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# ZnO, TiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>/Carbopol hybrid nanogels for the cleaner process of paper manuscripts from dust stains and soil remains

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## Abstract

There are many paper manuscripts at museums, stores, and libraries that have different stains. The dust stains and soil remains played an important role in the degradation of these manuscripts. Therefore, the cleaning process for these stains is important to process. Unfortunately, the removal of stains by some traditional techniques can be hazardous to the paper's fibers. Therefore, this study aims to evaluate innovative nanoparticle gels in the cleaning process of dust stains from paper manuscripts. The synthesized nanomaterials [Fe<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub>, and ZnO]/Carbopol hybrid nanogel were examined in order to investigate the surface morphology, determine the physio-chemical properties, for phase structure, using scanning electron microscope (SEM), transmission electron microscope (TEM), AFM, DLS, XRD, and Zeta potential. Some stained paper samples were prepared and exposed to accelerated thermal aging at 100 °C for 72 h. The evaluation of the cleaning by nanogel was performed by different analytical procedures containing investigation with a USB digital microscope, SEM, color change, mechanical properties, and ATR-FTIR analysis. The results of this study showed that ZnO/Carbopol hybrid nanogel at high viscosity gave the best results in the cleaning process of mud stains through the ability to dismantle mud particles and increase surface contact with the solvent. The aged treated sample with high viscosity form of ZnO NPs/carbopol hybrid nanogel gave the highest tensile strength value of (56.0 N). The treated samples with the high viscosity form of ZnO NPs/carbopol hybrid nanogel gave the highest value of elongation (1.398%) before aging. It also does not affect the chemical composition of the paper after cleaning it, but rather on the whole, it bites the hydration of the paper, which positively affects the properties of the treated paper.

**Keywords** Paper conservation, Gel cleaning, Hybrid nanogel, Magnetite, Rutile, Zincite

## Introduction

There are many paper manuscripts housed in different stores, libraries, and museums are suffered from numerous kinds of stains resulting from different deterioration factors [1–4], especially dust stains and soil remains. A lot of pages of the manuscripts are extremely cockled which leads to the ingress of dust inside the text block. The dust has a particular challenge for historical libraries [5–7]. Dirt and soil remain leads to different signs of damage to paper manuscripts like a scratchy action for the paper's fibers and lead to weakness of paper manuscripts [5, 8–10]. Dust and soil remains may become acidic due to

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the absorption of atmospheric pollutants such as sulfur dioxide from the surrounding environmental conditions [11–13]. The previous gas ( $\text{SiO}_2$ ) in combination with moisture can react with the metal compounds (Iron) found on the surface of the paper manuscripts in dust form and converted to sulfuric acid which is absorbed by paper sheets and consequently, weakness of its mechanical properties and flexibility [14, 15].

Dust and soil remain found on the paper manuscript's surface and often contain mold spores, particularly in an uncontrolled environment. Additionally, the components of dust can provide a nutrient source for insects and microorganisms [14, 16]. The dust and soil remaining can absorb moisture from the surrounding environmental conditions which facilitate penetration of particulates of dust inside the paper sheets, consequently making it difficult to clean by the surface cleaning methods. The presence of surface dust leads to the staining of the paper sheets and reduces the artistic and historical values of paper manuscripts [17]. The removal of dust from the manuscripts, books, and other contents of libraries needs a high cost [18]. Cementation of dust occurred at high humidity, where calcium ions can leach from dust particles and redeposit forming microcrystalline calcite which cements the dust particle to the substrate and the hygroscopic feature of paper-enhanced cementation [19, 20], where at high humidity, dust adheres very successfully to paper manuscripts. Many of the bacteria present in these materials, and particularly in archive materials, grow using very low concentrations of nutrients and may cause chemical and esthetic biodeterioration, as well as facilitating the last development of other microorganisms such as fungi, which are well-known detriogens [21]. Their initial growth on materials is usually due to other organic material present in the dust, not to the nutrients in the supports [22].

Due to the previous, the dust stains and soil remains must be removed and cleaned from paper manuscripts. The cleaning process is one of the most vital processes for the treatment of paper manuscripts [23, 24]. Unfortunately, some traditional methods such as solvents and chemical bleaching used for cleaning some stains lead to damage to the fibers of the treated paper [25] and most organic solvents (such as toluene) used in the treatment of paper manuscripts lead to degradation of the treated paper manuscripts, where these solvents led to an acceleration of oxidation and hydrolysis processes of paper [1].

One of the most important disciplines in cultural heritage conservation sciences these days is research into more effective, and stable time, new conservation treatments [26, 27]. The use of gel is considered one of the most important processes used for cleaning paper manuscripts because it is easy and securely controlled [1] and

it does not need liquid treatments [28]. Accordingly, the gel of some nanoparticles (NPs) such as ZnO,  $\text{TiO}_2$ , and  $\text{Fe}_3\text{O}_4$  gel have been evaluated for cleaning paper manuscripts in the present work. Out of our knowledge, gels contain ZnO NPs,  $\text{TiO}_2$  NPs, and  $\text{Fe}_3\text{O}_4$  NPs have never been applied in cleaning paper manuscripts prior to this study.

ZnO NPs were chosen in this study due to its advantages such as being affordable and having many active sites with high surface reactivity [29, 30]. ZnO NPs showed high absorption efficacy of light radiations, environmental safety, high homogeneity, relatively low process temperature and UV protection [31, 32] and antibacterial properties [33].

In nanoscale and microscale formulations, ZnO NPs are now being investigated as antibacterial agents [34]. When used in conjunction with components for biosensing and wound healing, ZnO NPs can trace minute amounts of biomarkers associated with different illnesses [35]. Additionally, it has been revealed that ZnO NPs may deliver and detect medicines [36]. ZnO NPs have superhydrophobicity, low electron conductivity, and excellent heat resistance [37, 38], which give it multifunction purpose in medical application [39].

Excellent reusable self-cleaning capabilities of ZnO NPs were demonstrated, and these capabilities are crucial for stain removal because they prevent dust or dirt accumulation on the treated surface [40, 41]. ZnO NPs give protection and preservation of paper works against deterioration factors and it uses as a protective coating on the surface of paper fibers [42]. When ZnO NPs were applied to the paper surface for the coating to improve the surface strength and softness [43–45] and protect paper from the damaging effects of UV light, air pollutants, and micro-organisms like fungi and bacteria [45, 46].

$\text{TiO}_2$  is a white non-combustible and odorless powder [47]. It is one of the most important inorganic minerals due to the potential applications of  $\text{TiO}_2$  NPs in different fields, non-toxicity, stability and optical, and adsorption properties [47, 48]. Additionally,  $\text{TiO}_2$  is super hydrophobic material [49].  $\text{TiO}_2$  NPs have been made using green, chemical, physical, and biological synthesis techniques. Green methods have been found to be more effective than chemical synthesis techniques because they use fewer precursors, use less time, and use less energy [50, 51].

Iron oxide nanoparticles ( $\text{Fe}_3\text{O}_4$  NPs) are widely studied in various fields of research like magnetic resonance (MR) imaging applications [52], platforms for tumor imaging and therapy or improved and targeted cellular absorption by alterations to the surface layer coating [53], customized medication delivery and environmental cleanup [54] and antimicrobial bioactives [55, 56].  $\text{Fe}_3\text{O}_4$