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Synthesis, Characterisation and Utilisation of Magnetic Fe_3O_4 – TGT Nanocomposite in the Removal of Pb(II) from Aqueous Solutions

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Abstract: Magnetic Adsorption Separation (MAS) method is an ideal substitute for the environmental clean-up process. Magnetic material embedded with natural litter material is a facile route to achieve maximum adsorptive ability at a lower dosage, contact time and increased chance of metal-laden adsorbents' recovery from aqueous matrices. In the present study, the synthesis of Fe_3O_4–TGT composite (TGT- C2) by the auto combustion method and its employment for Pb(II) removal from aqueous solutions is discussed. TGT- C2 is characterised using VSM (Vibrating Sample Magnetometer), SEM (Scanning Electron Microscope), Particle Size Analyzer, EDAX (Energy Dispersive X-ray Spectrometer) and FTIR (Fourier Transform Infra Red Spectrophotometer) techniques. TGT- C2 is found to be magnetic in nature and their saturation magnetization (Ms)/ Coercivity (Hc) values are calculated as 1.54 emu g^{-1}/139.83 G, respectively, being less than bare Fe_3O_4. The synthesised nanocomposite registered a maximum of 98% sequestration of Pb(II) ions under the optimised conditions of 100 mg/L initial metal ion concentration, 10 min agitation time, 50 mg dosage and pH 5 environment. Isothermal verification, the kinetics of adsorption and successive desorption/ regeneration cycles were performed. The outcomes support the preparation of bio-nanocomposites from animal waste was successful in the efficient trapping of divalent metal ions.

Key words: Nanocomposite, magnetic nature, litter material, characterisation, sequestration.

Introduction

Heavy metals are considered hazardous pollutants due to their toxicity even at low concentrations and non-biodegradable nature. These metallic elements are an intrinsic component of the environment. A variety of natural processes are responsible for their acute availability even at trace levels in various parts of the biosphere (Mohammed et al., 2011). Rapid industrialisation and their waste discharges have resulted in an unprecedented increase in a heavy metal influx into natural water bodies. The toxic effects of heavy metals while exceeding their tolerance levels affect the normal metabolic process.

Lead is the most abundant element on earth with the properties viz., heavy, soft, highly malleable, bluish–grey colour metal, stable at two oxidation states (+2 and +4). The major sources of lead pollution to the environment is from the industries of batteries, paint pigments, PVC plastics, X-ray shielding, crystal glass, pesticides, E-waste, smelting operation, ceramics, bangle industry, auto mobile exhaust (Zhang et al., 2015). Excess concentrations of Pb(II) than the prescribed limits (> 0.01 mg/L) lead to haematological, gastrointestinal and neurological dysfunction. The most insidious characteristic of lead is the ability to replace calcium in the bones and form a semi-permanent reservoir for long term release after its initial absorption.

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Hence, it has become a necessary and challenging task to treat heavy metal-contaminated wastewater prior to its discharge into the environment. Several methods for the removal of heavy metals, such as chemical precipitation, coagulation-flocculation, ion exchange and membrane filtration have been reported with their inherent advantages and widespread limitations in their applications (Madhava Rao et al., 2008).

The adsorption method finds to be an inevitable alternative to remove the toxic substances polluting the environment. Advantages of the adsorption process over other methods include simple design, easy operation, minimum capital investment, operational cost and selective trapping of metals even at lower concentrations (Barakat**,** 2011). Even though numerous low cost adsorbents from a variety of sources have been explored due to enormous surface areas per unit weight, in recent times, the search for effective/no-cost/ recoverable adsorbents has intensified.

New functional nanocomposite materials with impregnated nanoparticles are at the forefront of nano-based water treatment methods. A combination of both nano-sized and magnetic properties exhibited by the modified materials seek recent attention as novel sequestrants. The hybrid composites exhibit better efficiencies viz., extremely small size, high surface area/volume ratio, and easy recovery of the adsorbents through an external magnetic field, thus improving the possibilities of reuse than those of conventional materials/products available in the market for heavy metal removal (Horst et al., 2016). More insight is arrived from novel metal oxides and animal litter-based nanocomposites, through auto combustion technique from the present work. Herein, Goat Teeth, a butcher waste are modified and subjected to the preparation of nanocomposite.

Experimental Section

Preparation of Treated Goat Teeth (TGT)

Goat Teeth (GT), causing solid waste disposal problems collected from localities of Coimbatore, Tamil Nadu, India, stockpiled from local carnage, isolated from jaw bones under running water and sun dried for 10 days. Goat Teeth consist of a high percentage of mineral contents, especially exchangeable Ca^{2+} ions and organic/ bio-chemical materials viz lipids, collagen, proteoglycan (chondroitin sulphate, keratin sulfate). Hence, GT was soaked in 0.1N HCl for a period of 4 hrs, after segregating into 0.18 mm particle size using Scientific Test Molecular Sieves. The treated goat teeth (TGT) were washed several times and air dried (Anuradha et al., 2017).

Synthesis of TGT- C2 [TGT- Magnetite (Fe_3O_4) Nanocomposite]

Ferric benzoate nano precursors were prepared through one-pot synthesis as follows:

Ferric nitrate and benzoic acid solutions were prepared as per the literature, mixed and stirred in a magnetic stirrer for 20 min. Yellow crystals of Iron (III) benzoate dihydrate were formed, later filtered, washed thoroughly with hot distilled water and air dried (Ranjithkumar et al., 2014).

A specific dose of TGT was added to ferric benzoate solution after several trials and stirred for 6 hrs, later subjected to auto combustion. The obtained powder material was reheated in a muffle furnace for 2 hours which resulted in the in-situ surface formation of magnetic TGT - Fe_3O_4 nanocomposite (TGT- C2). The schematic preparatory procedure of TGT – C2 has been picturised in Figure 1.

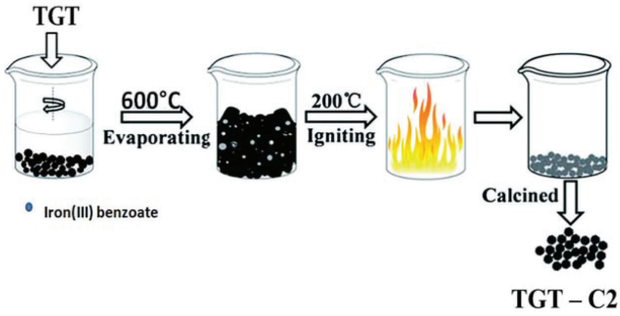

Figure 1: Preparation procedure - TGT- C2.

Characterisation Techniques

Magnetic property, nanoparticle nature, surface morphology and the elemental constituents exhibited by synthesised composite are characterised through various analytical techniques. The instruments employed for analyses include Vibrating Sample Magnetometer (Lakeshore 7410), Scanning Electron Microscope (JEOL model JSM-6390 LV), Particle Size Analyzer, EDAX Spectrometer, FTIR Spectrophotometer, X-ray Powder Diffraction Analyzer.

Adsorbate Preparation

A stock solution of 1000 mg/L Pb(II) was prepared by dissolving the appropriate dosage of lead nitrate in double distilled water (Distillon 4DQ). Aliquots of adsorbate solutions of varying concentrations were prepared through progressive dilutions of the stock solutions.

Batch Experiments

The adsorption capacity of TGT- C2 was experimentally verified following Batch mode for 100 mg/L concentration of Pb(II) aqueous solution at pH 5.5. 50 mL of the sorbate species was agitated at a pre-fixed time interval of 10 minutes and pH 5 environment for different doses varying between 25 and 100 mg with increments of 25 mg. The initial and residual Pb(II) concentrations were recorded using Atomic Absorption Spectrophotometer: **Shimadzu (AA 6200)** at 283.3 nm λ_{max} and 0.7 slit width.

Desorption/Regeneration Studies

The economic viability of chosen material was ensured via consecutive desorption/regeneration studies by batch experiment using 0.1 N HCl as the desorbing agent.

Data Analyses

Pb(II) removal in terms of percentage and the amounts adsorbed in terms of sorption capacity, were calculated using the following equations:

$$\% \text{ adsorption} = \frac{(C_i - C_e)}{C_i} \times 100$$

$$q_e = \frac{V(C_i - C_e)}{W}$$

[C_i/C_e - initial/equilibrium metal concentrations (mg/L), V - volume of the solution (L), W - mass of the adsorbent (g)]

The adsorptive nature of the studied system was established using Isothermal (Langmuir, Freundlich) and Kinetic (Pseudo first order, Pseudo second order) parameters. The batch experimental data were applied to the equations (Table 1) and plots were drawn to verify the applicability of above named models.

Table 1: Adsorption isotherm/kinetics factors

Models	*Equation*	*Plots*	*Constants*
Langmuir Isotherm	$(C_e/q_e) = (C_e/q_0) + (K_L/q_0)$	C_e vs (C_e/q_e)	q_m. b, R^2
Freundlich Isotherm	$\log q_e = \log K_F + (I/n) \log C_e$	$\log C_e$ vs $\log q_e$	K_F.1/n, R^2
Pseudo First Order	$\log(q_e - q_t) = \log q_e - K_f t / 2.303$	$\log (q_e - q_t)$ vs t	q_{e1}, K_f, R^2
Pseudo Second Order	$t/q_t = 1/(K_s q_e^2) + (1/q_e) t$	t/q_t vs t	q_{e2}, K_s, R^2

Results and Discussion

Magnetic Sensitivity Test

A magnet was placed externally near bottles containing TGT- C2 composite solution. Figure 2 manifests the attraction of black material towards the magnet within a short span of time, confirming the highly sensitive magnetic flux, in the aqueous matrix.

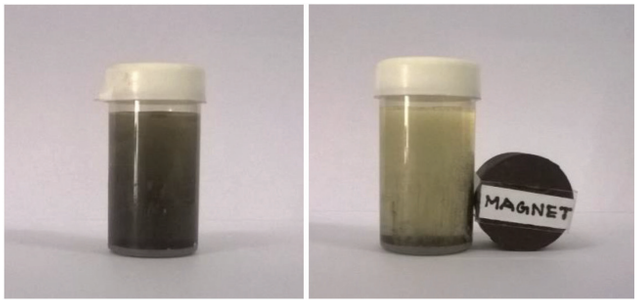

Figure 2: Magnetic separation – external magnetic field.

VSM Analysis

The magnetic property of the nanocomposite was characterised employing VSM (Vibrating Sample Magnetometer) technique with a 15 kOe magnetic field at 298K. Figure 3 exhibits the magnetisation (M-H) curve of TGT C2 as characterised by an S-like hysteresis loop, confirming the ferromagnetic nature. Saturation magnetisation strengths (Ms) and coercivity (Hc) values derived from the hysteresis loop are listed in Table 2. Ms value of TGT-C2 (1.54 emu/g) is markedly less in comparison with bare magnetite (92 emu/g) (Ristić et al., 2013), which could be due to the encapsulation of TGT within iron oxide particles. Also, a greater Hc value (139 Oe) supports the property of a specific magnetic field.

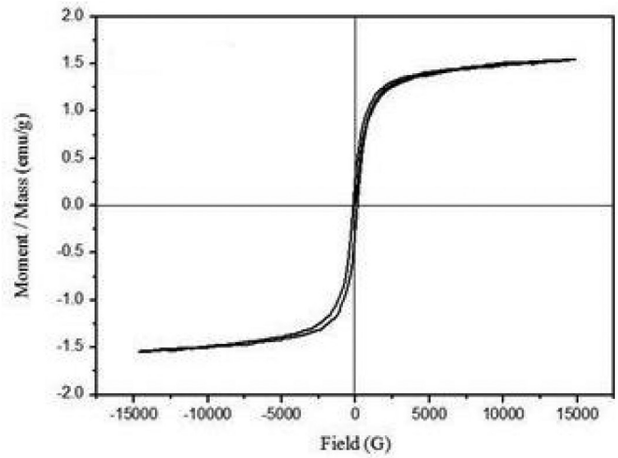

Figure 3: Magnetisation curve – TGT C2.

Table 2: VSM measurements

Magnetic Parameters	*TGT- C2*
Magnetisation (Ms) (emu g^{-1})	1.54
Coercivity (Hc) (Oe)	139.83

SEM/Particle Size Analyser Techniques

SEM micrograph (Figure 4a) reveals a homogeneous non-sphere/plate-shaped rough surface of iron oxide particles dispersed onto the TGT surface. The particle size analyser data evidenced the nano size of TGT- C2 as 57.35 nm (Figure 4b) which could be possible due to auto combustion synthetic route.

EDAX Study

EDAX spectra (Figure 5b), show the presence of Fe and C obviously, in TGT- C2 against its counterpart (TGT) in Figure 5a. Also, a decline in the % weight of elementals viz., Ca, P, O in Figure 5b, confirms their participation in composite formation.

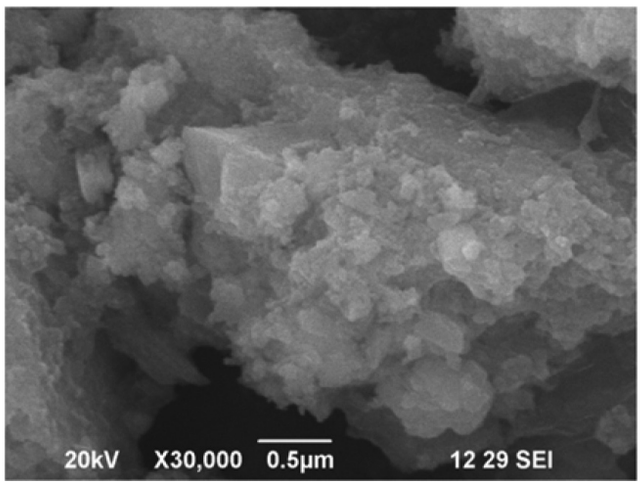

Figure 4a: SEM image – TGT C2.

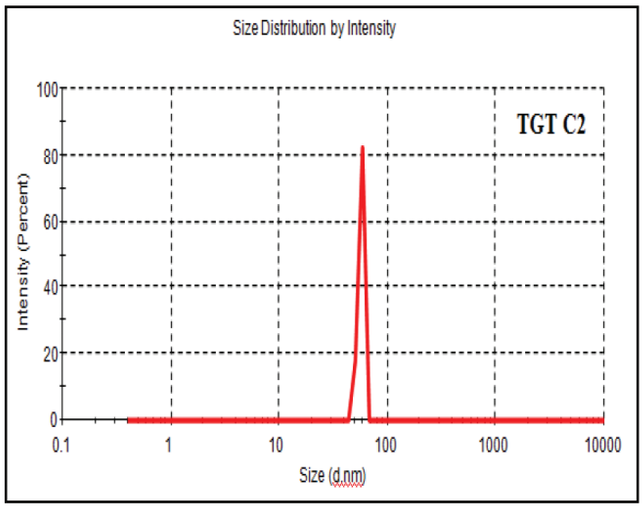

Figure 4b: Particle size Analyser data – TGT C2.

FTIR Technique

FTIR spectra of TGT, TGT- C2 are shown in Figure 6. Peak shifts from 556 cm^{-1} to 581 cm^{-1} (characteristics of PO_4^{3-} group), and 1515 cm^{-1} to 1456 cm^{-1} (characteristics of CO_3^{2-} group) indicate the successful doping of iron

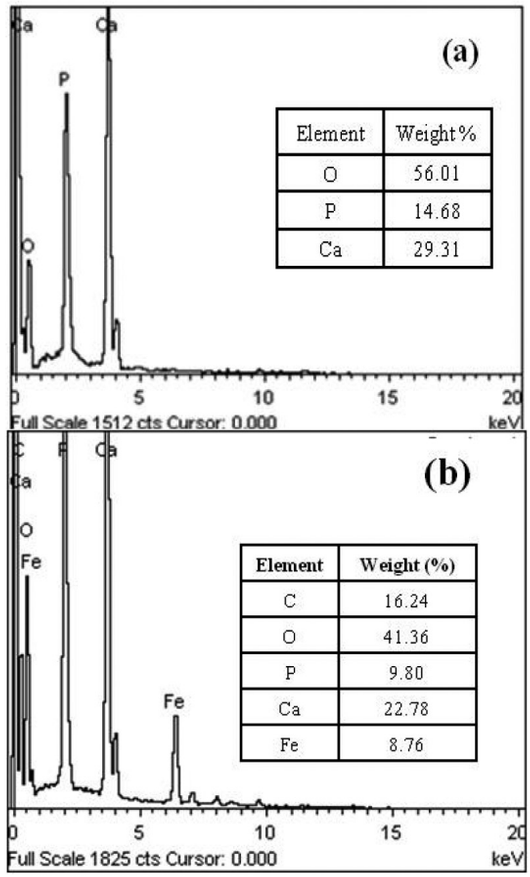

Figure 5: EDAX spectra: (a)TGT (b)TGT -C2.

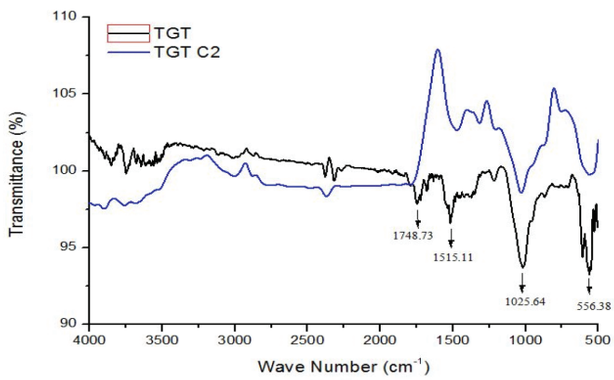

Figure 6: FTIR spectra.

oxides with the hydroxyl apatite of TGT. Asymmetric P-O stretching and peak occurrence corresponding to the –OH group at 1025 cm^{-1} and 1748 cm^{-1} are identical to that of TGT, emphasising the functional group identity of the parent precursor.

Batch Studies

Pb(II) sorption characteristics of TGT- C2 verified through batch experiments are listed in Table 3, for different doses (25-100 mg: 25 mg interval) of TGT-C2, where other parameters were pre-fixed (pH: 5.5, Adsorbate Volume/Concentration: 50 mL/100 mg/L, Contact Time: 10 min). The percentage removal of Pb(II) is observed to be maximum at 50 mg TGT- C2 dosage itself, beyond which the least increase in the removal process had occurred. This exhibits the better efficiency of TGT-C2 at lower doses under optimised conditions.

Table 3: Batch study

TGT C2 dosage (mg)	*Percentage removal (%)*
25	86.38
50	98.40
75	98.26
100	98.28

Desorption and Regeneration Studies

Desorbing ability of loaded metals and the regenerating capacity of TGT – C2 in consecutive cycles, determined by batch mode studies are shown in Table 4. A very low desorption rate is recorded invariably at successive processes without major variations in adsorption capacities. This could be attributed to the immobilising nature of TGT- C2, i.e., a high ratio of exchangeable calcium ions. Results evidenced that the parental TGT's (Anuradha et al., 2017) property has not been altered by the composite preparation. As far as the regeneration capability of TGT is concerned, the adsorption values observed in the three consecutive cycles, have less difference in the amounts adsorbed, (97.56: 97.10: 96.77) disclosing the excellent reusability of material.

Table 4: Desorption and regeneration study

[Pb(II) - TGT C2]	*Amount adsorbed (mg/g)*	
	Adsorption	*Desorption*
Cycle 1	97.56	0.23
Cycle 2	97.10	1.46
Cycle 3	96.77	2.39

Isothermal and Kinetic Verifications

(a) Isothermal Models

Langmuir, Freundlich isotherms were applied to the experimental data and the isothermal constants, and correlation coefficients (R^2) were calculated from linear plots (Figures 7 and 8) using isothermal equations (Table 1) which are summarised in Table 5. Langmuir constant (q_m) calculated as 98.03 mg/g for Pb(II) from the graphical representations exhibit good agreement with the adsorption capacities of TGT- C2 as per batch results (97.56 mg/g). Langmuir constant [b (L/g)] relating to the free energy of sorption being smaller (0.39) value implies greater affinity of adsorbent towards the selected metal ion through saturated monolayer sorption. Correlation coefficient R^2 values about 0.99 exhibiting linearity of the plots favour the fit in of the Langmuir model to Pb(II) – TGT C2 system. A smaller K_F (sorption capacity) value indicates the high adsorption process while a 1/n (sorption intensity)

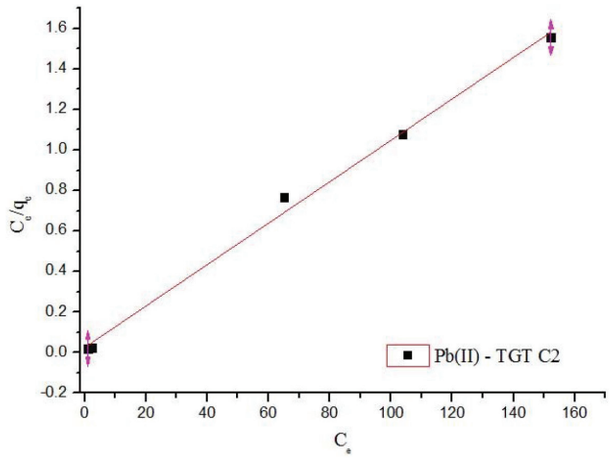

Figure 7: Langmuir plot.

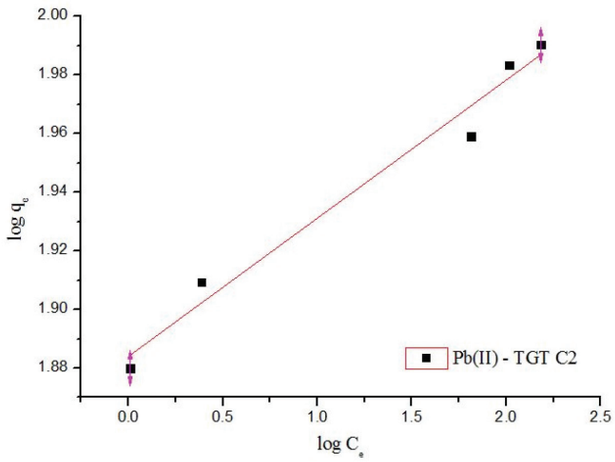

Figure 8: Freundlich plot.

value lying between 0.1 and 1.0 favour physisorption. Approximity of the R^2 values to unity and less linearity than the Langmuir model, favour lesser multilayer adsorption.

Table 5: Isothermal constants [Pb(II)- TGT C2]

Langmuir			*Freundlich*		
q_m *(mg/g)*	*b (L/g)*	R^2	K_f *(L/mg)*	*1/n*	R^2
98.0392	0.3968	0.9959	76.5597	0.0472	0.9772

(b) Pseudo Models

Table 6 shows data for pseudo-first/second order kinetic models at optimised concentrations using kinetic equations (Table 1) were employed to sketch out the respective plots (Figures 9 and 10). The resulting data reveal R^2 values nearness to unity, in the case of pseudo second order model than its counterpart being more suitable to describe the adsorption kinetics.

Table 6: Kinetic constants

Pb(II)- TGT C2	
Pseudo First Order	
q_e (mg/g)	8.43
K_f (min^{-1})	14.90
R^2	0.9370
Pseudo Second Order	
q_e (mg/g)	98.42
K_s (g/mg min)	3.62
R^2	0.9998

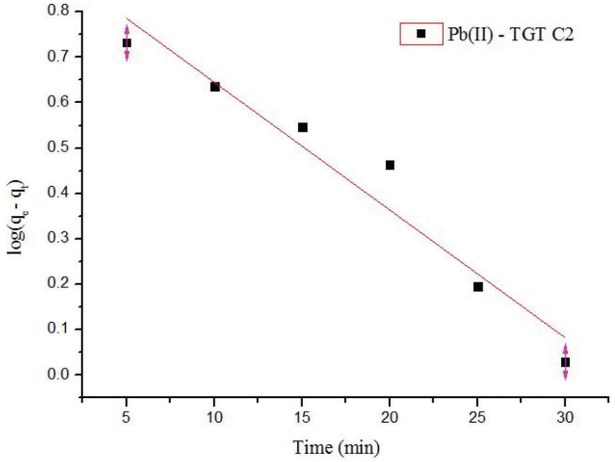

Figure 9: Pseudo first order kinetics.

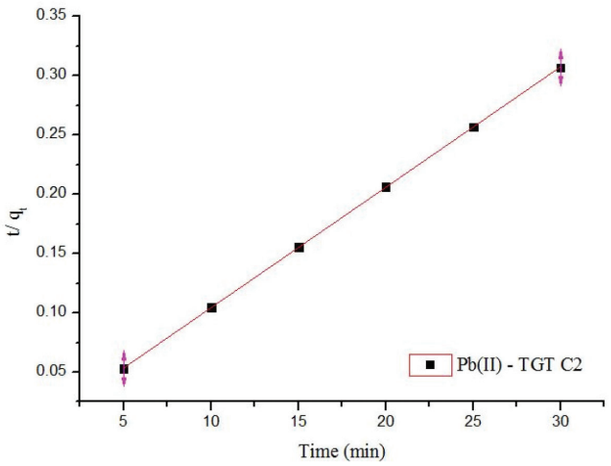

Figure 10: Pseudo second order kinetics.

Conclusion

Stable TGT- C2 - magnetic nanocomposite was synthesized through an efficient auto combustion technique without employing toxic chemicals. Fe_3O_4 encapsulated Treated Goat Teeth matrix possessed excellent nanosized magnetic properties confirmed by corresponding characteristic analyses. Batch results revealed TGT- C2 as a promising material to adsorb Pb(II) ions from an aqueous stream. Isothermal studies exhibited the best linear fit for the Langmuir plot suggesting a monolayer sorption mechanism and Pseudo second order kinetic mode was favoured for the chosen system. The more appreciable reusability of the exhausted material was assured by desorption and regeneration experiments.

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Contents