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Surface functionalized magnetic nanoparticles for separation of beta-blocker Propranolol from aqueous solution

Sudipa Ghosh*[1], Quek Jee Teck [1], M. S. Uddin[2], K. Hidajat [1]

[1]Department of Chemical and Biomolecular Engineering
National University of Singapore Engineering Drive 4, Singapore 117576
[2]Department of Biotechnology Engineering
International Islamic University Malaysia
P.O. Box 10, 50728 Kualalumpur
E-mail: sudipa047@yahoo.com

Abstract: The present study investigates adsorption separation of beta-blocker (β-blocker), propranolol utilizing surface functionalized magnetic nanoparticles (MNPs) from phosphate buffer solution. Surface of MNP is functionalized with silica and carboxymethyl-β-cyclodextrin (CMCD) to scrutinize sorption removal characteristics. Modified MNPs are characterized by Fourier Transform Infrared (FTIR) Spectroscopy, Transmission Electron Microscopy (TEM) etc. Adsorption of propranolol onto magnetic nanoadsorbents is found to be dependent on solution pH and adsorption capacity of adsorbent increases as pH increases from 3 to 9 and then reaches plateau at pH 11. It appears that modified hydrophobicity of beta-blocker, propranolol affects interaction with cyclodextrin functionalized magnetic nanoparticles as well as adsorption capacity of the pollutant. Equilibrium data in aqueous solution is well represented by Freundlich isotherm model. XPS analysis reveals that propranolol adsorption on magnetic nanoparticles involves nitrogen atoms in side chain of propranolol to form surface complexes. Finally, desorption studies are carried out in different concentration of methanol solution and 50% methanol solution was found to be effective for almost complete desorption.

1. INTRODUCTION

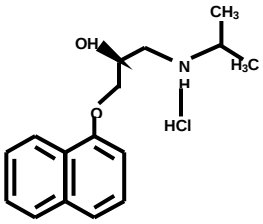
In the recent decades, pharmaceutical compounds received immense concern as emerging micropollutants for the contamination of aquatic environments [1]. Among the pharmaceuticals, beta-blockers (sometimes written as β-blockers) or beta-adrenergic blocking agents constitute a class of drugs used for various indications. As beta adrenergic receptor antagonists, they are widely used to treat a variety of cardiovascular diseases by diminishing the effects of epinephrine (adrenaline) and other stress hormones on the β-adrenergic receptor in the body, primarily in heart [2]. Propranolol, a β-adrenergic blocking agent, is widely used in the treatment of cardiovascular diseases (hypertension, cardiac arrhythmia). Propranolol is available in generic form as propranolol hydrochloride; some of the properties of propranolol hydrochloride are presented in **Table 1**. It is considered to be of low volatility, highly persistent [3, 4], and bioaccumulative [5]. Moreover, it was found that propranolol had the highest acute and chronic toxicity within the class of the β-blockers [6]. So development of more effective technologies to remove propranolol from aqueous environment is of prime importance.

Among the other methods, photo degradation has been utilized by many researchers as a way of removal of β-blockers from aqueous solution [7]. But photo degradation is accompanied by many disadvantages such as high energy consumption, generation of secondary products, complicated reaction pathways. Compared to other methods, adsorption has become one of the most promising techniques for removal of pharmaceuticals from aqueous solution, due to its convenience, less/ no energy consumption, efficacy etc. Recently, many studies have focused on use of superparamagnetic nanoparticles as alternative adsorbents for sorption separation/ removal of organic and inorganic contaminants [8, 9] etc. These superparamagnetic materials possess an advantage that they do not retain any magnetization after removal of external magnetic field. In addition, it is desired that the magnetic nanoparticles remain nonaggregated and are stable against oxidation from the point of these technological and medical applications. If considered as surface modifying agent, silica particles are not toxic and are also highly biocompatible. They are regularly used as food additives and components of vitamin supplements. In addition, amorphous silica particles have surfaces decorated with hydroxyl groups which not only render them intrinsically hydrophilic but also provide platform for further surface functionalization. On the other hand, cyclodextrins (CDs) are torus shaped cyclic oligosaccharides consisting of α-(1, 4) linked glucose units. A characteristic feature of cyclodextrin is the presence of an internal hydrophobic cavity with a remarkable capacity to form inclusion complexes [11]. Studies have been reported for adsorption of β-blocker propranolol onto other adsorbent such as modified attapulgites [12], cyclodextrin polymer [13]. However to the best of our knowledge, reports about silica and cyclodextrin coated magnetic nanoparticles used in separation of β-blocker are rather limited.

* Corresponding Author: Sudipa Ghosh
E-mail: sudipa047@yahoo.com

The primary objectives of this study were to investigate the sorption behavior of propranolol onto silica and cyclodextrin derivative-carboxymethyl-β-cyclodextrin modified magnetic nanoparticles to evaluate their feasibility for removing propranolol from aqueous solution in ppm concentrations.

Table 1. Physicochemical properties of propranolol.

Compound	Molecular structure	MW (g/mol)	LogK_{o_w}	pK_a	Log$D$ at pH 3, 7 and 9	Water solubility (mg/L at 25^{o}C)
Propranolol hydrochloride		295.8	3.48[a]	9.42[a]	-2.94[a] 1.06[a] 2.92[a]	150

[a] Data from reference [14]

2. Materials and Methods

2.1 Reagents and samples

The following chemicals were used in this study: Iron (II) chloride tetrahydrate (98%) (Alfa Aesar), iron (III) chloride hexahydrate (98%) (Alfa Aesar), citric acid (99%) (Alfa Aesar), cyanamide (98%) (Alfa Aesar), ammonium hydroxide (25%) (Merck), propranolol hydrochloride (99%) (Sigma-Aldrich), tetraethyl orthosilicate (TEOS) (99%) (Fluka), β-cyclodextrin hydrate (99%) (Sinopharm Chemical). 2-propanol (99.9%) (Fisher Scientific) and acetone (99.5%) (Merck), methanol (99.5%) (Merck) were distilled before use. All the chemicals were of analytical grade and were used as received without further treatment.

2.2 Methods

2.2.1 Synthesis of bare and coated magnetic nanoparticles: Nanosized bare magnetic particles were synthesized by chemical co-precipitation method and the procedure of silica coating follows a modified stöber method as mentioned in our previous work [15]. A solution of the magnetic nanoparticles was prepared by mixing 1 g dry bare MNPs in 200 mL (0.3M) of citric acid and the resulting solution was sonicated for 1 hr followed by mechanical stirring for 12 hrs at 400 rpm at room temperature. Citric acid modified nanoparticles (CMPs) were washed several times with distilled water, isolated with help of a magnet and dried at 60 °C in vacuum for 2 hrs.

Subsequently, 1g of CMP was mixed with 40 mL deionized (DI) water and 200 mL of 2-propanol and sonication for 15 mins was carried out to maintain proper dispersion. Under continuous mechanical stirring, 20 mL of ammonia solution (25%) and 1.5 mL tetraethyl orthosilicate (TEOS) were added. The reaction was allowed to proceed at room temperature at 650 rpm for 6 hrs. The silica coated core shell magnetic nanoparticles (Fe_3O_4/SiO_2 MNPs) were isolated by magnetic decantation to remove the unbound silica particles and at vacuum after being washed with de-ionized water, 2-propanol and acetone.

A derivative of β-cyclodextrin, carboxymethyl-β-cyclodextrin was synthesized according to the method proposed in our previous work [15]. 1 g of dry Fe_3O_4/SiO_2 MNPs were mixed with 20 mL of sodium phosphate buffer (0.03M, pH~6) and sonicated for 15 mins. Then 125 mg of cyanamide was dissolved separately in 5 mL of the same buffer solution and added to the previous mixture. Further sonication was done for 15 mins and finally 25 mL of CMCD solution (50 mg/mL in same buffer solution) was added and the reaction was continued for 2 hrs. The final product of CMCD coated magnetic silica nanoparticles (Fe_3O_4/SiO_2/CMCD MNPs) were washed several times with sodium phosphate buffer.

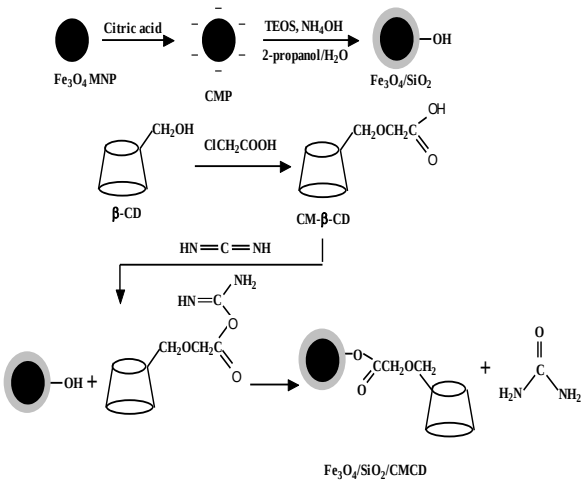


Fig. 1: Scheme representation of silica and CMCD coating on bare magnetic nanoparticles.

2.2.2 Characterization of magnetic nanoparticles: A Field Emission TEM (JEOL 2011F) (at an acceleration voltage of 200 kV) was used to determine size and morphology of the magnetic nanoparticles. The TEM samples were prepared by coating a copper grid (200 mesh and cover with formvar/ carbon) with a thin layer of diluted particle suspension. The copper grid was then dried at room temperature for 24 hrs before the measurement. The Shimadzu infrared spectrometer (Model No. 8400) was used to characterize all the synthesized particles at room temperature using KBr pellets over a broad wavelength ranging from 400 to 4000 cm^{-1}. XPS measurements were made on an Axis Ultra DLD (Kratos) spectrometer with Al mono Kα X-ray source (1486.71 eV photons) at a constant retard ratio of 40. The sample was mounted on the standard sample studs by means of double sided adhesive tape. The core-level signals were obtained at a photoelectron take-off angle 90° (with respect to the sample surface). The X-ray source was run at a reduced power of 75W. The pressure in the analysis chamber was maintained at 2×10^{-8} Torr or lower during each measurement.

2.2.3 Adsorption and desorption experiments: Effect of pH on adsorption of propranolol was examined over the pH range from 3-11 at initial concentration of 50 ppm. Three buffer systems, i.e., 0.01 M sodium acetic acid buffer (pH 3, 4), 0.01 M mono/disodium phosphate buffer (pH 6, 7), and 0.01M tris–HCl buffer (8, 9, 11), were used for the experiments. Adsorption of beta-blocker, propranolol hydrochloride was investigated using a batch equilibrium mode by adding 60 mg of wet Fe_3O_4/SiO_2/CMCD MNPs into 4 mL of propranolol hydrochloride solutions with different concentrations (10– 50 ppm). Samples for equilibrium adsorption studies were prepared in de-ionized water. Solution pH was adjusted by adding 0.01M NaOH or 0.01M HCl.

After preparation of propranolol solution, samples were stirred by a horizontal laboratory shaker at 230 rpm and after the equilibrium was reached, MNPs were removed by magnetic decantation from the solution before measurements. Some initial kinetic studies were done and it showed that adsorption reached equilibrium within 1 hr. Residual concentrations of propranolol hydrochloride in solutions were determined by Shimadzu UV–visible spectrophotometer (Model 1800) and absorbance values were recorded at 289 nm. The amounts of solute adsorbed per unit mass of adsorbent were calculated from the differences between initial and the final solute concentrations in solution before and after adsorption following equation 1.

$$Q_e = \frac{(C_i - C_e)\times V}{w} \qquad (1)$$

where Q_e (mg/g) is the adsorption capacity of the sorbent, V (mL) is the volume, C_i and C_e (mg/mL) are the initial and final solution concentration of propranolol hydrochloride and w (mg) is the dry mass of the solid.

Desorption studies of beta-blocker, propranolol was carried out using three different composition of alcohol solution, 10% methanol solution, 30% methanol solution and 50% solution when adsorption was carried out at pH 7 (sodium phosphate buffer solution). After equilibrium was achieved for adsorption, supernatant was separated from magnetic particles by the help of a magnet. Then particles were washed using Mili Q water. Magnetic particles containing propranolol was then mixed with 5mL alcohol solution. After 1 hr incubation at 25°C, supernatant was collected and analysed with UV spectrometer at 289nm.

3. Results and Discussion

3.1 Characterization by FTIR spectroscopy

The FTIR spectra of bare MNPs, CMPs and Fe_3O_4/SiO_2/CMCD MNPs are presented in **Fig. 2**. When compared, it can be inferred that the existence of the characteristic Si-O-Si stretching at 1088 cm^{-1} on Fe_3O_4/SiO_2/CMCD MNPs are evidences to confirm the formation of the silica shell [10, 16].On Fe_3O_4/SiO_2/CMCD MNPs, other characteristic absorption bands such as Si–OH stretching, Si–O bending and Si–O–Si bending, are shown at 958, 794, and 459 cm^{-1}, respectively [17]. Characteristic Fe-O peak of bare MNPs at 586 cm^{-1} is shifted to 584 cm^{-1} and 576 cm^{-1} in the spectrum of CMPs and Fe_3O_4/SiO_2/CMCD MNPs, respectively. Thus, undoubtedly it can be said that the silica shell is linked to the surface of the magnetic nanoparticles by Fe-O-Si chemical bond. The most important asymmetric and symmetric C-H stretching bands are found at 2855 and 2924 cm^{-1} respectively, which prove successful grafting of CMCD on silica coated magnetic particles [10].

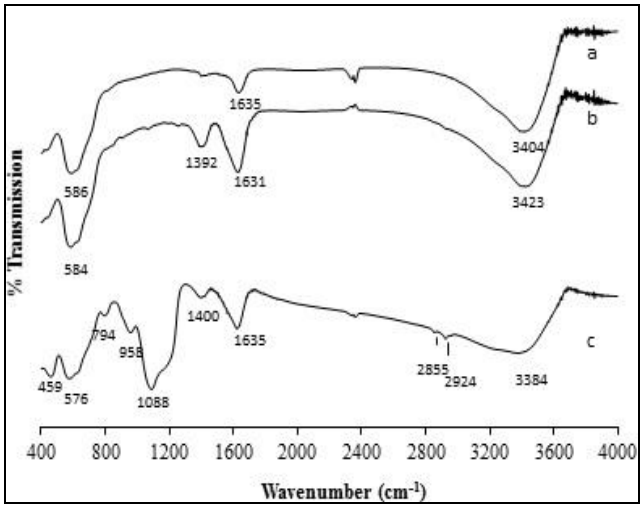


Fig. 2: FTIR spectra of (a) bare MNPs, (b) CMPs, (c) Fe_3O_4/SiO_2/CMCD MNPs.

3.2 TEM images

TEM images of bare MNPs, CMPs and Fe_3O_4/SiO_2/CMCD MNPs are presented in **Fig. 3**. From **Fig. 3(a)** and **Fig. 3(b)**. It is clear that the synthesized bare nanoparticles and CMPs are well dispersed, but also in some areas aggregates of larger particles are observed. **Fig. 3(c)** depicts the TEM image of Fe_3O_4/SiO_2/CMCD MNPs. Images of bare and coated MNPs were taken using HRTEM (High Resolution Transmission Electron Microscope) machine and afterwards, size of at least 100 particles from different areas were measured and average size of the particles were calculated using equation 2:

$$d_i' = \frac{\sum(d_i \times n_i)}{\sum n_i} \quad (2)$$

where, n_i = No. of Particles within the same size range, d_i = Particle diameter of the same size range, d_i' =Average particle size. The average size of bare nanoparticles and CMPs are about 11 nm and 12 nm, respectively. It can be clearly seen that the samples are nearly all in core-shell structures and average diameter of the Fe_3O_4/SiO_2/CMCD MNPs is around 30 nm.

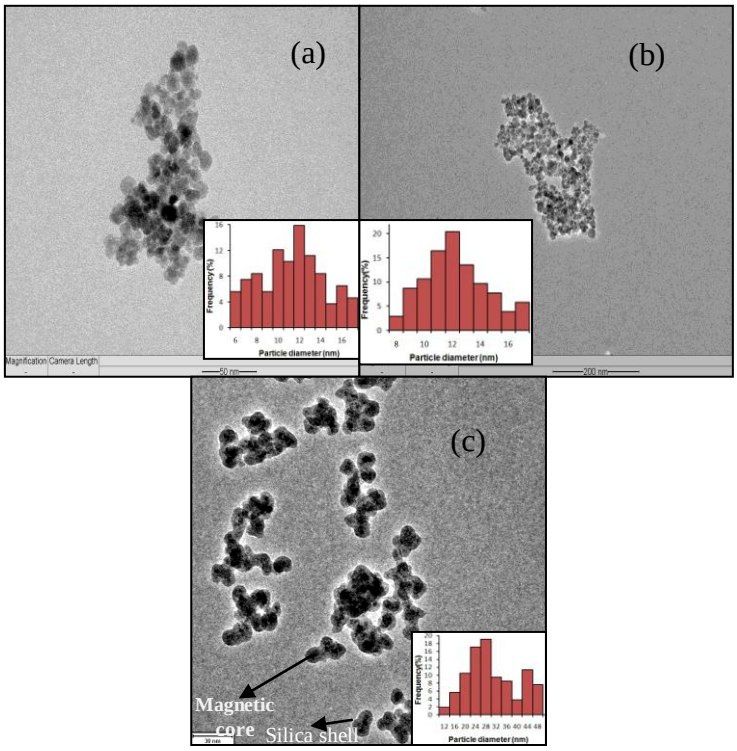


Fig. 3: TEM images of (a) bare MNPs (scale bar is 50 nm), (b) CMPs (scale bar is 200 nm), (c) Fe_3O_4/SiO_2/CMCD MNPs (scale bar is 30 nm).

3.3 Adsorption of propranolol

3.3.1 Effect of initial pH: The sorption of propranolol onto Fe_3O_4/SiO_2/CMCD MNPs as a function of initial solution pH was also investigated in the pH range of 3–11 (**Fig. 4**). As can be seen in **Fig. 4**, adsorption capacities of nanoadsorbents toward propranolol increase with increase in pH.

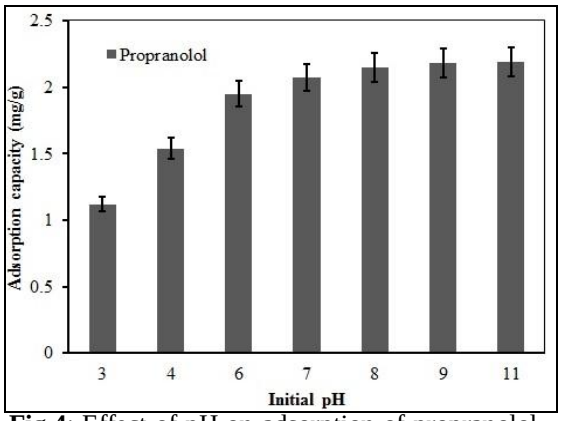


Fig.4: Effect of pH on adsorption of propranolol on the sorbents (T = 25°C, C_i = 50 ppm, sorbent dosage = 60 mg/4 mL).

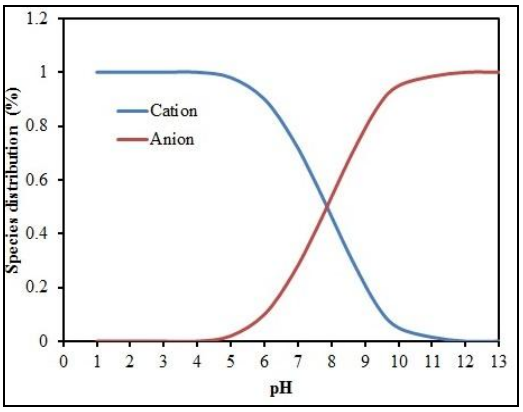


Fig. 5: Species distribution of propranolol.

In the case of propranolol (pK_a = 9.42), it exists as a neutral compound in the tested pH below its p*K*a and it exists as negatively charged molecule above its p*K*a [12]. Species distribution of propranolol has been depicted in **Fig 5**. Thus, adsorption of propranolol onto Fe_3O_4/SiO_2/CMCD MNPs can be controlled by both non-electrostatic and electrostatic interaction. In the prepared sample, propranolol was present in either neutral or ionized forms, depending upon the solution pH. It was reported that interaction forces between propranolol and cyclodextrin molecules are hydrogen bonding and hydrophobic interaction [13]. Adsorption capacity of the nano-adsorbent bearing cyclodextrin moieties toward β-blocker, propranolol is based on two factors, namely, the hydrophobicity of the drug (conditioned by the value of the octanol water partition coefficient, K_{ow}) and ionization of the molecule (determined by the values of pH and pK_a). Both parameters K_{ow} and pK_a can be taken into account for calculation of log*D*. Log*D* is a pH-dependent modified octanol water partition coefficient and is relevant for solutes that are partly dissociated or protonated [18]. It can be calculated using following equations 3 and 4. For acidic molecules Log*D* is determined as:

$$\log D = \log K_{ow} - \log\left(1 + 10^{(pH-pKa)}\right) \quad (3)$$

Whereas for basic molecules Log D is:

$$\log D = \log K_{ow} - \log\left(1 + 10^{(pKa-pH)}\right) \quad (4)$$

The modified Log*D* value of propranolol at pH 3, 7 and 9 are calculated as -2.94, 1.06, 2.92 [14]. According to the modified hydrophobicity values, hydrophobicity of propranolol increases from pH 3 to pH 9. Noteworthy, the chemical structure of Fe_3O_4/SiO_2/CMCD MNPs (**Fig. 1**) suggests that presence of ionizable groups on the surface is very limited. Thus, hydrophobic interaction between CMCD and propranolol molecules should be dominating. As a result, higher adsorption capacities of Fe_3O_4/SiO_2/CMCD MNPs toward propranolol at higher solution pH are justified.

3.3.2 Adsorption isotherm: Equilibrium isotherms for adsorption of propranolol in single solute system by both Fe_3O_4/SiO_2/CMCD MNPs and bare MNPs at pH 7 and 25°C are shown in **Fig. 6**. From the various isotherm equations that are used to analyze adsorption data in aqueous phase, the Langmuir-the theoretical equilibrium isotherm and the Freundlich-the empirical equilibrium isotherm are the most common models. The Langmuir model was originally developed to represent physisorption on a set of well-defined localized adsorption sites having the same adsorption energy, independent of the surface coverage and with no interaction between adsorbed molecules. On the other hand, the Freundlich isotherm, one of the more widely employed mathematical descriptions, usually fits the experimental data over a wide range of concentrations. This isotherm gives an empirical expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.The Langmuir equation can be expressed as [19]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m k_L} + \frac{C_e}{Q_m} \quad (5)$$

where Q_e is the amount of adsorbed material at equilibrium (mg/g), C_e the equilibrium concentration in solution (mg/mL), Q_m the maximum capacity of adsorbent (mg/g), and k_L is the "affinity parameter" or Langmuir constant (mL/mg).

The linear form of Freundlich equation, which is an empirical equation derived to model the heterogenous adsorption, can be represented as follows [20]:

$$\ln Q_e = \ln k_F + (1/n) \ln C_e \qquad (6)$$

where Q_e and C_e are defined as above, k_F is Freundlich constant (mL/g), and n is the heterogeneity factor. As can be seen from **Fig. 6 (a)**, the maximum adsorption capacities of Fe_3O_4/SiO_2/CMCD MNPs toward propranolol is 2.078 mg/g at 25°C and pH 7, whereas those using bare MNPs is 0.652 mg/g, at the same experimental condition. Thus, Fe_3O_4/SiO_2/CMCD MNPs could adsorb propranolol more than three times than that by bare magnetic nanoparticles indicating that the modification of magnetite surface with CMCD which has hydrophobic cavity could enhance the adsorption capacities. However, all the experimental data were fitted well to Freundlich isotherm model than Langmuir model (R^2 > 0.99). Thus, the adsorption process is governed by heterogenous adsorption.

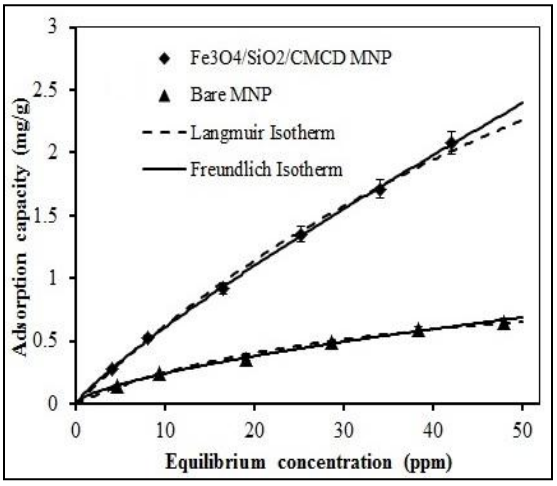


Fig. 6: Sorption isotherm of propranolol onto Fe_3O_4/SiO_2/CMCD MNPs and bare MNPs .

3.3 Investigation of Adsorption mechanism with XPS spectroscopy

To scrutinize adsorption mechanism of propranolol on magnetic nanoparticles, XPS analyses were carried out on propranolol and Fe_3O_4/SiO_2/CMCD MNPs after adsorption of propranolol and the corresponding results are shown in **Table 2**. There are major changes in the N 1s spectra of the propranolol before and after adsorption onto Fe_3O_4/SiO_2/CMCD MNPs, which indicates that the amino group of propranolol took part in adsorption and complex formation. Clearly, the spectrum of propranolol exhibits two N1s peaks at 398.4 and 400.5 eV which could be attributed due to N-H and N-C functional groups. After adsorption of propranolol onto Fe_3O_4/SiO_2/CMCD MNPs, the spectrum shows peak at 401.2 eV corresponding to the peak at 398.4 eV and peak at 402.3 eV corresponding to the peak at 400.5 eV in native propranolol. However, binding energy (BE) of the peaks shifted to higher eV after adsorption compared to that of the native propranolol molecule. The significant change in BE of N1s indicates propranolol-magnetic nanoparticle complex formation occurred. Because of the favorability of amide bond formation, free electron density of nitrogen atom is greatly reduced. As a result, the BE of N 1s increased considerably. Furthermore, O1s spectra of Fe_3O_4/SiO_2/CMCD MNPs depicts two oxygen peaks at 530.3 eV and 532.8 eV due to presence of C=O and C-O-H/C-O-C group, respectively which originates from presence of CMCD on nanoparticles' surface. After adsorption of propranolol on magnetic nanoparticles' surface, binding energy of C-O-H/C-O-C group shifted to higher eV which represents that interaction with the secondary hydroxyl group of the cyclodextrin outer rim on the magnetic nanoparticles took place (data shown in **Table 2**). Apart from these, there are no major changes in C 1s spectra.

Thus, from XPS analysis, it can be surmised that the hydrophobic part of propranolol penetrated into the hydrophobic cavity of CMCD and nitrogen molecule was involved into hydrogen bond formation. Structure of beta cyclodextrin and adsorption mechanism is depicted in Fig. 7.

Table 2. XPS data analyses for adsorption of propranolol.

Element	Binding energy (eV)		
	Fe_3O_4/SiO_2/CMCD MNPs	**Propranolol**	**Fe_3O_4/SiO_2/CMCD MNPs after adsorption of propranolol**
N1s	-	398.4 (N-H) 400.5 (N-C)	401.2 (N-H) 402.3 (N-C)
C1s	284.6 (C-C/C-H) 286 (C-O/C-O-C) 287.9 (C=O) 288.7(COO^-)	284.6(C-C/C-N) 286.2 (C-O/ C-O-C)	284.8(C-C/C-N) 286.3(C-O/C-O-C) 288.1(C=O) 288.9(COO^-)
O1s	530.3(C=O) 532.8(C-O-H/C-O-C)	532(C-O-H/ C-O-C)	530.75(C=O) 533.6(C-O-H/C-O-C)

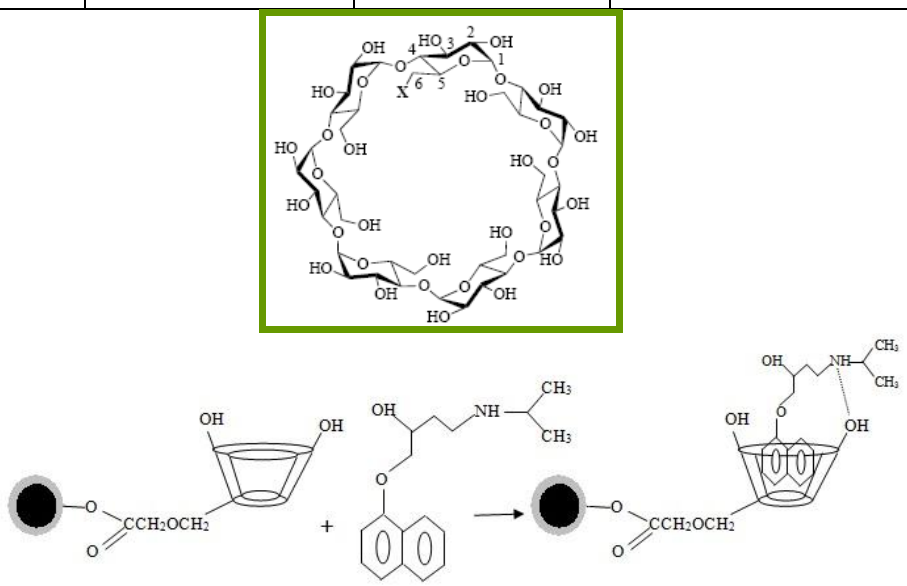


Fig. 7: (a) Structure of beta cyclodextrin, (b) simplified schematic showing adsorption mechanism of propranolol onto Fe_3O_4/SiO_2/CMCD MNPs.

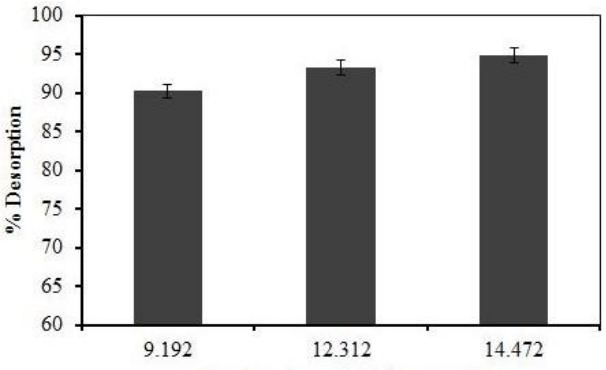


Fig. 8: Desorption of propranolol from Fe_3O_4/SiO_2/CMCD MNPs as a function of loading of adsorbent. Adsorption condition: propranolol 50 ppm; pH 7; temperature 25°C, contact time 5 hrs. Desorption condition Fe_3O_4/SiO_2/CMCD MNPs; 50% methanol solution, temperature 25°C, contact time 6 hrs.

3.5 Desorption studies

The success of an adsorption process usually depends on regeneration step of the adsorbent from economic point of view. There are a number of regeneration techniques such as thermal, steam, acid, base, and solvent regenerations. In this study, acetonitrile and methanol and were used as desorbing agents for propranolol. Among these, methanol solution was found as effective desorbing agent. Desorption of propranolol from nanomagnetic particles was carried out separately by 10%, 30% and 50% methanol solutions at equilibrium and 25°C and 20%, 50%, 94% desorption of propranolol were obtained, respectively. **Fig. 8** shows the result of desorption studies of propranolol after adding 50% methanol solution at equilibrium with respect to solid loading. Around 94% desorption of propranolol was achieved using 50% methanol solution when 14.47 mg of solid adsorbent was added.

4. Conclusions

In summary, silica and carboxymethyl-β-cyclodextrin functionalized Fe_3O_4 magnetic nanoparticles were synthesized and utilized for adsorptive removal of propranolol. Results from effect of pH study show that adsorption capacities of the particles increased as solution pH was increased and the behavior was dominated by hydrophobic interaction between propranolol and the nanoadsorbents. Adsorption capacities of as synthesized particles were compared to bare nanoparticles and it was found that the adsorption capacity was three times higher than that. All the adsorption equilibrium data were fitted well to Freundlich isotherm model thus showing heterogeneous adsorption. XPS spectroscopy were applied to investigate the adsorption mechanism and it was found that the hydrophobic portion of propranolol penetrated completely into the cyclodextrin cavity and amino group of propranolol interacted through hydrogen bond formation with the secondary hydroxyl group of cyclodextrin cavity. Finally, desorption studies show that the nanoadsorbents could be regenerated using methanol solution and using 50% methanol solution almost complete regeneration of the adsorbent was achieved. Thus, the as-synthesized CMCD functionalized magnetic nanoparticles with all significant properties would have great potentials in adsorptive separation/ removal of beta-blocker

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