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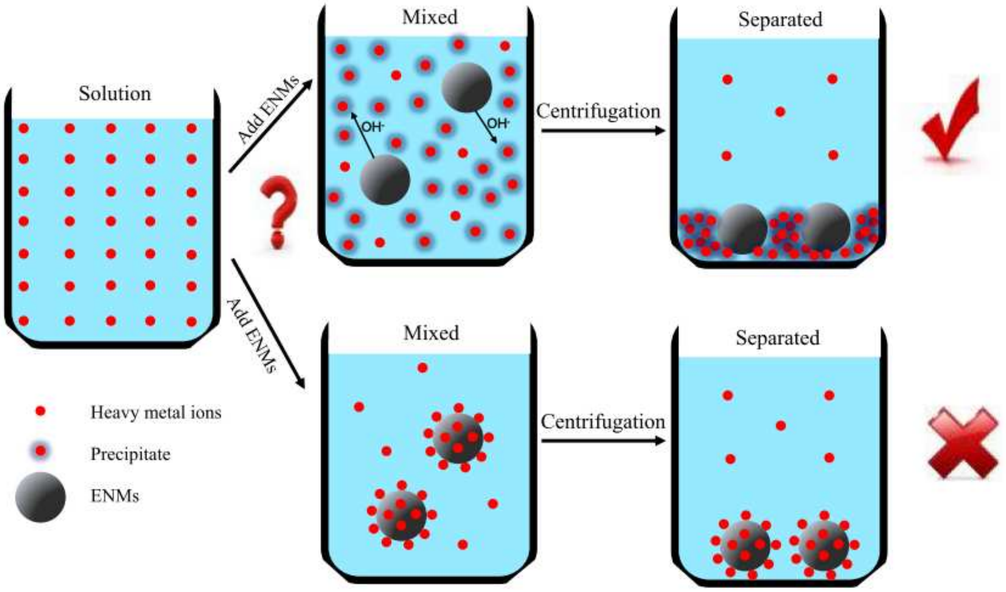

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Are Engineered Nanomaterials Superior Adsorbents for Removal and Pre-concentration of Heavy Metal Cations from Water?

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Abstract: We provide herein evidences that the removal of metal ions with engineered nanomaterials (ENMs) including carbon nanotubes (CNTs) and nano-oxides should be largely attributed to precipitation by forming the metal hydroxides rather than adsorption, implying ENMs cannot be the superior adsorbents.

Engineered nanomaterials (ENMs), including carbon nanotubes (CNTs) and nano-oxides, offer the features of large specific surface areas and surface hydroxyl and carboxyl groups, and thus have attracted great interest for application as superior adsorbents for the removal and pre-concentration of heavy metal ions from water based on previous studies (*1-9*). Various mechanisms, including electrostatic attraction, ion exchange, chemical complexation, and cation-π interaction have been proposed to interpret the adsorption of metal ions on ENMs (*2-9*). A number of studies have focused on elucidating the role of ENM characteristics (surface area, pore size distribution, sorbent mass, and surface total acidity) and solution properties (ionic strength, pH, initial sorbate concentration, and temperature) in the adsorption process (*2-12*). However, we observed in this study, that the reported sorptive removal of heavy metal ions from water by ENMs may be artificial. Instead, the removal of heavy metal ions should be attributed primarily to precipitation, a well-known mechanism for the removal of heavy metal ions by formation of metal hydroxyl precipitates in water rather than to adsorption on the ENMs.

As one point of evidence presented herein, the pH-dependent percentage removal curves of heavy metal ions (i.e., Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+}) in the presence of CNTs (i.e., graphitized CNTs, purified CNTs, and carboxylated CNTs) or nano-oxides (i.e., SiO_2, TiO_2, and Al_2O_3) are found to overlap with the precipitation curves of these metal ions over the pH range of 2 to 12 (Figures 1 and S1). The percentage removal of metal ions with or without ENMs increases gradually from about 0% to ~99% with variation of the solution pH from 2 to 8, and is subsequently maintained at ~99% with further increment of the pH up to 12. This increase in the percentage removal of metal ions with increasing pH in the presence of ENMs has been attributed to the adsorption of the ions by ENMs in previous studies (*2-12*) given that the species distribution of metal ions and the dissociation of surface functional groups and the surface charges of ENMs vary with the solution pH. The low percentage removal of metal ions in acidic solution was attributed to competitive sorption between the metal ions and H^+/Na^+ on the adsorbent surface or to electrostatic repulsion given that the metal ions and the ENM surface sites are both positively charged at solution pH values lower than the points of zero charge (pH_{pzc}) of the ENMs. The increased percentage removal of metal ions with increasing pH was attributed to electrostatic attraction and the formation of metal-ligand composite complexes between metal ions and the negatively-charged ENM surface sites given that the surface functional groups of the ENMs are progressively deprotonated, and thus the ENM surface sites are negatively charged at solution pH values higher than the pH_{pzc} of the ENMs. If adsorption due to electrostatic attraction and the formation of metal-ligand composite complexes are the operative mechanisms in the removal of metal ions from water (*2-12*), ENMs with more functional groups and more negative charges in basic solution, such as carboxylated CNTs (C-CNTs), nano-SiO_2, nano-γ-Al_2O_3,and nano-TiO_2 (Table S1), should lead to a higher percentage removal of metal ions than the graphitized CNTs (G-CNTs), purified CNTs (P-CNTs), and nano-α-Al_2O_3. Moreover, the adsorption of metal ions by nano-SiO_2 and C-CNTs should increase at lower pH compared to adsorption on other ENMs due to their lower pH_{zpc} values and the electrostatic attraction mechanism (Tables S1 and S2). However, analysis of the adsorption of a given heavy metal ion by three CNTs and seven nano-oxides (Figures 1 and S1) did not demonstrate these phenomena. Competition of water molecules with metal ions on the oxidized sites of the ENM surface may account for the insignificant adsorption of metal cations on the surface oxidized ENMs, because oxygen-containing groups on the ENM surface are hydrophilic and can form strong H-bonds with water molecules to suppress adsorption (*13,14*). An increase in the percentage removal of Mn^{2+} in the presence of oxidized CNTs was observed at pH > 8.0 but not at pH > 3.5 in a previous study (*16*), which also indicates that the dissociation of surface functional groups and the consequent generation of negatively-charged ENM surface sites is not responsible for the increased percentage removal of metal ions with increasing pH because dissociation of the -COOH groups to -COO^- groups is initiated at pH > 3.5 (*2*).

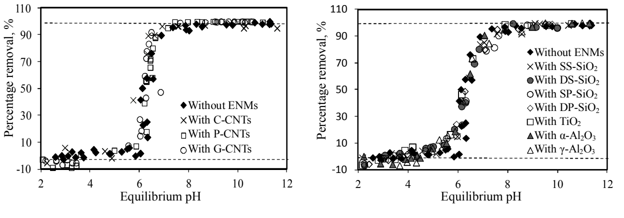

Figure 1. The pH-dependent percentage removal curves of Cu^{2+} (30 mg/L) in the presence of 200 mg CNTs (i.e., C-CNTs, P-CNTs, and G-CNTs) or 200 mg nano-oxides including nano-SiO_2 (i.e., SS-SiO_2, DS-SiO_2, SP-SiO_2, and DP-SiO_2), nano-TiO_2, and nano-Al_2O_3 (i.e., α-Al_2O_3 and γ-Al_2O_3) in 8 mL solution. The pH-dependent percentage removal curve of Cu^{2+} without engineered nanomaterials (ENMs), i.e., the precipitation curve, is also plotted as a reference.

However, the increased percentage removal of Mn^{2+} at pH > 8.0 could be attributed to the precipitation of Mn^{2+}considering that precipitation of $Mn(OH)_2$ from a solution of Mn^{2+} (0.1 mol/L) is effective at pH 8.0 based on the solubility product (K_{sp}) of $Mn(OH)_2$ of 2.1×10^{-13}. In addition, the affinity of the metal ions for oxidized CNTs follows the order: $Cu^{2+} > Pb^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$at pH 9.0 (*15*). This order is in accord with the K_{sp} values of these metal ions, where the $Cu(OH)_2$ precipitate has the lowest K_{sp} value (1.6×10^{-19}) whereas the $Mn(OH)_2$ precipitate has the highest K_{sp} value.

As further evidence substantiating precipitation as the operative mechanism of metal ion removal by ENMs, the pH-dependent percentage removal curves of heavy metal ions are found to be independent of the loading of CNTs (i.e., 10, 50, and 200mg in 8mL solution) and nano-oxides (i.e., 5, 25, 200, and 500 mg in 8mL solution) (Figures 2 and S2), which is not in agreement with the reported results (*16-18*). One of the most important characteristics of the adsorption mechanism is that the concentration of adsorbate adsorbed on the adsorbent (i.e., the amount of adsorbed adsorbate normalized by the mass loading of adsorbent) at a given equilibrium concentration, and consequently the sorption isotherms, are independent of the adsorbent loadings used in sorption experiments (*19*). Therefore, if the adsorption mechanism is operative, the percentage removal of heavy metal ions should increase with increasing adsorbent loading, which was not the case observed in this study (Figures 2 and S2). Moreover, the increase in the concentration of metal ions adsorbed and the slope of the isotherm for $^{243}Am^{3+}$ with increasing CNT loading (*20*) indicates that the $^{243}Am^{3+}$ removal cannot be attributed primarily to sorption on the CNTs (*19*). However, the lack of dependence of the percentage removal of heavy metal ions on the loading of CNTs and nano-oxides is congruent with the well-known mechanism of precipitation of heavy metal ions by formation of metal hydroxyl precipitates, for which the percentage removal of heavy metal ions is dependent on the solution pH (i.e., OH^- concentration) only.

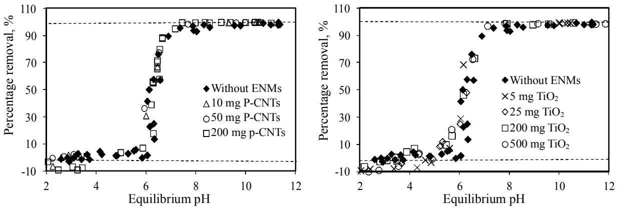

Figure 2. The pH-dependent percentage removal curves of Cu^{2+} (30 mg/L) with variation of the loading of P-CNTs or nano-TiO_2 in 8 mL solution. The precipitation curve of Cu^{2+} (i.e., without ENMs) is also plotted as a reference.

As further evidence, the pH-dependent percentage removal curves of heavy metal ions are also independent of the initial concentrations of heavy metal ions (i.e., 30 and 200 mg/L) (Figures 3 and S3), implying a linear relationship between the metal ion removal and the concentration of heavy metal ions at a given pH. The isotherms of Co, Cu, and Pb acquired in the presence of oxidized CNTs at pH 9.0 were in fact linear as evidenced by the exponent coefficients of about 1.0 (from 0.944 to 1.049) for the data fitted to the Freundlich model (*15*). Linear isotherms were also obtained for $^{243}Am^{3+}$ in the presence of CNTs at pH 6.5 (*20*). These linear isotherms imply that the mechanism for removal of metal ions is precipitation rather than adsorption since isotherm nonlinearity is one of the most important characteristics of the adsorption isotherm (*19*). Moreover, the re-release of metal ions from the solid to the aqueous medium by adjusting the solution pH with acids is also congruent with the precipitation mechanism, i.e., the acids facilitate re-dissolution of the metal hydroxide precipitates (*4*). The predominant removal of metal ions by precipitation could be used to interpret the large variation of the reported the removal percentages (from ~ 0% to 100%) and sorption capacities (from several mg/g to thousand mg/g) of metal ions in the presence of ENMs given that the experiments were conducted at various solution pH with various initial concentrations of metal ions (*2-9*). The largest sorption capacity of 2762 mg/g was observed in a recent study (*21*) for Pb^{2+} on a hybrid and nanostructured vaterite-poly(ethyleneimine). With the precipitation mechanism, it is clear that the removal efficiency of the adsorbents for metal ions is higher (i.e., higher removal percentages) at higher pH and a larger quantity of metal ions can be removed (i.e., larger sorption capacities) at higher initial concentrations. The predominant removal of metal ions by precipitation could also be effectively used to interpret the observations regarding the re-use of ENMs, i.e., ENMs could be used for more than 200 cycles subsequent to regeneration using acids without any changes in their sorption behavior (*22,23*)based on the insignificance of metal ion removal by sorption.

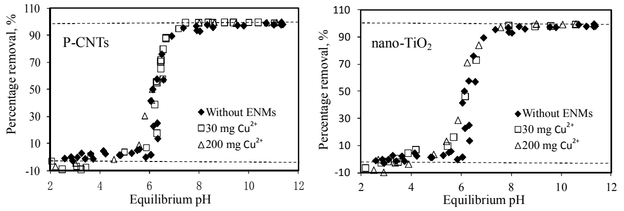

Figure 3. The pH-dependent percentage removal curves of Cu^{2+} at 30 mg/L and 200 mg/L in the presence of P-CNTs or nano-TiO_2 in 8 mL solution. The precipitation curve of Cu^{2+} (i.e., without ENMs) is also plotted as a reference.

Based on re-evaluation of the literature, we propose that the short-fall in the interpretation of the heavy metal ion removal on nanomaterials by invoking the adsorption mechanism in previous studies was derived from ignoring changes in the solution pH after mixing the metal ion solution with the nanomaterials or to erroneous interpretation of the pH changes after mixing the metal ion solutions with nanomaterials, and consequently the ignoring or underestimation of the precipitation of metal hydroxides. In most previous studies, only the initial pH of the solution was reported and used to interpret the adsorption of metal ions (*2-9,18*). Changes in the pH of the metal ion solution after mixing with ENMs were observed in this study (Figures 4 and S4), as was also observed in several previous studies (*16,17,20,24-27*). If the pH changes, especially the final pH, are ignored, one can artificially conclude that metal ions are adsorbed on ENMs because of the significant deviation of the percentage removal curves of the metal ions in the presence of ENMs from the precipitation curves (Figures 4 and S4) under such circumstances. However, one of the most important characteristics of the adsorption mechanism is that the pH sensitive adsorption behavior is dependent on the final pH at the sorption equilibrium but not the initial pH (*13,14,19*). When the final pH is considered, the pH-dependent percentage removal curves of heavy metal cations (i.e., Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+}) in the presence of CNTs (i.e., graphitized CNTs, purified CNTs, and carboxylated CNTs) and nano-oxides (i.e., SiO_2, TiO_2, and Al_2O_3) overlap with the precipitation curves of the heavy metal ions over the pH range of 2 to 12 (Figures 1 and S1), indicating the insignificance of adsorption. The changes in the pH after mixing the metal ion solutions with ENMs were attributed to adsorption via the ion exchange mechanism and the cation-π interaction mechanism. The lowering of the final solution pH at the sorption equilibrium relative to the initial solution pH was attributed to the exchanged H^+ of the ENMs that were released into the solution via ion exchange with metal ions (*24-26*), whereas the increase in the solution pH after mixing with the ENMs was attributed to the simultaneous adsorption of metal ions and H^+(acting as electron pair acceptors) by cation-π interaction with delocalized π electrons (acting as electron pair donors) of the ENMs, such as graphene nanosheets, resulting in an increase in the solution pH from 4.0 to 4.87 and higher(*27*). However, the changes in the pH after mixing with ENMs were also observed for water without metal ions at the initial water pH of 4.0 and 6.0 in this study (Tables S1 and S2), indicating that the pH changes may result from the release of H^+ or OH^- groups of the ENMs rather than the other mechanisms suggested (*24-27*), where the ENMs act as a buffer. For example, the pH of the metal ion solution after mixing with ENMs (such as nano-SP1-SiO_2 and nano-DP1-SiO_2 (Table S2)) falls from neutral to lower pH could be due to the release of H^+ of the ENMs. However, the pH of the solution increases from 4.0 to higher pH after mixing with ENMs (such as CNTs, TiO_2, Al_2O_3, nano-SS1-SiO_2, and nano-DS1-SiO_2) (Tables S1 and S2) could be due to the release of OH^- of the ENMs. In addition, the previously reported increase in the percentage removal of heavy metal ions as the adsorbent loading increased (*16-18*) could be attributed to a larger change in the pH of the solution to highly alkaline with the addition of more ENMs. Moreover, the observed nonlinear isotherms could also be attributed to the change in the solution pH from neutral/basic to acidic, which decreases the precipitation of metal ions (Figures 1 and S1) and thus the removal of ions from water given that solutions with higher metal ion concentrations are generally more acidic due to the saturated H^+ in the metal salts, added to prevent deterioration.

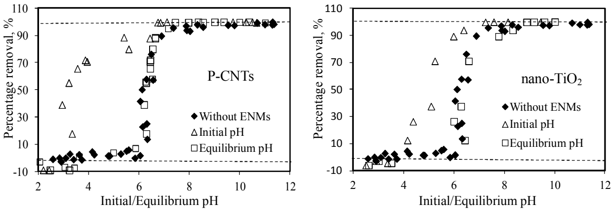

Figure 4. Percentage removal of Cu^{2+} (30 mg/L) versus initial/equilibrium pH in the presence of P-CNTs or nano-TiO_2 in 8 mL solution. The precipitation curve of Cu^{2+} (i.e., without ENMs) is also plotted as a reference.

Another possible reason for the erroneous interpretation that adsorption is the operative mechanism of metal ion removal from solution by ENMs is the disregard of the fact that impurities in the nanomaterials can form precipitates with heavy metal ions. During synthesis of CNTs, transitional metal catalysts (such as molybdenum) will deposit at the tip of the nanotubes or intercalate in the center of the nanotubes (*14,28*). As a case in point, it was observed that metal impurities (e.g., $MoO4^{2-}$) which can release into solutions from purchased CNTs during the sorption to form $PbMoO_4$ precipitates with Pb^{2+} (*28*). Chemical precipitation, i.e., $PbMoO_4$ formation between Pb^{2+} and CNTs-released $MoO4^{2-}$ and subsequent precipitation in the sorptive solutions, was the dominant mechanism for the apparent removal of Pb^{2+} from solution by the reported CNTs (*28*).

Modification of ENMs is one prospective means of enhancing the sorptive removal of metal ions from wastewater (*3,29,30*). For example, by coating Fe_3O_4 magnetic nanoparticles with humic acid (HA), the prepared Fe_3O_4/HA complex exhibited remarkable enhancement of metal ion removal by adsorption (*29*). However, the adsorption capacity of the HA-coated ENMs for metal ions was much lower than that of bulk HA (*31*), implying that modification of the ENMs was not necessarily a promising way to confer superior metal ion adsorption properties on the ENMs.

In conclusion, the awareness of the importance of precipitation of metal hydroxyls in the removal of heavy metal ions from water in the presence of nanomaterials leads us to deduce that the removal of heavy metal ions from water in the presence of ENMs should be attributed primarily to precipitation of metal hydroxyls or formation of precipitates of the metal ions with impurities present in the ENM, rather than to adsorption of these metal ions on the ENMs, i.e., ENMs(including CNTs and nano-oxides) are not superior adsorbents for the removal and pre-concentration of heavy metal ions from water. The erroneous interpretation that heavy metal ion removal occurs via the adsorption mechanism on ENMs in previous studies is largely attributed to disregard of the changes in the solution pH after mixing with the nanomaterials or release of impurities in the ENM, and consequently to the disregard or underestimation of the formation of metal precipitates.

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Notes and References

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Electronic Supplementary Information available: Material and methods, Two Tables and Four Figures.

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