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Silica-titania hybrid nanoparticles for the extraction of zinc ions from water samples

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Graphical Abstract

ABSTRACT

This study prepares and evaluates the performance of the hybrid nanoparticles as absorbent to extract selected heavy metal ion namely zinc from water samples. SiO_2–TiO_2 hybrid nanoparticles was prepared using sol-gel method which used the combination of titania and silica sols. Titania sol was prepared at a molar ratio of 1 $TiCl_3$: 3 NaOH, while silica sol was prepared at molar composition of 1 TEOS: 2 H_2O: 2 C_2H_5OH: 0.5 HCl. The prepared solid was characterized using XRD, FTIR, nitrogen adsorption analysis and SEM. XRD results showed that the sample is amorphous due to the presence of silica in the sample. Low-intensity peaks of are observed at 2θ 28.302º, 41.887º, and 68.585º indicating the presence of titania as minor component. Nitrogen adsorption analysis revealed that SiO_2-TiO_2 hybrid nanoparticles have mesoporous structure with type IV isotherm and average pore sizes of 12.45 nm. The BET surface area of SiO_2-TiO_2 hybrid nanoparticles is 129.326 m^2/g and t-Plot has proved that SiO_2-TiO_2 hybrid nanoparticles only composed of mesopores. Several extraction conditions were optimized namely pH level, shaking time and mass of adsorbent. The SiO_2-TiO_2 hybrid nanoparticles adsorbent has demonstrated to be potentially applicable for the removal of zinc ion from water samples.

Keywords: silica-titania hybrid nanoparticles, dispersive-solid phase extraction, zinc extraction, heavy metal in water.

1. INTRODUCTION

Unscrupulous discharge of untreated effluents can cause water contamination by toxic heavy metals [1]. Water pollution with heavy metals has been threatened aquatic live and also human health even if they are present in low concentrations [2]. Zinc is a heavy metal that belongs to the periodic table group 12, together with the two toxic metals cadmium and mercury. Zinc is relatively harmless as compared to several other metal ions with similar chemical properties, and is an essential trace element in human body [3, 4]. However, accumulation of zinc in human body can be toxic. Excess amount of zinc can cause system dysfunctions which leads to impairment of growth and reproduction, kidney failure, anemia, kidney failure, and diarrhea [5]. Thus a simple and rapid microextraction technique is required to regulate and monitor these types of pollutants.

Dispersive solid phase extraction (DSPE) is one of the simplest extraction techniques with wide range of selectivity due to its various types of adsorbents. DSPE is one of the favourable options as it eliminates the multiple steps of SPE [6]. DSPE or also can be termed as solid-liquid extraction adopting the principle of transferring analytes from the aqueous phase to the active sites of the solid phase [7].

Researchers have sought after various composites as potential adsorbents to cater to the microextraction of metals. Hybrid nanoparticles are composites that consist of two or more different constituents at nanometer level. By mixing different constituents, it will lead to the formation of composite having new combination properties of the two constituents. SiO_2–TiO_2 hybrid nanoparticles are a newly developed material and its properties and applications are still not well investigated. Thus, it was of interest to synthesize and apply the adsorbent for the extraction of targeted analyte, zinc ion in water samples.

2. EXPERIMENTAL

The experiment was divided into three main stages. The first stage was focused on the prepared of SiO_2–TiO_2 hybrid nanoparticles and characterization of SiO_2–TiO_2 hybrid nanoparticles prepared by using XRD, FTIR, nitrogen adsorption analysis, and SEM. The second stage was focused on the DSPE optimization of SiO_2–TiO_2 hybrid nanoparticles in extraction of zinc from water by optimizing several parameters including sample pH, mass of sorbent, and extraction time. Optimization of parameters were carried out one at a time while other parameters were kept constant.

In order to validate the method used in this study, validation parameters such as LOQ, LOQ, precision, and linearity were studied. The LOD and LOQ were determined using 3 times and 10 times the standard deviation of the lowest concentration detectable using DSPE-AAS method. The precision was done intra and inter day intervals and were calculated based on percentage of relative standard deviation of known concentrations. The real sample analysis were evaluated based on recovery of known amount spiked in the samples. The last stage was focused on real sample analysis. Water samples from UTM Lake, Sungai Skudai, and laboratory tap water were used in this stage, and each samples were spiked with 0.2 and 0.4 ppm of zinc. All analysis of heavy metal were measure by using Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometer.

3. RESULTS AND DISCUSSION

3.1 Characterization of SiO_2-TiO_2 Hybrid Nanoparticles

3.1.1 Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FTIR) is was used to determine the type of bond and functional group present in the solid of SiO_2-TiO_2 hybrid nanoparticles prepared. This measurement was done carried out in the wavenumber range between 4000 cm-1 to 400 cm-1 and KBr method was used in the preparation of sample before being analysed. **Figure 1** shows the infrared spectra of SiO_2-TiO_2 hybrid nanoparticles. Broad absorption peak at wavenumber 3455.43 cm-1 was is observed, which assigned for to the hydrogen bonded OH due to the presence of water molecule. SiO_2-TiO_2 hybrid has Si-O-Si absorption at 1024.96 cm-1. Ti-O-Ti adsorptions were observed for at 777.99 cm-1

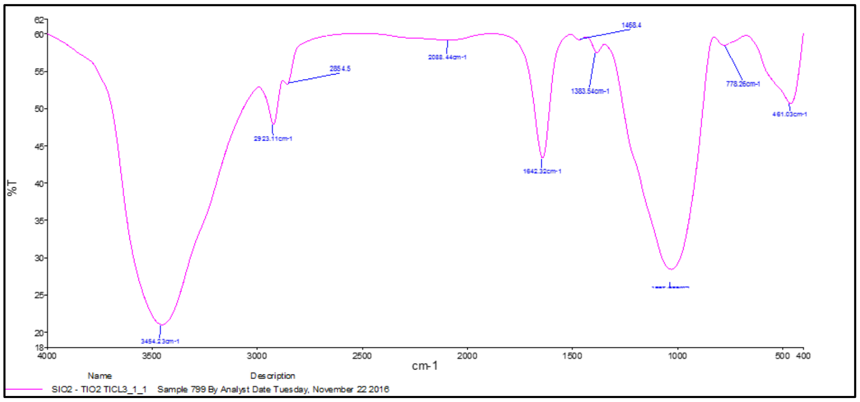

Figure 1: IR spectrum for silica-titania hybrid nanoparticles

3.1.2 Nitrogen Adsorption Analysis

In order to determine the BET surface area, type of pore, pore volume and pore width of the SiO_2-TiO_2 hybrid nanoparticles, nitrogen adsorption analysis was used. The nitrogen adsorption analysis for the isotherm, t-plot, and BJH desorption pore volume of SiO_2-TiO_2 hybrid nanoparticles are shown in **Figure 2 (a), (b),** and **(c)**.

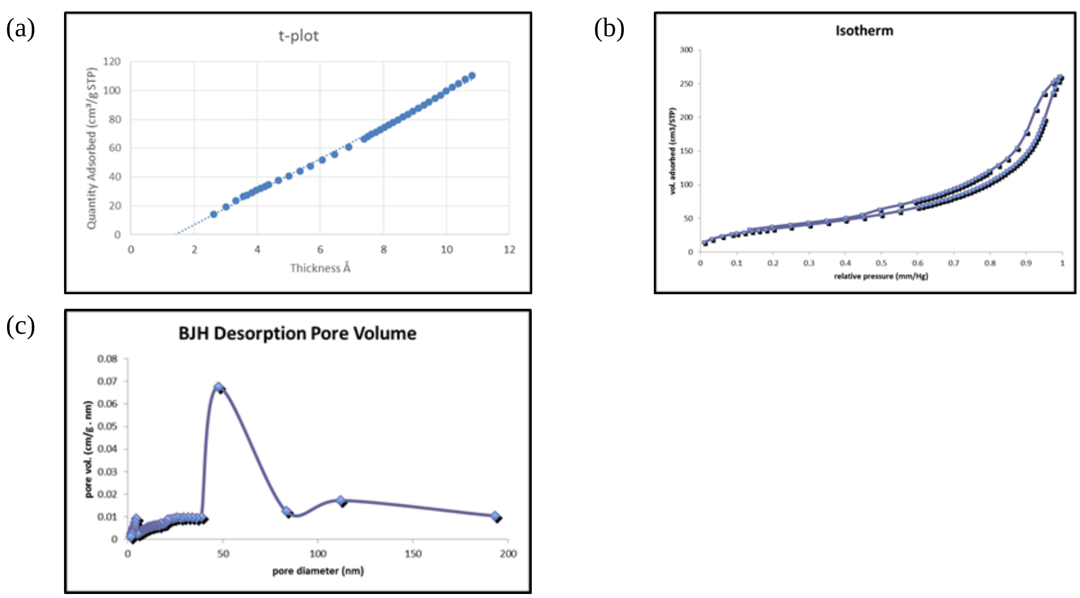

Figure 2: Nitrogen adsorption analysis data for SiO_2-TiO_2 hybrid nanoparticles (a) t-Plot, (b) Isotherm, (c) BJH desorption pore volume

The isotherm plot in **Figure 2 (b)** shows that SiO_2-TiO_2 hybrid nanoparticles has a BET surface area of 129.3260 m^2/g with a type IV physisorption isotherm, which indicates that SiO_2-TiO_2 hybrid nanoparticles has pores in mesoporous size range and has capillary condensation. The hysteresis loop follows type H3 hysteresis loop which associated with capillary condensation in solids consisting of slit shape pores with non-uniform size and shape.

From the BJH desorption pore volume (**Figure 2c**), the average pore width of SiO_2-TiO_2 hybrid nanoparticles is 100.993 Å with pore volume of 0.407415 cm^2/g. The pores formed on the adsorbent will help in the entrapment of the analytes onto the surface of the particle, leading to an increased extraction efficiency.

t-Plot in **Figure 2(a)** describes the microporous surface area of the samples, which can be determined from the extrapolation to the y-axis. The BET surface area of this hybrid nanoparticles is 129.3260 m^2/g, which is lower than the surface area of silica-titania hybrid prepared for pH sensing studies, which is 489 m^2/g. This was probably because of different types of chemical and synthesis approach during the preparation processes.

3.1.3 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) was used to analyze the morphology and shape of the particle structure as well as to quantitatively show the size of the particle. The SEM micrograph of SiO_2-TiO_2 hybrid nanoparticles sample is shown in **Figure 3**. From the micrographs, it is clear that some of the particles are agglomerated forming bigger particles. This will lower the surface area of the absorbent which affect the efficiency of the absorbent. The average width and length of the particles is 125 and 160 nm respectively.

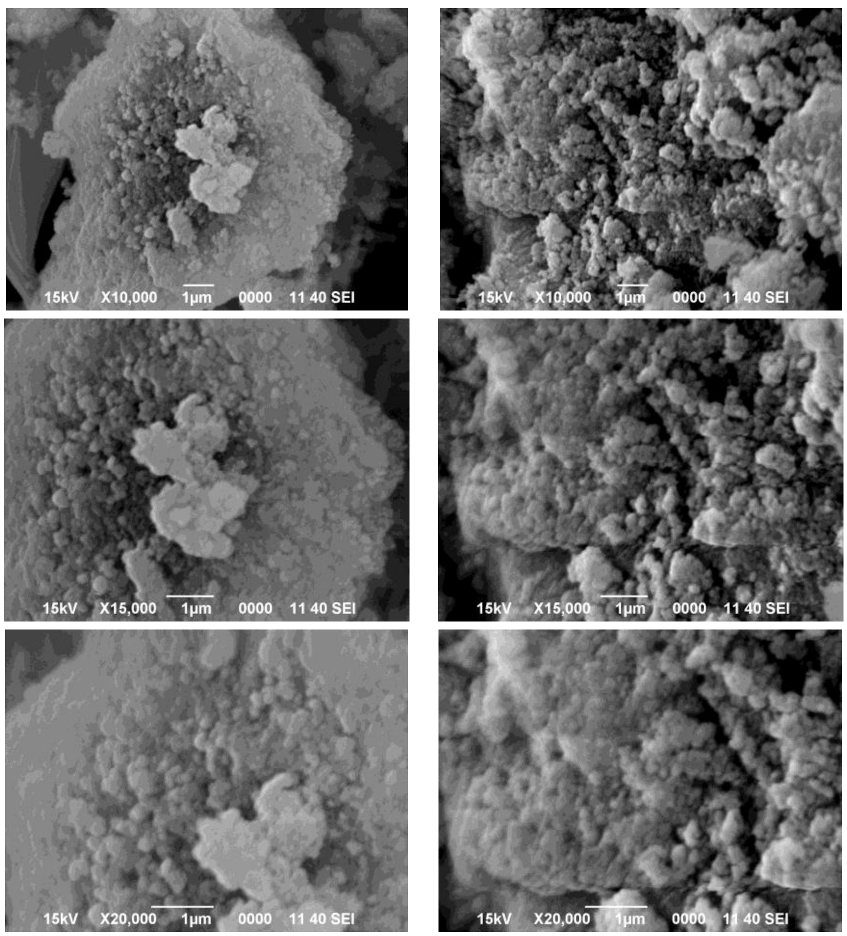

Figure 3: SEM micrographs of SiO_2-TiO_2 hybrid nanoparticles

3.1.4 X-Ray Diffractogram (XRD)

X-ray diffractometer was used to identify the phase of a crystalline of SiO_2-TiO_2 hybrid nanoparticles. The x-ray diffractogram of SiO_2-TiO_2 hybrid nanoparticles is shown in **Figure 4**. From the XRD pattern, it shows the amorphous of structure of silica in the SiO_2-TiO_2 hybrid nanoparticles. This is due to the nature of synthesis method which is not using heat treatment method. However, the sample is not highly amorphous as pure silica due to the presence of TiO_2 in the sample. The peaks of the XRD pattern for TiO_2 is visible although not prominent since silica is majority on the surface of the sorbent. From the XRD pattern, low intensity peaks at 2θ 28.302º, 41.887º, and 68.585º correspond to the peaks of TiO_2 in the sample.

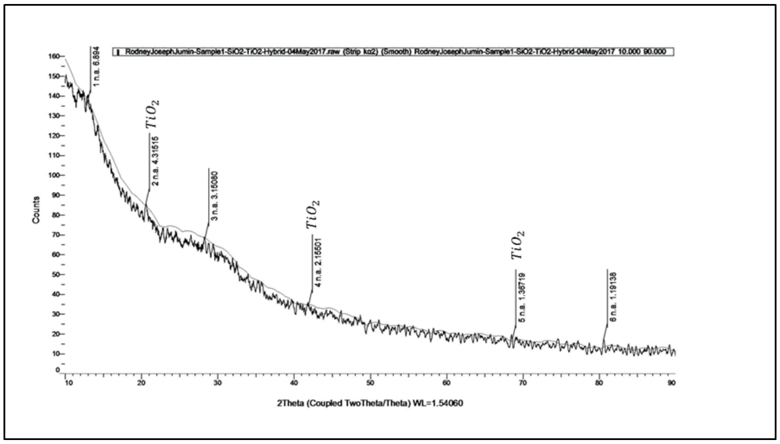

Figure 4: X-ray Diffractogram of SiO_2-TiO_2 hybrid nanoparticles

3.2 Optimization of Metal Ion Extraction

3.2.1 Effect of Sample pH

The effect of zinc adsorption on the adsorbent was studied over the pH range of 3-7 as shown in the **Figure 5**. The uptake of the metal ions is directly proportional to the pH level, and the highest extraction efficiency was 3.50 at pH 7. The uptake of metal was slower at lower pH possibly due to the presence of protons in the solutions which leads to the competition between protons and the metal ions. The pH study is not performed at pH above 7 because insoluble metal hydroxides start to form from the solutions.

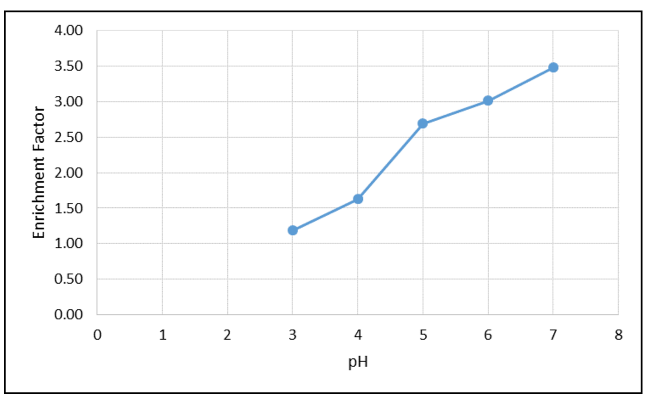

Figure 5: Effect of initial pH on adsorption of zinc ions

3.2.2 Mass of Sorbent

The effect of mass of sorbent was studied with different masses of sorbent in the range of 10-40 mg. The results showed that the absorption of metal ions increased with the increasing mass of sorbent (**Figure 6**). The highest enrichment factor for zinc ions is 3.75 at 30 mg of sorbent.

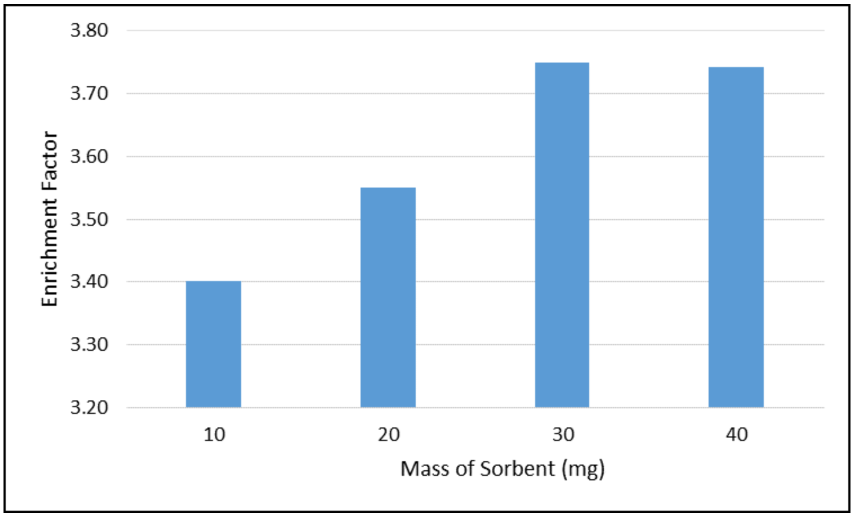

Figure 6: Effect of mass of sorbent on adsorption of zinc ions

3.2.3 Shaking Time

Figure 7 shows the effect of shaking time on the adsorption of zinc ions on the adsorbent. The effect of shaking time was studied in the range of 5 min to 40 min. It shows that the adsorption of metal ions was increased from 5 min to 10 min of shaking time, and decreased at shaking time above 10 min. The optimum shaking time for the extraction of zinc ions is 10 min. Further shaking did not give any significant changes in terms of extraction efficiency.

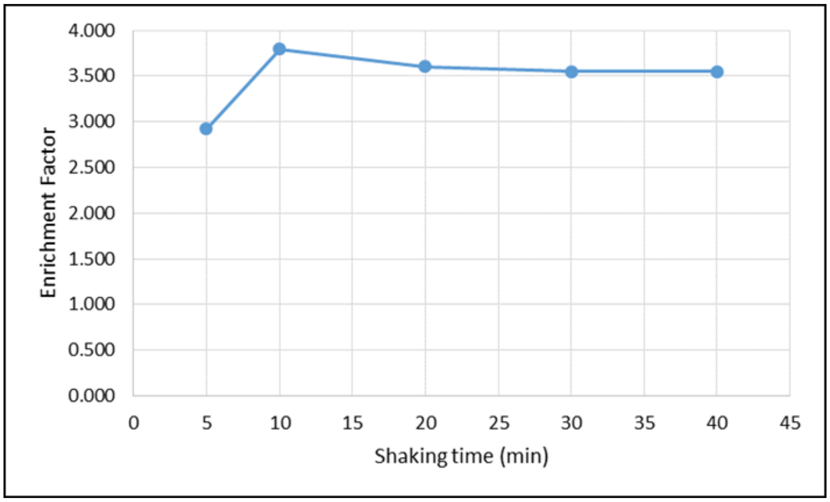

Figure 7: Effect of shaking time on adsorption of zinc ions

As a summary, the DSPE optimum conditions were: sample pH of 7.0; mass of sorbent, 30 mg; extraction time, 10 min. The optimum condition were used for validation and real sample analysis.

3.3 Method Validation

The developed method was further validated in terms of linearity, precisions, LOD and LOQ. The applicability of DSPE method using SiO_2-TiO_2 hybrid nanoparticles was validated using deionized water. The LOD and LOQ were calculated based on 3 and 10 standard deviations from the lowest concentration detectable by AAS. Table 1 shows the validation data of DSPE using SiO_2-TiO_2 hybrid nanoparticles with deionized water. All the validation results were in acceptable range.

Table 1: Validation data of DSPE using SiO_2-TiO_2 hybrid nanoparticles with deionized water

Sample	**Number of replicates**	
Working range		0.1 – 0.5 ppm
Regression		0.995
Limit of detection (LOD)		0.03 ppm
Limit of quantitation (LOQ)		0.10 ppm
Precision at		0.25 mg/L
Intra-day	3	2.19%
Inter-day	3	5.25%
Trueness/accuracy	3	101.56%

3.4 Real Sample Analysis

The water samples were obtained from laboratory tap, Skudai River, and UTM Johor Bahru Lake. Each sample was spiked with 0.2 and 0.4 ppm of zinc. The optimized conditions were applied in the extraction of the samples. The results of the extraction are shown in Table 2.

Table 2: Recovery studies on DSPE of SiO_2-TiO_2 hybrid nanoparticles using spiked tap water, river water, and lake water samples (n=3)

Sample	**R^2**	**Spiked concentration (mg/L)**	**Average recovery (%)**	**RSD (%)**
Tap water	0.996	0.2	110.16	1.86
	0.996	0.4	87.94	0.70
River water	0.996	0.2	99.93	6.73
	0.996	0.4	90.89	0.46
Lake water	0.996	0.2	94.15	2.55
	0.996	0.4	99.64	0.70

The analysis results showed that zinc was detected in all three types of real water samples, and the percentage of recovery for 0.2 mg/L spiked tap water was the highest (110.16%).

4. CONCLUSION

SiO_2-TiO_2 hybrid nanoparticles were successfully prepared via sol-gel method. The prepared material was found possess different characteristics from its precursors SiO_2 and TiO_2 that enhances its capability for the extraction of targeted metal ion, zinc in aqueous matrix. The prepared material was then used for the extraction of zinc ions in aqueous matrix using dispersive solid phase extraction (DSPE) method. Several parameters were optimized in DSPE of SiO_2 – TiO_2 hybrid nanoparticles. The optimum condition was as followed: pH of sample, 7.0; mass of sorbent, 30 mg; extraction time, 10 min. The optimum parameters were used to validate the method and in the analysis of real sample. The LOD and LOQ is 0.03 mg/L and 0.10 mg/L respectively, and the accuracy is 101.56%. Zinc was detected in all three real samples, namely lake water, river water, and tap water. The SiO_2-TiO_2 hybrid nanoparticles adsorbent has proved to be potentially applicable for the removal of zinc ion from water samples.

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