Anchoring \( \text{H}_3\text{PW}_{12}\text{O}_{40} \) on aminopropylsilanized spinel-type cobalt oxide (\( \text{Co}_3\text{O}_4\text{-SiPrNH}_2/\text{H}_3\text{PW}_{12}\text{O}_{40} \)): A novel nanohybrid adsorbent for removing cationic organic dye pollutants from aqueous solutions

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In this work, phosphotungstic acid (\( \text{H}_3\text{PW}_{12}\text{O}_{40}; \text{PW}_{12} \)) was chemically anchored on aminopropylsiloxane functionalized spherical \( \text{Co}_3\text{O}_4 \) nanoparticles (\( \text{Co}_3\text{O}_4\text{-SiPrNH}_2 \)) and the resultant nanocomposite (\( \text{Co}_3\text{O}_4\text{-SiPrNH}_2/\text{PW}_{12} \)) was fully characterized. The results demonstrated successful anchoring of \( \text{PW}_{12} \) on the surface of \( \text{Co}_3\text{O}_4\text{-SiPrNH}_2 \) nanoparticles. The \( \text{Co}_3\text{O}_4\text{-SiPrNH}_2/\text{PW}_{12} \) nanohybrid indicated a specific surface area of 42.14 m\(^2\) g\(^{-1}\), which was greater than that of pure \( \text{PW}_{12} \) (ca. 5 m\(^2\) g\(^{-1}\)). The adsorption efficiency of this novel adsorbent nanomaterial was evaluated for removing methylene blue (MB), rhodamine B (RhB) and methyl orange (MO) dyes from aqueous solutions. The hybrid nanomaterial exhibited a high adsorption rate and selective adsorptivity for the cationic MB and RhB dyes compared to those for anionic MO dye. The prepared hybrid nanomaterial removed over 98% of MB within 12 min. The effects of initial pH, contact time, adsorbent dosage, and temperature were investigated on the adsorption process. The adsorption capacity of nanohybrid for cationic MB dye was 38.46 mg g\(^{-1}\). Also, adsorption kinetics indicated that the adsorption by \( \text{Co}_3\text{O}_4\text{-SiPrNH}_2/\text{PW}_{12} \) was well-modeled using pseudo-second-order kinetic model. Finally, thermodynamic parameters revealed that the adsorption was endothermic and spontaneous. The adsorption rate and ability of the \( \text{Co}_3\text{O}_4\text{-SiPrNH}_2/\text{PW}_{12} \) were enhanced as compared with \( \text{Co}_3\text{O}_4 \) and \( \text{Co}_3\text{O}_4\text{-SiPrNH}_2 \) samples due to enhanced electrostatic attraction interaction. The nanohybrid was easily separated and reused without any change in structure. Thus, it could be a promising green adsorbent for removing organic pollutants in water.

KEYWORDS
adsorption, aminosilanized cobalt oxide, dye pollutants, novel hybrid adsorbent, phosphotungstic acid

1 | INTRODUCTION

Water pollution is one of the most serious public health issues worldwide.\(^1\) Uncontrolled industrial development leads to disposal of many organic compounds including organic dyes and surfactants.\(^2\) Most of the organic dyes are toxic and carcinogenic as well.\(^3\) The increasing environmental concerns make it necessary to implement certain steps towards eliminating dyes from wastewater before discharging it in the mainstreams.\(^4\) Among
various methods used to treat the dye-containing wastewater, including biological treatment, ion exchange, coagulation or filtration,\textsuperscript{[5]} adsorption is the most widely used method because of the flexibility in design and operation, and comparatively low cost of application.\textsuperscript{[6]} Many types of materials have been used as adsorbent for water purification, such as clays, activated carbons, polymeric materials, etc.\textsuperscript{[7]} However, these adsorbents have shown either a relatively low adsorption capacity or difficulty in separation. Thus, it is necessary to seek new adsorbents with a large specific surface area, high adsorption capacity, fast adsorption rate and selective adsorption ability.

Polyoxometalates (POMs), as a class of discrete anionic metal oxides with unique physical and chemical properties, controllable shape and size and high electronegative have been used in many research fields, including chemical analysis, biochemistry, ion selective membranes, sensors, catalysis, and proton exchange membranes.\textsuperscript{[8]} Until now, many researchers have still been using heteropolyacids in their recent works. Nevertheless, the main obstacles for using homogeneous POMs catalysis in industries are difficulty/inconvenience of separation and recovery of the POM catalysts due to high solubility in polar solvents such as water, dimethylformamide as well as acetonitrile, and their low surface area (5-8 m² g⁻¹), limiting the accessibility of the active sites and ultimately their utility for different applications.\textsuperscript{[9,10]} To overcome these obstacles, two approaches have been suggested. The first involves fixating POMs on supports such as SiO₂, Al₂O₃, TiO₂, CoO₄, ZrO₂ etc.\textsuperscript{[11–14]} The second option is to use POM salts by substituting the protons (H⁺) with large cations such as Cs⁺, NH₄⁺, Rb⁺ and Tl⁺.\textsuperscript{[29]} Generally, physically adsorbed POM on the support surface is not stable and can leach out easily. Therefore, the most effective approach is immobilization through chemical bonding via functionalized silica. For example, Zheng et al. and Hamadi et al. reported immobilization of POM on imidazole functionalized silica coated Fe₃O₄ and CoFe₂O₄ nanoparticles, respectively.\textsuperscript{[30,31]} The PM was bonded strongly to these functionalized supports through ionic interaction with strong σ-donor amine groups, blocking leaching of the catalyst in polar solvents. In a similar study, molybdovanadophosphoric acid was chemically anchored to a modified SBA-15 surface.\textsuperscript{[32]} Also, Amini et al. immobilized H₃PW₁₂O₄₀ and H₁₅P₅W₆O₃₄ on the inner surface of mesoporous MCM-41, fume silica, and silica-gel via chemical bonding to aminosilane groups.\textsuperscript{[33]} In recent years, POM-based inorganic-organic hybrid materials have been used as a new type of adsorbent for removing dyes. For example, Wang et al. prepared a series of POM@MOF composite material based on MIL-101 and various POMs (POM=K₄PW₁₂O₄₀, K₅SiW₁₂O₄₀) for rapid adsorption and selective separation of methylene blue (MB) from aqueous solutions.\textsuperscript{[34]} Zhang et al. developed a novel organic–inorganic hybrid compound, (4-Hap)₄[Mo₃O₉S₆] (4-AP=4-aminopyridine) via a hydrothermal method.\textsuperscript{[35]} According to the results, the compound demonstrated rapid and selective adsorption of MB with ultra-high efficiency and capacity. Sun et al. and Yang et al. also developed POM-based MOFs for selective adsorption of cationic dyes from aqueous solution.\textsuperscript{[36,37]}

Based on the above mentioned studies, it can be concluded that metal oxides cannot be directly used as supports to prepare POMs-based composites, which are normally fabricated by wet impregnation method. It can be explained that the structure of POMs can be decomposed due to the surface alkalinity of some metal oxides. For example, Marci et al. reported binary materials which were prepared by impregnation of H₃PW₁₂O₄₀ on Al₂O₃ as support and concluded that the Keggin-type POM anion was completely degraded when supported on Al₂O₃.\textsuperscript{[15]} So, it is necessary to explore more efficient routes for POMs loading on metal oxides that not only keep the structure intact and avoid solubilisation during the adsorption process, but they also offer more convenience in view of separation, recovery and recycling of POM.

Spinel-type cobalt oxide (Co₃O₄) is a transition metal oxide with high thermal and chemical stability, low solubility, as well as interesting electronic, magnetic and catalytic properties.\textsuperscript{[38–48]} Due to these excellent characteristics such as its resistance to severe acidic and basic conditions, it can be applied as an appropriate support for immobilizing POMs. Accordingly, in this paper, we have prepared a new nanohybrid consisting of phosphotungstic acid (H₃PW₁₂O₄₀; PW₁₂) coupled with Co₃O₄ nanoparticles. Initially, the surface of Co₃O₄ nanoparticles was modified by 3-aminopropyltriethoxysilane (APTES) to provide desired binding sites. The APTES group covalently bounded to Co₃O₄ is a strong base which makes a strong electrostatic interaction with PW₁₂ via acid-base reaction. The as-synthesized Co₃O₄–SiPrNH₂/PW₁₂ nanohybrid was tested as a novel adsorbent for removing organic dye pollutants from aqueous solution. To the best of our knowledge, coupling POMs with Co₃O₄ to remove pollutants from water has not been reported yet.

2 | EXPERIMENTAL

2.1 | Materials and characterization techniques

Cobalt(II) chloride hexahydrate (98.5%), 3-aminopropyltriethoxysilane (APTES, 98%) and phosphotungstic acid (HPW, 98%), methylene blue (MB, C₁₈H₁₈ClN₂O₃, 99%), Rhodamine B (RhB, C₂₈H₂₃ClN₂O₃, 98%), and methyl orange (MO,