CHAPTER 4

CONCLUSIONS

MNPs were synthesized by the chemical co-precipitation of iron(II) and iron(III) ions. SEM and TEM analysis revealed that the MNPs are nearly spherical particles with average diameter of 20 nm. Surface modification of the MNPs with APTES under the optimized conditions (30% v/wt (mg) of APTES/MNPs, 5 h, room temperature) yielded high load aminopropyl magnetic silica for further applications.

Molecularly imprinted silicas for nicotinic acid (NA) were developed based on the modified MNPs using the combination of molecular imprinting strategy and sol-gel process. Three M-MISs (M-MIS 1-3) were synthesized using the NA, NAM and 3-APY as template molecules. APTES and tetraethoxyorthosilicate (TEOS) were used as the functional monomer and cross-linker, respectively.

Binding efficiency of all the synthesized M-MISs with their corresponding templates was evaluated using UV-Vis spectrophotometric technique. M-MIS 1 synthesized from NA template showed the best binding characteristic with its template, whereas the rest of M-MISs showed lower binding capacity. Various solvent systems comprising of 6:1(v/v) EtOH:H_2O, 1:1(v/v) EtOH:H_2O, EtOH, MeOH, MeCN and 4:1 (v/v) MeCN:H_2O were screened to obtain suitable media for the rebinding of NA onto M-MIS 1. Among the tested solvents, EtOH was the best media

to provide the highest binding efficiency of M-MIS **1**. Fast adsorption kinetic was also observed in this solvent as the binding of NA to M-MIS **1** reached equilibrium with in 15 min.

Langmuir isotherm and Scatchard analysis were ultilized to evaluate the recognition properties of M-MIS **1**. Information regarding the chemical interaction was obtained from Scatchard analysis whereas the Langmuir adsorption isotherm provide evidence on the physical adsorption. The adsorption behavior of NA onto M-MIS **1** fitted to Langmuir equation revealed a homogeneous distribution of molecularly imprinting adsorption sites on the M-MIS surface. From this plot, the values of Q_m and K_d calculated were 1666.67 µmol/g and 0.0382 µmol/ml, respectively. The saturation binding data were further processed with Scatchard equation to estimate the binding affinity of imprinted magnetic nanoparticles. The value of Q_m and K_d can be estimated from linear line of Scatchard plot resulting in Q_m is 345.43 µmol/g and K_d of binding sites is 0.5208 µmol/ml. It can be implied that the binding for NA molecule with M-MIS seems to involve both mechanisms: the chemical interaction and the physical adsorption.

The selectivity of the M-MIS **1** was also investigated by UV rebinding of NA and it's structural analogues comprising of BZA, C-NA, NTA, NAM and 3-APY. Interestingly, NA exhibited selective binding superior to other analogue compounds. This data indicates that recognition site of M-MIS 1 are complementary both in shape and functional groups to NA template molecule.

The presence of a magnetic component in the imprinted silica not only allows the ease of their removal from the binding matrix using an external magnet but also the ability to potentially reuse of the used M-MIS. The reusability of M-MIS was therefore investigated. The result showed that M-MIS **1** can be reused for NA adsorption without significant loss in its binding performance after four repeated cycles.

Another application of the modified MNPs was in the synthesis of magnetic poly(allylmorpholine *N*-oxide) which can be used for the oxidation of organic halides to the corresponding carbonyl compounds. M-NMO was synthesized via modification of aminopropyl magnetic silica nanoparticles with acrylic acid then grafted with polymeric chain of allylmorpholine. Under three polymerization conditions, three bacth of poly(*N*-allymopholine) modified magnetic silica nanoparticles (M-NMM **1**, **2** and **3**) were obtained. The corresponding M-NMOs were then readily obtained upon oxidation of M-NMM with *m*CPBA or H_2O_2.

M-NMOs were examined effective loading as oxidant agents for the oxidation of benzyl chloride and benzyl bromide. The results showed that M-NMO **2** exhibited the highest effective loading 2.0 and 2.2 mmol/g according to best performance in oxidizing both benzyl chloride and benzyl bromide into benzaldehyde, respectively. The preparation method was proven to have a great influence to oxidative efficiency of M-NMOs. Moreover, DMSO and DMF were found to be good solvent for M-NMO oxidation of benzyl chloride.

In continuation of the work described in this study, the following suggestions for further work are made:

1)   The NA selective M-MIS may be applied as solid phase extraction of NA to determine the amount of NA or use as sorbent assay for detection of NA in biological samples.

2)   In case of the poly(allylmorpholine N-oxide) modified silica magnetic nanoparticles, the polymerization method may be improved to allow long chain of allylmorpholine grafted onto MNPs surface leading to high loading of required functional groups.

3)   Method for accurate loading estimation of morpholine N-oxide on the MNPs surface has to be investigated.