model coefficient, calculated from adsorption kinetic experiments (Tran et al., 2017), were also extracted.

To assess whether CPNs were benchmarked and tested for water treatment applications, we recorded whether the following experiments were performed in addition to those described above: i) pollutant adsorption from varying solution chemistry (pH and ionic strength), ii) pollutant adsorption from 'real water' (wastewater, natural water, or synthetic 'real water', i.e., deionized water containing multiple pollutants and background solutes), iii) regeneration of spent CPNs, iv) adsorption experiments in fixed-bed columns, v) experimental comparison of CPNs to commercially used sorbents, and vi) cost evaluation.

The complete database and references for the articles used in this meta-analysis are included in the Supplementary Material.

2.3. Statistical analyses

2.3.1. Principal component analysis (PCA)

We tested for an association between minerals, functional groups, pollutant properties (class, charge), CPN fabrication methods, and Langmuir coefficients using principal components analysis (PCA). PCA results were computed (after scaling) using FactoMineR, an R package for multivariate analysis (Lê et al., 2008)

and visualized using statistical tools for high-throughput data analysis (Kassambara, 2017). Confidence ellipses were used to visualize whether categorical groups were significantly different from each other and defined as regions containing 95% of all samples that can be drawn from the underlying Gaussian distribution. Variables with $n \langle 10$ observations or p-values$\rangle$ 0.05 were excluded.

2.3.2. One-way analysis of variance (ANOVA)

We used one-way ANOVA models to identify the main effects of mineral, pollutant properties (class, charge), and CPN fabrication method, on our dependent variable of interest (Q_{max} and K_L). We compared ANOVA results with those from linear mixed-effect models (LMER) using the lme4 package (Bates et al., 2007). LMER models were constructed as above but included study ID as a categorical random effect to account for the nonindependence of observations originating from the same study. For all models, Q_{max} and K_L values were transformed to fit assumptions of normality using the log10 scale. Normal distributions were evaluated using Shapiro-Wilk tests and QQ-plots. Estimated marginal means were computed using the emmeans package (Lenth et al., 2018), and coefficients (b_i-b_j) were back-transformed in the manuscript for ease of interpretation (Lane, 2002). P-values were calculated using Tukey's HSD method for comparing a family of estimates.

2.3.3. Multiple linear regression (MLR)

We constructed multiple linear regression models using CPN and pollutant properties as covariates for predicting variation in Q_{max} and K_L. Dummy variables were made from categorical variables, excluding those with fewer than 10 observations. We used exhaustive (forwards and backwards) stepwise AIC (Akaike Information Criterion)-selected linear regression models to identify relationships between our dependent variable of interest (Q_{max} or K_L) and potential predictor variables, for two common pollutant classes (heavy metals and cationic dyes). We analyzed subsets of the database so mutually exclusive variables were not included in the same model (for example, heavy metals, which are always positively charged, and oxyanions, which are always negatively charged). Stepwise multiple linear regressions were conducted following reported procedure (Lynch et al., 2019) using the stats package in R (Team, 2013). We normalized dependent variables using the boxcox power transformation to yield normally distributed errors, assessed using Shapiro-Wilk tests of the residuals, Q-Q plots, Studentized Residuals, and non-constant variance scores. Best-fit model results, AIC scores, and boxcox λ values are reported in the Supplementary Material (Table S5).

3. Results

3.1. Dataset

Our literature search yielded 158 experimental observations from 99 published papers. For comparison, similar meta-analyses of adsorption systems consisted of $n = 44$, $n = 195$, and $n = 63$ observations (Benstoem et al., 2017; Kumar et al., 2019; Mejias Carpio et al., 2018). For each of the observations we compiled information and the following data were included in statistical analyses: clay and polymer type, CPN fabrication method, and pollutant class, charge, and molecular weight. Data on CPN surface area, surface charge, and polymer content—potentially important variables describing CPN properties—were available for a limited number of observations and therefore not included in the formal meta-analysis.

Principal component analyses examining Freundlich ($n = 46$) and pseudo-second-order kinetic ($n = 98$) model coefficients, and thermodynamic parameters ($n = 54$) as adsorption metrics, were constrained by few observations and reported in the Supplementary Material (Figures S2-S4). We ultimately restricted our PCA, ANOVA, and MLR analyses to Langmuir model coefficients (Q_{max} and K_L) ($n = 141$) due to the low number of observations of the adsorption metrics.

To assess the percentage of observations that report CPN benchmarking and application testing, we recorded if the following experiments were performed: pollutant adsorption from 'real water', regeneration of spent CPNs, adsorption in fixed-bed columns, experimental comparison of CPNs to commercially used sorbents, and cost evaluation.

3.2. Synthesis of data on CPN adsorption performance

#### 3.2.1. Pollutant adsorption by CPNs versus common sorbents

Our survey indicates the Langmuir adsorption capacities (Q_{max}) of CPNs for several commonly studied organic (dyes) and inorganic (heavy metals and oxyanions) pollutant classes exceeded or equaled those of other sorbents, including biochar, activated carbon, and modified chitosan (Fig. 2 and Table S1). K_L values were often not reported for these sorbents and therefore not included. Although variation in solution chemistry and experimental conditions affects adsorption coefficients (Wang and Giammar, 2019), we observed significant differences in Q_{max} among sorbents ($P < 0.0001$) and significant interactions between sorbent and pollutant class ($P < 0.01$) across this large dataset, which encompassed multiple experimental conditions ($n = 308$ observations).

While some sorbents have a high Q_{max} because they are chemically compatible with one specific pollutant class—for example activated carbons for dyes (Mezohegyi et al., 2012; Yagub et al., 2014) or graphene oxides for heavy metals (Peng et al., 2017)—the high Q_{max} of CPNs for each pollutant class stems from their tunability, or chemical compatibility, with a wide range of pollutants. CPNs are also superior sorbents than their clay mineral building blocks. The Q_{max} of CPNs, averaged over all three pollutant classes is 1.72 mmol/g and the K_L is 201.45 L/mmol. For comparison, the Q_{max} of smectite for Cu^{2+} and methylene blue—the most widely studied mineral, heavy metal, and cationic dye in our survey—is 0.45 mmol/g and 0.9 mmol/g, respectively, while the K_L is 1.9 L/mmol and 3.2 L/mmol, respectively (Almeida et al., 2009; Bhattacharyya and Gupta, 2006). The advantage of positive CPNs over bare smectite (which bears a negative surface charge) would likely be more pronounced for the adsorption of anionic pollutants.

3.2.2. Visualizing relationships among variables

To identify parameters driving the high Q_{max} of CPNs, we used principal component analysis (PCA) to assess relationships between CPN properties, pollutant properties, and Langmuir model coefficients. Within ordination space, dimensions 1 and 2 together explained 25% of the variance (Fig. 3 and Table S2). Based on 95% confidence intervals (visualized as shaded ellipses), dyes and heavy metals were significantly different from each other and from micropollutants and oxyanions (micropollutants and oxyanions were not significantly different). Q_{max} loaded in the opposite direction from oxyanions and micropollutants, suggesting adsorption capacity for these classes was lower, though Q_{max} values accounted for only 5% of the variability across the first two dimensions. In contrast, K_L values accounted for 10% of the variability along dimension 2 alone, suggesting the affinity of dyes and high M_w pollutants for the tested CPNs, especially those based on smectites, were higher than average. The positive correlation between M_w and K_L ($P < 0.0001$; Figure S5) supports established evidence that adsorption affinities increase with M_w (Breen, 1999). This trend may be related to the energy gain of high M_w pollutants dehydrating and forming multiple interactions with the sorbent surface.
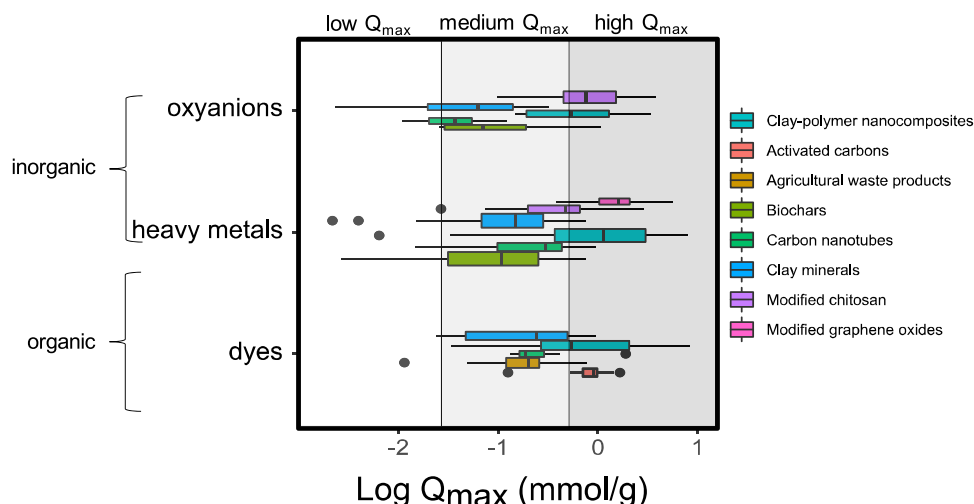
Fig. 2. Langmuir adsorption capacity (Q_{max}) of some common sorbents for selected heavy metals (Pb^{2+} and Cu^{2+}), oxyanions (Cr(VI)), and dyes (methylene blue and crystal violet), emphasizing the higher capacity of clay-polymer nanocomposites (CPNs). Boxplot widths are drawn proportional to the square-root of the number of observations within each sorbent class (including only sorbents with more than 10 observations).
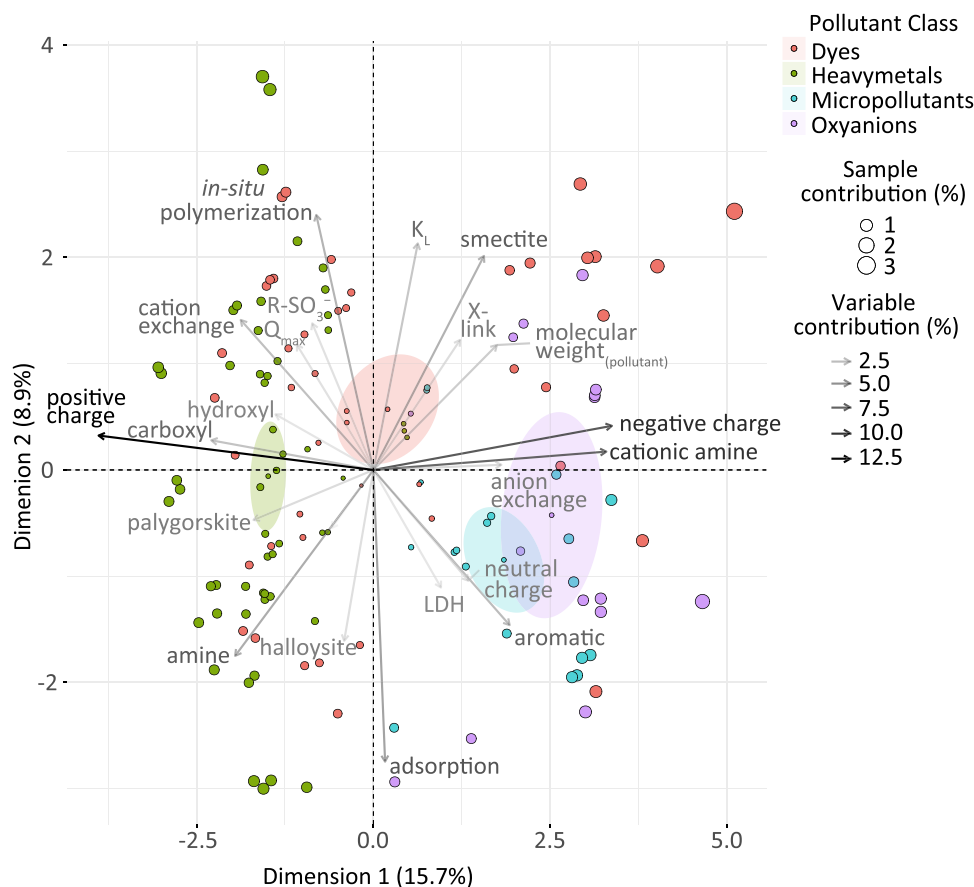
Fig. 3. Principal component analysis (PCA) of clay-polymer nanocomposites (CPNs), polymer functional groups, pollutant charges, and adsorption equilibrium coefficients. Variables with a significance level of < 0.01 are shown; each circle represents a sample, colored by pollutant class. The percent contribution of individual variables and samples to principal components 1 and 2 are shown with vector shade and symbol size, respectively. Shaded ellipses display 95% confidence intervals. X-link: cross-linking fabrication; $R-SO_3^-$: sulfonate functional group. Results of the PCA analysis are reported in Tables S2a and S2b.

Fabrication methods influence the chemical and structural properties of CPNs, thereby influencing their adsorption performance (see Section 3.3.3). Fabrication using the *in-situ* polymerization approach was positively correlated with dimension 2 (0.55) and explained 14% of the variance, loading with Q_{max}, and sulfonate and cation exchange functional groups (Fig. 3 and Table S2). In contrast, adsorption fabrication methods were negatively corre-

lated with dimension 2 (−0.67) and explained an additional 20% of the variance. Along with cross-linking, fabrication methods explained 38% of the variance, indicating their crucial role in CPN adsorption performance.

Oxyanions were strongly related to CPNs bearing cationic amine functional groups, which accounted for 15% of the variability across dimension 1, while micropollutants were associated with aromatic

Table 1

Linear and linear mixed effects regression results for Langmuir adsorption capacity (Q_{max}, $n = 141$), and affinity (K_L, $n = 138$).

| Effect | | Adsorption capacity Q_{max} | | | | Adsorption affinity K_L | | | |
| | | Linear model | | Mixed effect model | | Linear model | | Mixed effect model | |
	DF	F ratio	P value	F ratio	P value	F ratio	P value	F ratio	P value
Clay mineral	5	0.85	0.51	0.31	0.91	2.87	**0.02**	1.77	0.13
Fabrication method	3	10.54	**<0.0001**	5.25	**0.002**	3.22	**0.03**	1.83	0.15
Pollutant class	3	6.98	**0.0002**	2.87	**0.04**	6.46	**0.0004**	4.42	**0.005**
Pollutant charge	2	7.85	**0.0005**	2.51	0.09	4.91	**0.009**	2.02	0.14
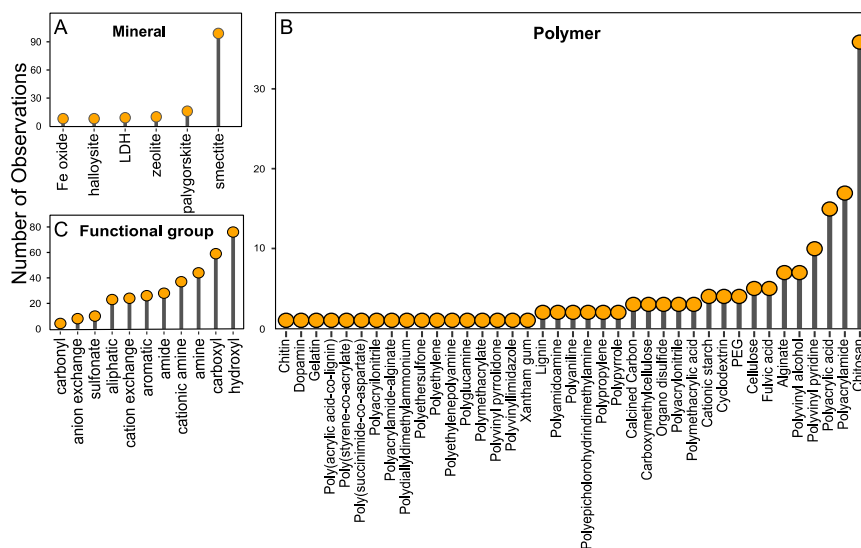
Fig. 4. Summary of CPN building blocks: (A) clay minerals, (B) polymers, and (C) polymer functional groups.

functional groups, accounting for 10% of variance explained across the first two dimensions (Table S2). In contrast, heavy metals were associated with amine, carboxyl, and cation exchange functional groups, which together accounted for 17% of the variability across dimension 1. Together, these results reveal that observations are separated across pollutant class and charge, polymer functional group, and fabrication method, demonstrating that CPNs can be rationally designed to maximize chemical interactions between the polymer and targeted pollutant.

3.2.3. CPN building blocks

At their simplest form, CPNs consist of a clay-mineral functionalized with a polymer. We present these CPN "building blocks" and discuss how various fabrication methods shape the structure and properties of CPNs. We then assess their contribution to adsorption performance, using one-way ANOVA (Table 1 and Table S4) and stepwise multiple linear regressions (Table 2 and S5).

3.2.3.1. CPN building blocks – clay minerals. Clay minerals are well-known sorbents with exhaustively characterized adsorption sites (Gaines and Thomas, 1953; Ikhsan et al., 1999). Our survey shows that most CPNs were designed using six different mineral classes (Fig. 4A). Smectites, phyllosilicates based on Si tetrahedra and Al octahedra (2:1), were the most commonly used mineral (63% of observations), likely because they easily disperse in water and polar organic solvents (Gardi and Mishael, 2018; Herrera et al., 2004), and possess a large total surface area (710 m^2/g) and cation exchange capacity (0.85 meq/g) (Borden and Giese, 2001). These traits are well suited for the adsorption of cationic and neutral

polymers (Deng et al., 2006), and the exchange sites serve as additional adsorption sites for cationic pollutants such as heavy metals (Barbier et al., 2000). Other clay minerals included palygorskite (10%), zeolite (6%), layered-double hydroxide (LDH) (6%), Fe-oxide (5%), halloysite (5%), kaolinite (3%), and K-feldspar (2%). While Fe-oxides are not clay minerals, they are mineralogically related and widely reported as useful sorbents for water treatment (Xu et al., 2012).

Although smectites were the most prevalent clay building block, several interesting studies selected less explored clay minerals, including zeolites, LDHs, and palygorskites. Zeolites are aluminosilicates based on Al and Si tetrahedra that form microporous, negatively charged frameworks, containing exchangeable metal cations. Zeolite pores can serve as adsorption sites that target a specific pollutant or a broad mixture of pollutants, based on the uniformity of their structure (Rossner et al., 2009). In contrast to most clay minerals, synthetic LDHs possess a positive surface charge because of partial substitution of trivalent for divalent cations in the brucite-like layers (Goh et al., 2008). This allows for facile functionalization of LDHs with anionic (bio)polymers such as alginate and fulvic acids, and subsequent removal of cationic pollutants (Li et al., 2018). Palygorskites are fibrous clay minerals, with high porosity (0.38–0.58 cm^3/g), high specific surface area (173 m^2/g) (Dogan et al., 2006) and abundant surface Si-OH groups that can be hydrolyzed to obtain pH-dependent charged groups (Liu et al., 2015), or grafted with organo-silanes as a first step for surface-initiated polymerization (Chen et al., 2009; Xue et al., 2011).

Due to small sample sizes ($n \leq 5$) K-feldspar and kaolinite were excluded from ANOVA models. Despite large differences in their structure, surface area, and exchange capacity (Table S3), Q_{max} values did not differ across mineral classes in the standard

Table 2

Results of stepwise multiple linear regression models. Coefficient estimates (β values) are multiplied by a factor of 10 and italicized if they are statistically significant at $P < 0.05$ and bolded at $P < 0.001$. na indicates the variable was not included in the best-fit model, as evaluated using AIC model selection criteria. Dependent variables were transformed (boxcox power function) to meet assumptions of normality. The standard error for estimated coefficients, boxcox λ values, model F-statistics, and degrees of freedom are reported in Table S5.

|	pollutant class	intercept	adsorption	in-situ polymerization	carboxyl	hydroxyl	amide	cation exchange	molecular weight	null AIC	final AIC	adjusted R²
Q_{max}	cationic dyes	11	−1.09	−2.39	1.38	1.98	na	na	−0.01	−106.99	−118.69	0.41
	heavy metals	99.56	−40.39	14.87	na	na	10.21	10.33	0.04	−153.21	−233.82	0.77
K_L	cationic dyes	16.32	na	na	−1.94	na	na	na	na	−83.14	−84.84	0.08
	heavy metals	95.52	na	7.81	na	na	−8.2	−7.23	−0.08	−201.11	−209.55	0.21

($P = 0.5$) or random mixed effects ($P = 0.9$) model (Table 1 and Figure S6). K_L values varied across mineral class ($P = 0.02$), but all pairwise comparisons were insignificant. Similar CPN adsorption performances across clay building blocks is likely caused by the dominating influence of polymer functional group chemistry (Ray et al., 2019), CPN surface charge (Shabtai and Mishael, 2016), and CPN structure (Levy et al., 2019; Shabtai and Mishael, 2018). In addition, the paucity of experimental evidence for clay minerals other than smectite limits insight on the advantages of alternate mineral building blocks.

3.2.3.2. CPN building blocks – polymers. The polymer building block of CPNs constitutes the driving force behind pollutant adsorption as it contains numerous, and often diverse, adsorption sites in addition to those on the mineral surface. Functionalization of clay minerals with a polymer is often associated with desorption of water and ions from the mineral surface, significantly changing its surface chemistry. The polymer can change the mineral's surface charge (Seyrek et al., 2011), influencing the attraction and repulsion of charged pollutants (Chen et al., 2013; L. Li et al., 2018; M. Li et al., 2018). Polymers can also alter the mineral's crystal structure and surface morphology by intercalating between clay layers, exfoliating them, or agglomerating them into larger particles (Chen et al., 2008; Shaikh et al., 2017). These processes result from complex mineral-polymer interactions that can induce conformational changes of polymer chains on the mineral surface (Kohay et al., 2015). Implications for adsorption performance (Shabtai and Mishael, 2018, 2016) are discussed below (Section 4.2). Because these parameters are difficult to compare and often unreported, we focus instead on polymer functional group chemistry as a proxy for CPN-pollutant compatibility.

Our survey identified 39 polymer types (Fig. 4B). The most frequently studied were chitosan (23%), polyacrylamide (11%), and polyacrylic acid (10%). Chitosan is a water soluble (at low pH) biocompatible biopolymer with amino and hydroxyl functional groups. Polyacrylamide and polyacrylic acid are water soluble, easily cross-linked synthetic polymers that contain amide and carboxylic functional groups, respectively. Accordingly, the most common functional groups in CPNs are hydroxyl, carboxylic, amine, and cationic amine, along with aromatic, aliphatic, amide, and cation exchange groups (Fig. 4C).

Because CPNs contain combinations of two or more functional groups, we tested the effect of polymer functional group on adsorption metrics using stepwise multiple linear regressions (Section 3.5).

3.2.3.3. CPN fabrication method - building with the blocks. We identified four principal approaches to functionalizing clay minerals with polymers: adsorption, *in-situ* polymerization, cross-linking, and grafting (Figure S7). Most of the CPNs (40% of observations) were fabricated using direct polymer adsorption onto the clay surface by mixing a polymer solution with a clay dispersion. This method utilizes attractive electrostatic and non-specific (Van der Waals) interactions (van de Steeg et al., 1992) between polymers and clay mineral surfaces. Polymer adsorption is often driven by entropic gains associated with dehydration of large polymer chains as they adsorb on the mineral, and desorption of mineral bound water (Chen and Evans, 2004; Lee and Ruckenstein, 1988). The *in-situ* polymerization method (34% of observations) begins with mixing monomers or polymer precursors with dispersed clay, followed by the addition of a polymerization initiator (e.g., azobisisobutyronitrile or ammonium persulfate) (Zhu and Wilkie, 2000). The cross-linking method (10% of observations) consists of reacting a clay or clay-polymer mixture with a cross-linking compound (e.g., alginate or epichlorohydrin) that forms bonds between adsorbed polymer chains, polymer chains and clay, or that self-polymerizes,
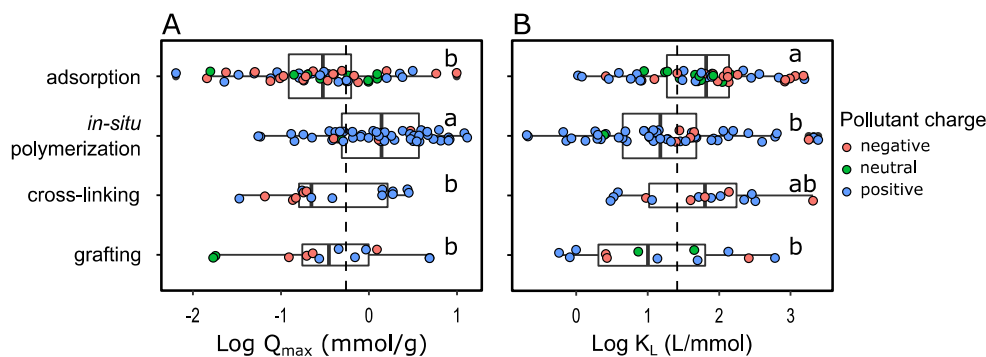
Fig. 5. Langmuir adsorption capacity (Q_{max}, panel A) and affinity (K_L, panel B) of CPNs fabricated using different approaches. Circles are colored according to pollutant charge, and boxplot widths are drawn proportional to the square-root of the number of observations for each fabrication method. Letters indicate Tukey's honestly significant differences between composite preparation methods ($P < 0.05$). Dashed lines represent the mean Log Q_{max} and Log K_L values across all observations.

and as a result reinforces the CPN structure (Tirtom et al., 2012). Cross-linked CPNs are often capable of swelling and adsorbing large amounts of water (hydrogels), which facilitates rapid pollutant transport to adsorption sites (Massaro et al., 2017). The grafting method (9% of observations) consists of covalently bonding a polymer to the mineral surface, or rarely, by grafting an initiator to the surface, followed by *in-situ* polymerization (Liu, 2007). The grafting approach achieves a chemically stable nanocomposite due to the covalent bonding of mineral and polymer building blocks. An additional 6% of observations used other fabrication methods such as electrospinning, melt-mixing, calcination, and gamma radiation (Figure S7), which may offer new pathways to CPN development, but were excluded from ANOVA models due to low sample size ($n < 5$).

Q_{max} values were significantly different across CPN fabrication methods ($P < 0.0001$), where the mean effect of *in-situ* polymerization was significantly higher than adsorption, cross-linking, and grafting (Fig. 5A, Table 1). In both the linear and linear mixed effects models, the mean effect of *in-situ* polymerization was 4.8 times that of adsorption ($P < 0.0001$) and associated with observations of positively charge pollutants (Fig. 5A and Table S4). To account for the fact that mostly positively charged pollutants were tested by *in*-situ polymerized CPNs, we also tested the interaction between CPN fabrication method and pollutant charge on Q_{max}. Q_{max} was significantly affected by the interaction between fabrication method and pollutant classes ($P = 0.01$). This could suggest that polymers employed for this type of CPN, such as polyacrylic acid and polyacrylamide, were especially suited for the adsorption of positively charged pollutants. We suggest that future studies investigate designing *in-situ* polymerized CPNs for removal of anionic pollutants as well. Including study ID as a random effect reduced differences in estimated means ($P = 0.002$), such that only *in-situ* polymerization and adsorption methods differed from each other (Table S4). The higher Q_{max} associated with *in-situ* polymerization is likely due to the high polymer loading achievable relative to other fabrication methods (Gardi and Mishael, 2018). Normalizing pollutant adsorption to polymer loading on the mineral (mass pollutant per mass polymer) would enable a direct comparison of CPN efficiency. In contrast, K_L is expected to be more influenced by polymer-pollutant interactions than polymer loading (Levy et al., 2019).

K_L values were also significantly influenced by CPN fabrication method ($P < 0.05$). Here, the mean effect of adsorption was 3 times greater than *in-situ* polymerization ($P < 0.05$) and associated with negatively charged pollutants (Fig. 5B, Tables 1 and S4). Difference in means did not remain significant when study ID was included as a random effect.

While higher Q_{max} values indicates a CPN can adsorb more pollutant molecules, higher K_L values are related to the nature of the interaction. We previously found that CPNs with higher K_L performed better in fixed-bed columns than CPNs or activated carbons with lower K_L but higher Q_{max} (Kohay et al., 2015; Shabtai and Mishael, 2018). A sorbent with high K_L is also likely to remove pollutants at low concentrations more efficiently than a sorbent with a similar Q_{max}, but a lower K_L. As a result, one must consider Q_{max} and K_L in tandem when testing a sorbent for water treatment (Wang and Giammar, 2019). For example, CNPs fabricated via *in-situ* polymerization may be appropriate in applications that require the removal of pollutants present at high concentrations (Wang et al., 2011). In contrast, CPNs fabricated via the adsorption method may be better suited for the rapid and complete removal of pollutants at trace concentrations (Guillossou et al., 2019).
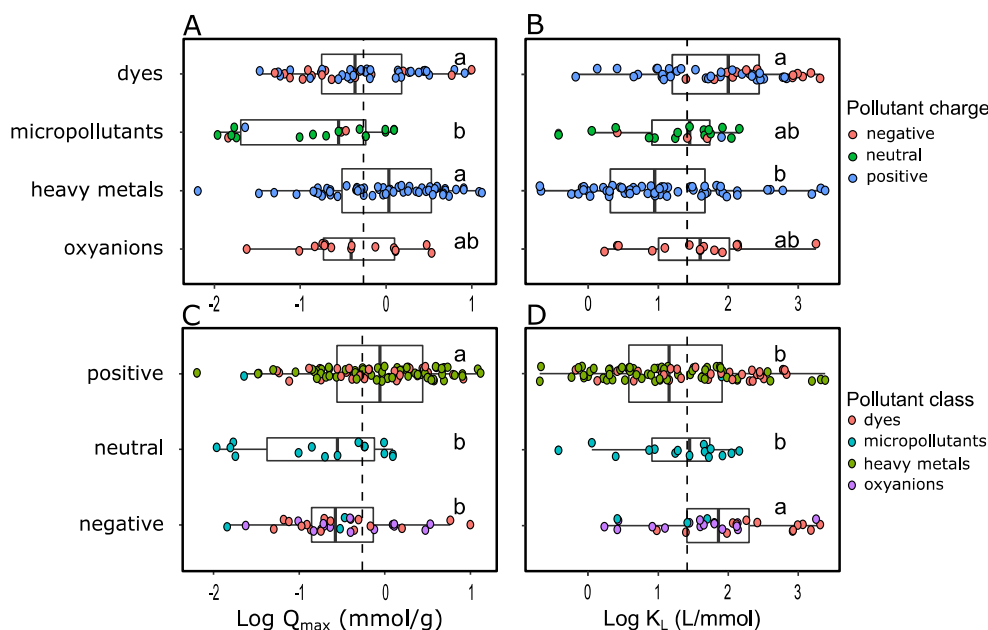
3.2.4. Pollutant class and charge

Surveyed studies tested the adsorption of 58 different organic and inorganic pollutants (Figure S8), which were binned into four classes (dyes, micropollutants, heavy metals, and oxyanions). Dyes ($n = 53$) are high molecular weight organic compounds that have *pi*-electron systems that can be excited by visible light, and often exhibit pH-dependent charge. Micropollutants ($n = 23$) are organic compounds, such as agrochemicals, pharmaceuticals, and polyaromatic hydrocarbons, which have a lower molecular weight, are mostly non-charged or negatively charged (in this study), and often have *pi*-electron systems. Inorganic pollutants include heavy metals (Ali and Khan, 2018) ($n = 65$) and oxyanions ($n = 17$). The most frequently studied pollutants were the heavy metals Cu^{2+} ($n = 16$), Pb^{2+} ($n = 15$) and Cd^{2+} ($n = 12$), the oxyanion Cr(VI) ($n = 10$), the dye methylene blue ($n = 19$), and the micropollutant bisphenol A ($n = 4$).

These heavy metals, oxyanions, and micropollutants are all EPA-regulated water pollutants or included in contaminant candidate lists (CCLs), and their removal from water warrants the development of novel sorbents. However, methylene blue is neither regulated nor included in CCLs, but receives disproportionate focus in the field of novel water remediation technologies (Bielska and Szymanowski, 2006; Houas et al., 2001; Rafatullah et al., 2010; Zhang et al., 2009), perhaps due to the ease with which it can be quantified, and to the vast existing literature that allows easy comparison of results. We strongly suggest future research limits its focus on methylene blue, and instead focus on persistent emerging micropollutants (Bai et al., 2018; Tran et al., 2018).

Q_{max} values were significantly influenced by pollutant class and charge ($P < 0.001$) (Fig. 6A and C, Table 1). Micropollutants had significantly lower Q_{max} values than dyes ($P = 0.03$) and heavy metals ($P = 0.0001$). Accordingly, Q_{max} values were higher for positively than neutral ($P = 0.003$) or negatively ($P = 0.02$) charged pollutants, with estimated mean effect sizes of 4.2 and 2.4, respectively (Table S4).

Fig. 6. Langmuir adsorption capacity (Q_{max}, A&C) and affinity (K_L, B&D) of CPNs for different pollutant classes and charges. Circles are colored according to pollutant charge (top panel) or pollutant class (bottom panel). Boxplot widths are drawn proportional to the square-root of the number of observations for each fabrication method. Letters indicate Tukey's honestly significant differences between composite preparation methods. Dashed lines represent the mean Log Q_{max} and Log K_L values across all observations.

K_L values were also significantly influenced by pollutant class ($P < 0.001$) and charge ($P < 0.01$) (Fig. 6B and D, Table 1). The mean effect of dyes was 6.5 times higher than heavy metals ($P < 0.001$) (Table S4). K_L values were significantly higher for negatively than positively charged pollutants ($P < 0.01$) (Fig. 6C, Table 1) (though post hoc tests did not reveal significant pairwise comparisons), suggesting negatively charged dyes and oxyanions drive high K_L values. These results correspond well to the PCA plot, which showed that K_L was associated with negatively charged dyes (Fig. 3), and to the regression between K_L and pollutant M_w (Fig S5), which was highest for dyes. When including study ID as a random effect, mean effects were diminished due to reduced degrees of freedom and large within- versus across-study variance, however trends were similar (Table 1). This variance highlights the need for testing CPN performance across labs using standardized protocols (see Section 3.6). Improving confidence in results within the field is essential for honing the design and technological adoption of novel materials.

### 3.2.5. Pollutant-functional group interactions

According to our survey, CPNs adsorb pollutants through several types of functional groups and participate in numerous chemical interactions. For example, charged carboxylate and cationic amines can form electrostatic and ion exchange interactions. This is useful for targeting heavy metals, oxyanions, and polar moieties in organic pollutants (El-Dessouky et al., 2018; Gardi and Mishael, 2018; Lozano-Morales et al., 2018). Polymer aromatic rings and aliphatic chains can interact with organic pollutants through hydrophobic and *pi-pi* interactions (Cao et al., 2009; Kohay et al., 2015). Amine and amide polymer functional groups can complex heavy metals (Cho et al., 2012; Kumararaja et al., 2018), and polymer hydroxyls can form H-bonds with various pollutant molecules. Potential mechanisms involved in pollutant adsorption by CPNs has been recently summarized (Mukhopadhyay et al., 2020).

Here, we used stepwise multiple linear regression (MLR) to evaluate whether specific pollutant-functional group interactions can explain the variance in Q_{max} and K_L across pollutant class and charge. We focus on heavy metals and cationic dyes because they have enough observations for robust analysis. We did not include a

formal analysis of oxyanions and micropollutants due to low samples size ($n = 17$ and $n = 23$, respectively).

3.2.5.1. Heavy metals.
Q_{max} values for heavy metals were best explained with a model specification including six explanatory variables (adjusted $R^2 = 0.77$, $P < 0.0001$) (Table 2 and S5). Q_{max} values were strongly, negatively correlated with adsorption fabrication method, but positively correlated with *in-situ* polymerization, cation exchange, and amide functional groups. Pollutant molecular weight and CPNs based on smectite significantly improved AIC scores, but the coefficients were not statistically significant and small in magnitude. K_L values were positively correlated with *in-situ* polymerization, but negatively related to the molecular weight of heavy metals, as well as cation exchange and amide functional groups (adjusted $R^2 = 0.21$, $P < 0.01$) (Table 2 and S5).

The effect of fabrication mode and polymer functional groups on Q_{max} is in line with PCA and ANOVA results (Figs. 3, 5, and Table 1), which suggest that *in*-situ polymerization may be the most advantageous fabrication approach for heavy metal removal. Considering the higher polymer content often achieved by this fabrication method, we suggest Q_{max} values should be normalized to polymer content (mass pollutant per mass polymer) to identify whether *in-situ* polymerization increases the number or accessibility of adsorption sites (Shabtai and Mishael, 2018) compared with CPNs fabricated by polymer adsorption. PCA plots revealed that heavy metal studies clustered around amine functional groups, or carboxyl and cation exchange groups, suggesting heavy metals are targeted through complexation and electrostatic/ion exchange mechanisms (Anirudhan et al., 2012), respectively. MLR results also suggest cation exchange and amide functional groups—which also form complexes with heavy metals (Boyd et al., 1979)—were associated with high heavy metal Q_{max}, but amide functional groups were also linked to low K_L values. This implies that CPNs with ion exchange/electrostatic and complexing capabilities (such as amide and carboxyl containing polymers) have excellent potential for heavy metal removal, but require more in-depth investigation (Ilgin et al., 2015).
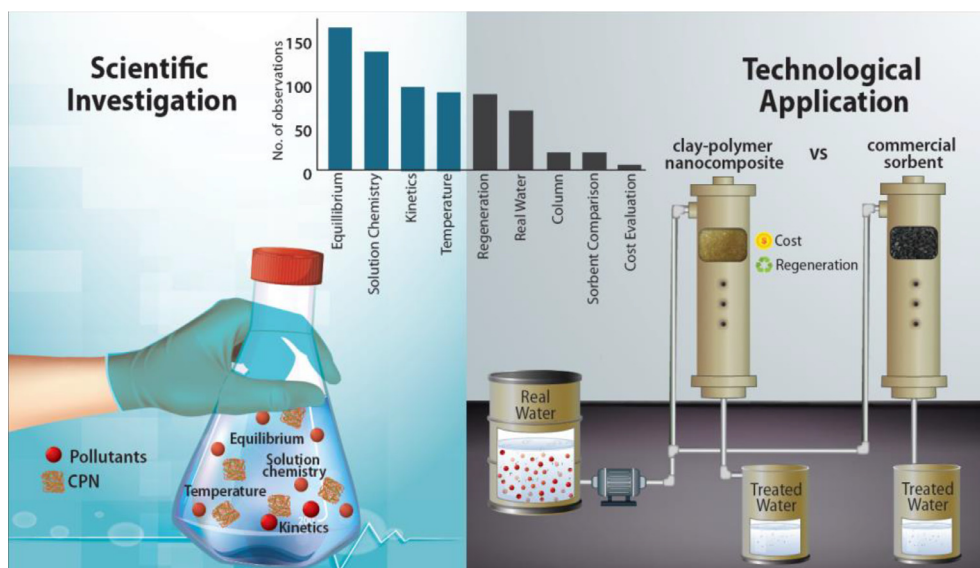
Fig. 7. Studying and testing pollutant removal from a "scientific investigation" perspective requires careful assessment of adsorption equilibrium and kinetics, and the effects of solution chemistry and temperature. Scaling from basic research to "technological application" requires directly testing CPN regeneration, adsorption from 'real water', performance in column mode, comparison to commercial sorbents, and cost evaluation. The number of observations per parameter tested in this meta-analysis are plotted.

3.2.5.2. Cationic dyes. Variation in the adsorption capacity of CPNs for cationic dyes was best explained by including four variables (adjusted $R^2 = 0.3$, $P = 0.001$) (Table 2 and S5). In this model, Q_{max} was positively correlated with polymer hydroxyl and carboxyl functional groups, and negatively correlated with *in-situ* polymerization fabrication. Pollutant M_W was also included in the best-fit model, but the coefficient was small. We could not identify a best-fit model to explain variation in K_L values of cationic dyes based on the tested CPN and pollutant properties (adjusted $R^2 = 0.08$, $P = 0.07$) (Table 2 and S5).

The MLR and PCA results (Fig. 3, Table S2 and Table 2 and S5) both indicate a positive association exists between cationic dyes and carboxyl and hydroxyl functional groups, indicating electrostatic/ion exchange, H-bonding, and other non-specific interactions. In contrast to heavy metals, *in-situ* polymerization was strongly negatively correlated with Q_{max}, suggesting this fabrication method reduces the accessibility of adsorption sites for dye pollutants. This could be the result of the large molecular size of dyes (Shabtai and Mishael, 2016) (e.g., 17 Å methylene blue (Greathouse et al., 2015) vs. 4.19 Å for Cu^{2+}) (Asthagiri et al., 2004) and the thick polymeric phase produced by *in-situ* polymerization (Shaheen et al., 2016). To investigate adsorption site accessibility, a molar calculation of adsorbed dyes per adsorption sites (assuming the composition and stoichiometry of the adsorption sites are known) is required (Shabtai and Mishael, 2018). However, this is seldom reported in the literature.

3.2.5.3. Oxyanions. Oxyanions were strongly associated with cationic amine groups, which is indicative of an electrostatic adsorption mechanism (Fig. 3 and Table S2). The above-average K_L values indicate that CPNs are an excellent sorbent for oxyanion removal (Gardi and Mishael, 2018), however lower than average Q_{max} values (and low number of observations) highlight the need for future research in this direction (Fig. 6A and B), perhaps focusing on CPNs fabricated via *in-situ* polymerization.

3.2.5.4. Micropollutants. Based on PCA results, neutral micropollutants were targeted via *pi-pi* interactions with aromatic functional groups (Cao et al., 2009; Keiluweit and Kleber, 2009), while negatively charged micropollutants could also be targeted via cationic amine functional groups (Ateia et al., 2019; Kohay et al., 2015).

The low Q_{max} of micropollutants (Fig. 6A) could suggest CPNs have been better tailored for targeting charged pollutants, which were primarily tested in this meta-analysis, and are less effective for uncharged micropollutants. However, this could also be an underestimation due to having only one observation of micropollutant removal by a CPN fabricated using *in-situ* polymerization (Guo et al., 2011), which has been shown to correlate with high Q_{max}. The total number of studies on micropollutants is small ($n = 23$), necessitating further research to optimize CPNs for their removal. A potentially useful approach may be functionalizing clays with aromatic polymers (Kong et al., 2019) and carbonaceous materials (Darder et al., 2018; Diagboya et al., 2020; Premarathna et al., 2019) that are capable of interacting with micropollutants containing aromatic functional groups.

Finally, the reviewed studies individually highlight the key role of chemical interactions between polymer functional groups and pollutants. Indeed, the results of this meta-analysis, based on those studies and applying multiple statistical approaches, validate this conclusion across a broad and diverse selection of CPNs and pollutant classes, and confirm its generality. However, most of the reviewed studies investigated a simplified system in equilibrium containing deionized water and a single pollutant (Fig. 7). The role of such chemical interactions may be less pronounced upon pollutant removal from 'real water' (i.e., higher ionic strength, competing pollutants, dissolved organics, etc.) via adsorption columns (non-equilibrium).

3.3. CPN testing and benchmarking

To translate optimistic results from lab-scale experiments to technological applications, CPNs must be tested under realistic conditions encountered in water treatment industries and benchmarked against existing commercial sorbents. The adsorption performance of novel CPNs should also be compared to other reported CPNs, such as the data compiled here. This can serve as a first step in evaluating their technological potential.

Fig. 7 summarizes the type and prevalence of experiments used to characterize, test, and benchmark designed CPN sorbents. We found that 85% of the observations investigated how solution chemistry (pH and ionic strength) affects adsorption ($n = 134$). These experiments are useful for understanding adsorption mech-

anisms and evaluating adsorption under different operating conditions. More than half of the observations included adsorption kinetic experiments ($n = 98$) to obtain a kinetic coefficient, and tested adsorption at different temperatures to determine the enthalpy of the reaction ($n = 92$). Approximately one third of the observations ($n = 54$) extracted thermodynamic parameters. While these experiments yield rich mechanistic and operational information, they do not address four key issues of CPN applicability in water treatment facilities: 1) adsorption of pollutants at relevant concentrations from real water matrices, 2) regeneration potential of spent CPN, 3) CPN granulation and performance in columns (or slurry, if relevant), and 4) side-by-side comparisons of pollutant removal efficiency and cost ,relative to commercially available sorbents at realistic operational conditions (e.g., flow rate, contact time). Based on our survey of review articles, we conclude that this knowledge gap is common across other fields of sorbent design (Bhatnagar and Anastopoulos, 2017; Gerente et al., 2007; Gupta et al., 2013; Wang and Giammar, 2019) and as such our following recommendations may be pertinent to a broad research area beyond that of CPNs.

4. Future perspectives

4.1. Technological application

In addition to thorough investigation of CPN properties and interactions with the targeted pollutants, CPN applicability most also be evaluated in realistic conditions.

1) Pollutant adsorption from 'real water' is often lower relative to deionized water due to the presence of background solutes that can compete for adsorption sites (Zietzschmann et al., 2014), block adsorptive pores (Quinlivan et al., 2005), and form complexes with pollutants in solution (Ruiz et al., 2013). Adsorption from real water was only tested in 41% of the observations ($n = 64$), and its effect (i.e., percent reduction in pollutant removal) was seldom quantified. We strongly encourage future studies test how effective sorbents are at removing pollutants from real water (e.g., municipal or industrial wastewater at environmentally relevant concentrations), and study pollutants that reflect current water treatment needs (Ray et al., 2019). With that said, 'real' water can vary from place to place, and while it is useful for evaluating CPN performance for a specific situation, the use of standardized challenge water (Andrew, 2002), and even standardized experimentation protocols (Ali and Gupta, 2007), can streamline comparison of novel sorbents.

2) Handling spent sorbents is an inherent challenge in adsorption technology. Spent sorbents can be disposed of as solid waste or regenerated and reused. For example, spent activated carbon is removed from its column and thermally regenerated, which is a major expense. Demonstrating the feasibility of CPN regeneration increases their economic competitiveness and reduces their environmental impact. *In-situ* regeneration in the column further establishes the potential of CPNs (Shabtai and Mishael, 2018, 2017). Sorbent regeneration was studied in 58% of the observations ($n = 98$). Chemical regeneration (desorption induced by acid, base, organic solvent, or electrolyte solution) was by far the most common approach investigated in the studies included here, often reaching almost complete desorption. Thermal, biological, and catalytic regeneration of clay-based sorbents have also been probed (Unuabonah and Taubert, 2014; Zhu et al., 2009). Regeneration experiments should determine the efficiency of chemical regeneration, i.e., what percentage is desorbed, whether adsorption is compromised by repeated adsorption-regeneration cycles, the kinetics of desorption, and the volume of regenerating solution needed. Chemical regeneration also throws light on the adsorption mechanisms at play (Is it pH dependent? Electrostatic? Hydrophobic?) and is therefore a valuable tool. Moving forward, efficient degradation of the regenerant pollutant solution should be investigated, as it is a key component of the adsorption-regeneration approach.

3) Commercial sorbents are most often applied in fixed-bed adsorption columns because separation, regeneration, and reuse of the spent sorbent are technically easier in column than in batch mode. Accordingly, CPNs should also be tested in columns, especially since sorbent capacity is often lower in column than batch mode (Ray et al., 2019; Shabtai and Mishael, 2018). However, only 13% of the observations ($n = 19$) tested CPN performance in columns, of which only two tested the CPN as a bead or granule. A major hurdle to applying CPNs (and many other novel sorbents) in fixed-bed columns, is their small particle size – nm to μm size range – and swelling properties, which limit water flow rate through the column. CPN granulation can potentially overcome this challenge, although the effect of granulation technique and adsorption kinetics must be carefully investigated (Du et al., 2017; Ouellet-Plamondon et al., 2012). For example, we recently reported a granulated CPN which was employed in adsorption columns for removal of dissolved organic matter from surface water. The mechanically stable granules enabled a high flow rate, and the columns were in-situ regenerated and re-used (Zusman et al., 2020).

4) Finally, since CPNs are proposed as alternative sorbents, they must be experimentally compared to conventionally used sorbents, e.g., ion-exchangers, activated carbons, or granular ferric oxides. Despite that, we found that only 13% of the observations ($n = 20$) performed side-by-side comparisons, which should ideally investigate the effect of background organic matter on column performance (Kohay et al., 2015; Ling et al., 2017). While activated carbons often have very high Q_{max} values, our work has shown that CPNs are advantageous in real water scenarios because, unlike activated carbon, their performance is less compromised in the presence of background organic matter (Kohay et al., 2015; Zadaka et al., 2009). CPNs can be designed to specifically remove background organic matter (Shabtai and Mishael, 2016), even simultaneously with micropollutants (Shabtai and Mishael, 2018, 2016). Employing CPNs in tandem with commercial sorbents could enhance the removal of pollutant mixtures since sorbents can have different affinities for different pollutants. This has been shown to optimize adsorption efficiency (Du et al., 2017; Zusman et al., 2020), and maintain column hydraulic conductivity, while utilizing existing infrastructure for operating columns with commercial sorbents. While beyond the scope of this analysis, we acknowledge that the environmental and economic performance of new materials and technologies ($n = 4$ observations) dictates their acceptance in the market and requires rigorous assessment (Alhashimi and Aktas, 2017; Kumar et al., 2019).

4.2. Scientific investigation

Although most of the research on CPN adsorbents focuses on the chemical parameters (pH, temperature, etc.) that influence pollutant adsorption (Fig. 7), we suggest that future research must also consider the overlooked aspect of polymer conformation on the clay mineral surface, and its influence on CPN adsorption performance. Polymer adsorption on a clay mineral often transitions from a flat conformation, as monomer "trains", to an extended conformation, as monomer "loops and tails" when 1) polymer loading increases (Kohay et al., 2015), 2) polymer charge density decreases (Levy et al., 2019), and 3) ionic strength increases (Shabtai and

Mishael, 2016). This transition from a "trains" to a "loops and tails" conformation does not only occur on the clay's external surfaces but usually induces intercalation between the clay platelets and may even induce platelet exfoliation.

Poly-4-vinylpyridine (PVP) is one of the few polymers that have been investigated for the effects of its conformation on the performance of PVP-based CPNs. The nitrogen atom in the pyridine monomers can be protonated (pKa = 3.55) (HPVP) (Gardi et al., 2015), yielding pH-dependent polycations, and functionalized with a methyl group (QPVP) (Kohay et al., 2015) or an ethanol group (OHPVP) (Levy et al., 2019), resulting in constant-charge polycations with tunable charge densities. Accordingly, we studied the interactions of PVP-based CPNs with micropollutants that can be targeted through *pi-pi* interactions, hydrogen bonding, and electrostatic interactions (Gardi et al., 2015; Kohay et al., 2015; Levy et al., 2019; Radian and Mishael, 2012). We used X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and thermogravimetric analysis to characterize polymer conformation, and show that it plays a pivotal role in CPN performance, along with polymer chemistry. We found that a "loops and tails" conformation created a nanostructure that increased the Q_{max} and K_L of QPVP-CPN and OHPVP-CPN for anionic micropollutants such as gemfibrozil, diclofenac, and ibuprofen (Levy et al., 2019; Shabtai and Mishael, 2016). In contrast, Lozano-Morales et al. found that a CPN bearing a highly-charged polycation in a "trains" conformation adsorbed the anionic micropollutants sulfamethoxazole and diclofenac better than a CPN bearing a low-charge polycation in a "loops-and-tails" conformation (Lozano-Morales et al., 2018). "Loops and tails" extending into solution may offer more diverse monomer-pollutant orientations (Kohay et al., 2019), while uncharged monomers in "loops and tails" segments may promote hydrophobic interactions with apolar pollutants (Lozano-Morales et al., 2018). Furthermore, adsorption sites in "loops and tails" were found to be inaccessible by larger dissolved organic matter compounds (Shabtai and Mishael, 2016). These few studies show the important, but understudied, role of polymer conformation on pollutant removal.

5. Conclusions

Design of novel and exciting CPNs, even if their initial performance requires tuning, is at the heart of scientific research in this field. Such pioneering studies can focus on selective pollutant adsorption and facile regeneration, perhaps using computer-aided design. Polymer loading, chemistry, and conformation on the clay surface should be thoroughly characterized in future studies, and the effects of these physicochemical properties on adsorption performance should be tested to optimize CPNs. Future research can also probe understudied minerals, polymers, and fabrication techniques to design CPN with new properties. More applicable studies should rigorously evaluate and benchmark these novel CPNs for the removal of emerging pollutants at environmentally relevant concentrations, and in realistic operational conditions. Community-wide adoption of standardized adsorption protocols, challenge waters, and reporting conventions will enable effective comparison of sorbent performance.

Finally, our database can be used as a searchable repository of adsorption data, aimed at supporting transdisciplinary comparisons and benchmarking that drives data-based discoveries for the material research and environmental remediation communities. We anticipate this work will inspire the design of smart and functional CPNs, which most certainly will mature into widely applied, real-world water treatment solutions.

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