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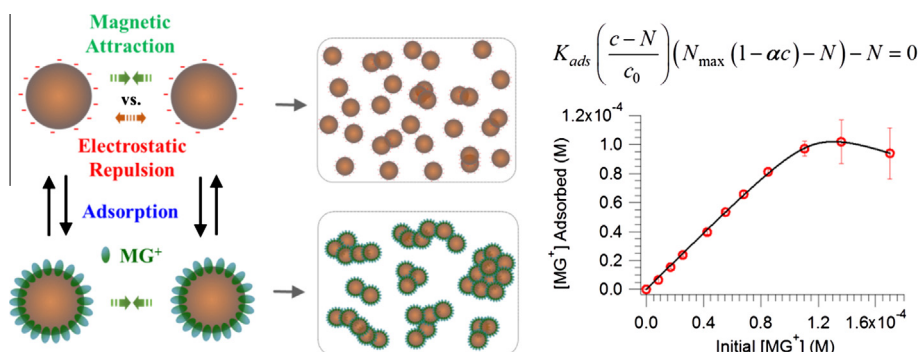
Magnetic vs. non-magnetic colloids – A comparative adsorption study to quantify the effect of dye-induced aggregation on the binding affinity of an organic dye



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GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Due to attractive magnetic forces, magnetic particles (MPs) can exhibit colloidal instability upon molecular adsorption. Thus, by comparing the dye adsorption isotherms of MPs and non-magnetic particles of the same size, shape and functional group it should be possible to characterize the influence of magnetic attraction on MP aggregation.

Experiments: For a range of particle densities, a comparative adsorption study of malachite green (MG⁺) onto magnetic and non-magnetic colloids was carried out using a combination of a separation technique coupled with UV–vis spectroscopy, optical microscopy, and polarization dependent second harmonic generation (SHG) spectroscopy.

Findings: Significant MP aggregation occurs in aqueous solution due to MG⁺ adsorption. This alters the adsorption isotherm and challenges the determination of the adsorption equilibrium constant, K_{ads} . The dye-induced aggregation is directly related to the MG⁺ concentration, [MG⁺]. A modified Langmuir equation, which incorporates loss of surface sites due to this aggregation, accurately describes the resulting adsorption isotherms. The K_{ads} of $1.1 (\pm 0.3) \times 10^7$ and a loss of maximum MP surface capacity of $2.8 (\pm 0.7) \times 10^3 \text{ M}^{-1}$ per [MG⁺] has been obtained. Additionally, SHG has been established as an effective tool to detect aggregation in nanoparticles.

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Abbreviations: MP, magnetic particle; PSC, polystyrene carboxylate particle; m-PSC, magnetic polystyrene carboxylate particle; MG⁺, cationic malachite green; [MG⁺], MG⁺ concentration; SHG, second harmonic generation.

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1. Introduction

Adsorption of molecules from solution phase to the surface of colloidal particles dispersed in a liquid medium is an important first step for many chemical processes in the realm of nanotechnology and environmental science [1,2]. For instance, the fundamental principle behind dye sensitized solar cells [3], trace analyte detection based on nano-sensors [4,5], and removal of aquatic contaminants using engineered nanoparticles [6,7] all entail adsorption of organic compounds from solution onto the colloidal surface. Thus, the determination of the molecular adsorption equilibrium constant, K_{ads} , or the binding affinity is essential in elucidating numerous environmental and industrial processes. Yet, the adsorption process is often complicated by colloidal aggregation. Due to high surface to volume ratio and attractive interactions between the particles, nanomaterials can exhibit a strong tendency to aggregate in solution [8,9]. Fig. 1a highlights the possible pathways associated with colloidal aggregation and dye adsorption processes. These pathways pose a challenge as it not only hinders the accurate determination of K_{ads} , but also alters the effectiveness of colloidal particles in removing organic contaminants. In addition, aggregation of natural colloids in the aquatic environment can affect the chemical reactivity, transport, and fate of particle-bound organic molecules [10–12]. As a result, it is imperative to understand the fundamental aspects of colloidal aggregation, especially when molecular adsorption takes place.

The demand to investigate aggregation behavior is further augmented by a recent surge in the production and application of a wide range of nanoparticles of varying size, composition, shape, structure, and surface modifications [8,9]. This is because the classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which describes colloidal stability in terms of the attractive van der Waals (vdW) and repulsive electrostatic forces in charged particles, is challenged when particles of unique composition and surface properties are considered [1,2,8]. An example of a nanomaterial that belongs to this category, and is the focus of this work, is the surface functionalized magnetic particle (MP). The MPs exhibit widespread applications in biomedical science [13,14], catalysis [15], and environmental remediation technology [7,16–18]. They are often composed of a metallic core such as magnetite, hematite, or zero-valent iron and are tailored with polymer-based coatings that can accommodate a surface functional group for specific binding. These particles exhibit long-range magnetic attraction in the

absence of applied magnetic field and are thus prone to form aggregates [10,11,19–22]. Additionally, surface properties, such as colloidal charge density, are subject to change when the target molecule binds to the particle. This can increase the probability of aggregation (Fig. 1a) and is of major concern in removing organic contaminants using MP-based adsorption technology. Non-functionalized MPs have been utilized in removing inorganic toxic heavy metals [23–25]; however, the use of functionalized MPs in removing organic dyes is lacking and systematic investigation of dye interaction with the surface of MPs is desirable [8,9]. Hence, we explore the following question – what is the relationship (if any) between organic dye adsorption and colloidal aggregation involving polystyrene carboxylate particles (PSCs)?

The aim of this work has been to investigate and quantify the influence of MP aggregation on the binding affinity of an organic dye. Accordingly, a comparative adsorption study of positively charged malachite green (MG^+ , Fig. 1b) to the polymer-based non-magnetic PSCs and magnetic PSC particles (m -PSCs) of the same size, shape, and surface carboxylic ($-COOH$) functional group has been carried out. Herein, we present a systematic characterization of the dye adsorption equilibrium and colloidal aggregation in m -PSCs using a combination of a magnetic separation technique coupled with UV-vis spectroscopy, optical microscopy, and surface selective [26–29] second harmonic generation (SHG) spectroscopy. It is revealed that m -PSCs aggregate and there is a direct relationship between aggregation and dye adsorption. The study provides fundamental insights into the nature of dye-induced aggregation and offers an approach to quantify K_{ads} when colloidal aggregation takes place and persists throughout the adsorption process. To the best of our knowledge, this is the first time a quantitative understanding of the dye-induced aggregation of magnetic colloids has been obtained using a multipronged experimental approach.

2. Materials and methods

2.1. Chemical and sample preparation

The polystyrene carboxyl iron microspheres (ProMag Series-COOH, m -PSC) and polystyrene carboxyl microspheres (non-magnetic PSC) were purchased from Bangs Laboratories, Inc. and have mean radius of 440 and 435 nm, respectively. Malachite Green Carbinol hydrochloride (dye content: 85%) was purchased from Sigma-Aldrich. The following sample preparation

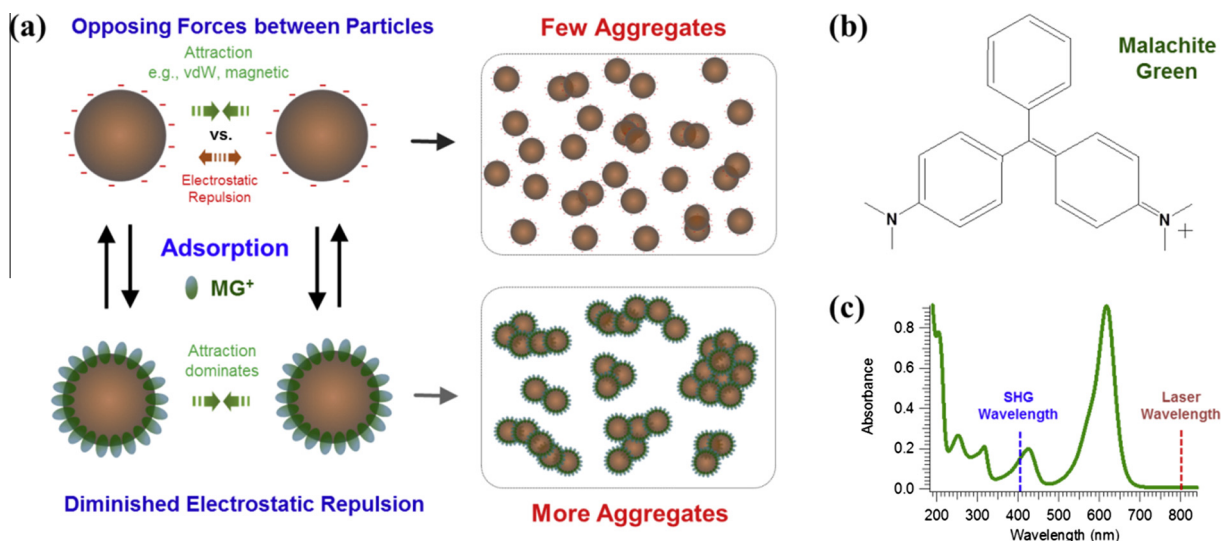


Fig. 1. (a) Schematic of malachite green, MG^+ , adsorption onto the surface of magnetic particles and the resulting number of aggregates. (b) Structure of positively charged MG^+ . (c) UV-vis absorption spectrum of MG^+ and the corresponding laser and SHG wavelengths.

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