Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

Superparamagnetic imposed diatom frustules for the effective removal of phosphates

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Experimental Details

A sample of diatoms (approx 80 mg) is exposed to an air plasma source at a frequency of 40 kHz at 110 W for five three minute periods with agitation after each ion bombardment. A stock solution was made up comprising 35 mg of $FeCl_2.4H_2O$ and 87.5 mg of $FeCl_3.6H_2O$ in 200 mL of Milli-Q water that has been purged with argon for at least 5 minutes. The stock solution is purged while the $Fe^{2+/3+}$ solution is mixed for a further 5 minutes. 40 mL of the stock solution is collected and kept under argon while 40 mg of plasma cleaned diatoms is added to this $Fe^{2+/3+}$ solution. The diatom $Fe^{2+/3+}$ suspension is kept under argon for a further 5 minutes to ensure all oxygen is removed from the system.

A solution of ammonia is made up with 5 mL of 30% ammonia added to 95 mL of DI water in a round bottom flask. Argon is bubbled through the ammonia solution and into the diatom/$Fe^{2+/3+}$ suspension resulting in controlled growth of magnetite nanoparticles.

Transmission electron microscopy (TEM) samples were prepared by dispersing the magnetite coated diatoms in argon purged water and diluting them until the water had a light brown tinge.

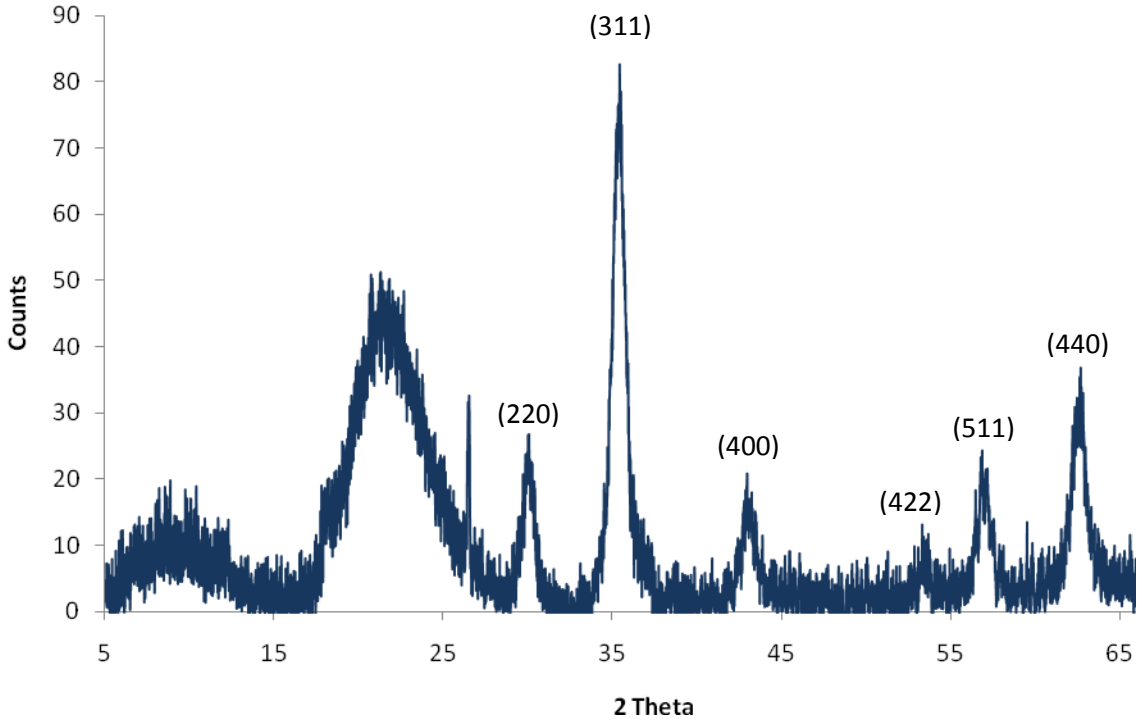
The solution was dropped cast onto a copper TEM grid using a pipette and left to dry in air. The samples were then viewed immediately, however if this was not the case, they were kept in an argon environment to minimise any oxidation.

Phosphate Analysis

Particle-free supernatants of each sample were subjected to phosphate tests via colorimetric ascorbic-acid test, also called orthophosphate method, which is a standard water analysis procedure[1] also recognized by the United States Environmental Protection Agency (USEPA). Chemical-kits in the form of powder pillows HACH®, PhosphoVer®3 Phosphate Reagent were employed before reading the phosphate concentration from a colorimeter (HACH® DR/870).[1]

1. APHA, Standard methods for the examination of water and wastewater, American Public Health Association, Washington DC, 18th edn., 1992 .

XRD



Powder XRD pattern for magnetite coated diatom frustules showing the Miller indices for each peak. The broad hump at around 20 is typical of the amorphous silica of diatomaceous earth.

Scherrer Equation:

$d=0.9\lambda/\Delta\cos\theta$

$\Delta = 0.896 \quad = 0.01564$ rad

$\theta = 36.44/2 \quad = 17.72$

$\lambda = 0.154$

$d = 20.6$ nm

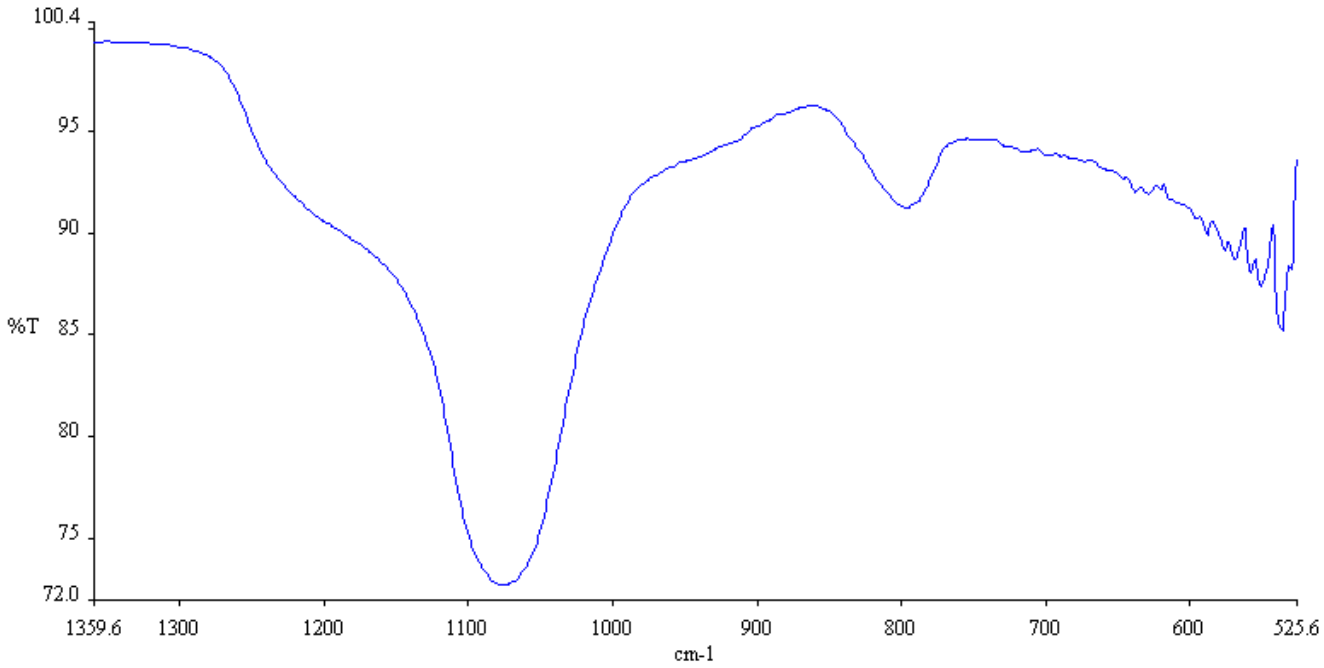
Size Distribution Analysis

<10	23
10 to 12	45
12 to 14	70
14 to 16	60
16 to 18	23
18 to 20	10
>20	6

Average : 13.53 nm

Standard Dev : 2.88 nm

FT-IR



FT-IR showing no characteristic stretching bands for Si-O-Fe at around 900 cm^{-1} or 680 cm^{-1}.